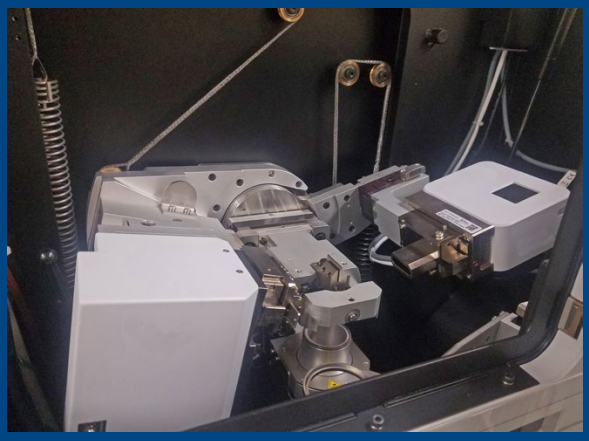
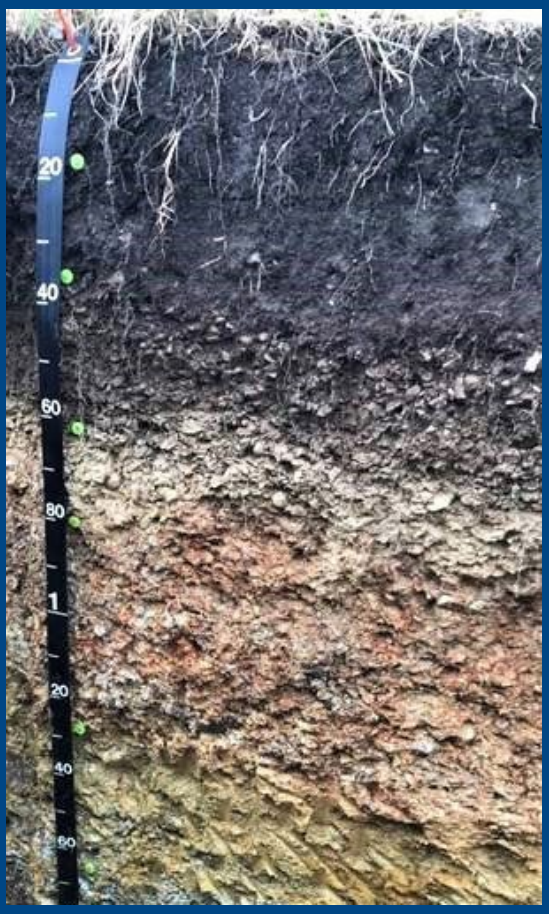
USDA Natural Resources Conservation Service
U.S. DEPARTMENT OF AGRICULTURE

Kellogg Soil Survey Laboratory Methods Manual

Soil Survey Investigations Report No. 42, Version 6.0

Part 1: Current Methods





Cover photos:

Top left.—Archive of soil samples at the Kellogg Soil Survey Laboratory. Samples date back to 1940.

Right.—Profile of a soil in the Olpe Series in Kansas.

Bottom left.—The interior of an x ray diffraction analyzer, which is used to determine crystallographic structure.

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KELLOGG SOIL SURVEY LABORATORY METHODS MANUAL

Soil Survey Investigations Report No. 42, Version 6.0
Part 1: Current Methods

Compiled by the staff of the Kellogg Soil Survey Laboratory and the National Soil Survey Center

Kellogg Soil Survey Laboratory
National Soil Survey Center
Natural Resources Conservation Service
U.S. Department of Agriculture
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PREFACE

Laboratory data are critical to the understanding of the properties and genesis of a single pedon, as well as to the understanding of fundamental soil relationships based on many observations of a large number of soils. The development of an analytical database and the soil relationships based on those data are the cumulative effort of several generations of soil scientists.

The purpose of Soil Survey Investigations Report (SSIR) No. 42, Kellogg Soil Survey Laboratory Methods Manual, is to document methodology and to serve as a reference for the laboratory analyst. This document is expected to continue to change over time as new knowledge and technologies result in the development of new methods and the modification or retirement of old methods. Part two of the manual documents obsolete methods. It provides a historical perspective, documenting the contributions of many soil scientists who have gone before. Many of these scientists are noted in the section on contributors.

CONTRIBUTORS

Scientists (past and current) and physical science technicians (current) are listed alphabetically. Each has provided lasting and valuable knowledge and insight to human understanding and appreciation of soil science.

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CURRENT METHODS OF ANALYSIS

SAMPLE COLLECTION AND PREPARATION (1)

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1. Introduction to Field Sample Collection and Preparation

Soil map-unit delineations are individual landscape areas defined during a soil survey. Recognized characteristics include landforms, landscape position, parent materials, and soil hydrology. Soil scientists capture these observations and other information through descriptions of soil map units and pedons. These descriptions convey relationships among soil properties, soil horizons, landscapes, geomorphology, and parent materials. Small areas of soil, known as pedons, are observed, described, and classified in detail. Observed pedons are commonly 1 to ≈7 m in size and are chosen to be representative of a map unit (10's to 1,000's hectares). These soils are identified by names that reference the national system of soil taxonomy (Soil Survey Staff, 2014a). Using this information, the United States National Cooperative Soil Survey (NCSS) Program has prepared soil maps for over 95 percent of the country.

Field and laboratory data are used to design map units. The data provide supporting information for scientific documentation and predictions of soil behavior. The coordination of mapping, sampling-site selection, and sample collection contributes to the quality assurance process for laboratory characterization (Burt, 1996). The primary objective of KSSL sampling programs is to select sites and pedons that are representative of a soil series or landscape segment and to collect samples that are representative of horizons within the pedon. In the laboratory, samples are homogenized to obtain a representative soil sample that is used in chemical, physical, and mineralogical analyses. Rigorous effort is made to keep analytical variability small. Because of the high precision of laboratory analyses, the principal variability in characterization data resides in sample variability; i.e., sampling is the precision-limiting variable. As a result, site selection, sample collection, and sample preparation are critical to successful soil analysis.

2. Scope and Field of Application

The objectives of a project or study govern the sampling strategy. A carefully designed sampling plan addresses site selection, depth of sampling, type

and number of samples, details of collection, and sampling and subsampling procedures. A complete description of the sampling site is critical because: (1) it provides a context for the various soil properties determined, and (2) it is useful in the evaluation and interpretation of the soil analytical results (Patterson, 1993). There are various kinds of sampling plans, e.g., intuitive and statistical, and many types of samples, e.g., representative, systematic, random, and composite. The KSSL has routinely used intuitive sampling plans based on the judgment of the field sampling team.

The Geomorphic Description Systems (GDS) is not discussed here. Refer to Wysocki et al., 2000; Schoeneberger et al., 2012; and Schoeneberger and Wysocki, 2012, for discussion of a comprehensive and consistent system for describing geomorphic and landscape attributes for soil survey. Also refer to the Glossary of Landform and Geologic Terms, National Soil Survey Handbook, Part 629 (USDA–NRCS, 2021).

2.1 Geomorphic Considerations for Sampling Sites

Soils form a vital, complex continuum across the landscape. On this landscape level, soils can be segregated into individual areas that have similar properties, and therefore, similar use and management. Soil scientists use multiple scales to study and group soils; these point observations and interpretations can be applied to larger land areas.

The quantitative understanding of soil landscape relationships involves planned, detailed studies (Ruhe et al., 1967; Daniels et al., 1970; Gamble et al., 1970; Parsons et al., 1970; Gile et al., 1981; Lee et al., 2001, 2003a, 2003b). Such studies are an important component of the National Cooperative Soil Survey. They quantify and explain the links between soil patterns and the following: stratigraphy, parent materials, landforms, surface age, landscape position, and hydrology. The required time and effort are significant, but studies of this nature provide the most rigorous, quantitative, and complete information about soil patterns and landscapes.

The occurrence of soils can be accurately predicted and mapped using observable landscape features (e.g., landforms, vegetation, slope position, parent material, bedrock outcrops, stratigraphy, drainage, and photo tonal patterns). During a soil survey, soil scientists develop a knowledge of soil occurrence based on landscape relationships. Soil occurrence is consistently linked to several geomorphic attributes. Among these are landform type, landscape position, parent material distribution, slope shape, slope gradient, and drainage pattern.

Several earth-science sources (Fenneman, 1931, 1938, 1946; Hunt, 1967; Wahrhaftig, 1965) identify and name geomorphic regions, which are grouped by geologic and landform similarity. The value of relating soil patterns to these regions becomes apparent. Such terms as Basin and Range, Piedmont, Columbia Plateau, and Atlantic Coastal Plain provide both geologic and geographic context for communicating regional soil-and-landform knowledge. This breadth of soil landscape knowledge is assembled into block diagrams,

map units, and pedon descriptions. A clear, concise geomorphic description effectively conveys soil location within a landscape to other soil scientists and to landowners.

Preliminary or initial knowledge about soil patterns is commonly based on landscape or geomorphic relationships. Observations during a soil survey refine existing landscape models or sometimes compel and create new models. Crucial problems can be addressed by an appropriately designed study of geomorphology, stratigraphy, or parent material. For example, a silty or sandy mantle over adjacent soils or landforms may be of eolian origin. A well-designed geomorphic study can test this hypothesis. In another geomorphic setting, soil distribution and hydrology may be controlled by stratigraphic relationships rather than by elevation or landscape patterns. A drill core or backhoe pit sequence can confirm or refute this idea.

2.2 Geomorphic Sampling Plan

Any study plan, site selection, or pedon sampling must consider and address the soil geomorphology, which serves several key functions in soil survey. The functions are:

- Provide a scientific basis for quantitatively understanding soil landscape relationships, stratigraphy, parent materials, and site history.
- Provide a geologic and geographic context or framework that explains regional soil patterns.
- Provide a conceptual basis for understanding and reliably predicting soil occurrence at the landscape scale.
- Communicate soil location within a landscape.

Sampled pedons represent a taxonomic unit and a landscape unit; both should be considered in site selection. A sampled landscape unit could be multi-scale. The unit could be a landform (e.g., stream terrace, dune, or drumlin), a geomorphic component (e.g., nose slope), a hillslope position (e.g., footslope), or all of these. A single landscape unit (e.g., backslope) may contain more than one taxonomic unit as well. As an example, soil patterns on landscapes follow catenary relationships. It is important to characterize not only the individual pedon properties but also the soil relationships higher and lower on the landscape. This goal requires that soils be sampled as a catenary sequence (i.e., multiple samples across the same hillslope). This sampling scheme is intensive, but it serves multiple purposes. A sample pedon or set of pedons provide vital characterization data; can quantify the catenary pattern and processes; and can provide an understanding of the entire soil landscape. For a characterization project, the dominant taxonomic unit within a given landscape unit is selected. The existence of other soils or taxa can and should be included in the soil description and the map unit description.

In a characterization project, the sample pedons should be representative of the landscape unit (e.g., stream terrace, backslope) on which they occur.

Every sampled pedon should include a complete description of both soil and geomorphology. In addition to representing the landscape, pedon descriptions and classifications—in conjunction with measured lab data—correlate pedons to named soil map units or a component within the map unit. Soil scientists can reliably scale-up pedon information to soil map units based on experience and the strong linkages among soils, landforms, sediment bodies, and geomorphic processes. Characterization projects are applicable and necessary to the Major Land Resource Area (MLRA) approach to soil survey. Soil survey updates by MLRA can and should involve similar studies.

2.3 Pedon, Water, and Biological Sampling

The pedon is presented in soil taxonomy (Soil Survey Staff, 2014a) as a unit of sampling within a soil. It is the smallest body of one kind of soil large enough to represent the nature and arrangement of horizons and the variability in the other properties that are preserved in samples (Soil Survey Division Staff, 1993). In the NCSS Program, laboratory pedon data is combined with field data (e.g., transects and pedon descriptions) to define map unit components, establish ranges of component properties, establish or modify ranges of properties for soil series, and answer taxonomic and interpretive questions (Wilson et al., 1994).

Water samples are analyzed by the KSSL on a limited basis in support of specific research projects. These projects are typically in conjunction with soil investigations. Examples have involved monitoring seasonal nutrient flux to evaluate movement of nitrogen and phosphorus via subsurface and overland flow from agricultural lands into waterways and wetlands.

Biological samples are also collected for analysis at the KSSL, either in conjunction with pedon sampling or for specific research projects. Measurable biological indices have been considered as a component to assess soil quality (Gregorich et al., 1997; Pankhurst et al., 1997). Many soil biological properties have been evaluated for potential use as indicators of soil quality/health (Doran and Parkin, 1994; Pankhurst et al., 1995). USDA–NRCS has used soil biology and carbon data in macro-nutrient cycling investigations, soil quality determinations, resource assessments, global climate change predictions, long-term soil fertility assessments, erosion impact analyses, conservation management practices, and carbon sequestration (Franks et al., 2001). Soil quality was identified as an emphasis area of USDA–NRCS in 1993.

All USDA–NRCS soil quality publications and technical notes are available at www.soils.usda.gov.

3. Principle

A sampling site that meets the project objectives is selected. The site is georeferenced (Lat/Long, Township/Range, GPS, UTM), and descriptions are made of the site position, geomorphology, and pedons. Complete soil descriptions include observations of soil properties, such as texture, color, slope, and depth,

Figure 1A–1.—Landscape of a site selected for sampling.

soil quality (soil erodibility and productivity), and soil-forming factors (climate, topography, vegetation, and geologic material). The sampled pedons should be representative of the landscape unit and can be multi-scale (fig. 1A–1).

A soil pit is excavated by hand tools or with a backhoe (fig. 1A–2). Soil horizons or zones of uniform morphological characteristics are identified for sampling (fig. 1A–3). After the horizons or layers are identified, photographs are taken of the landform segment and the soil profile. A vertical scale is included (fig. 1A–4).

Representative samples are collected using horizon boundaries to define the vertical limits and lateral short-range variability limits. The horizon or layer samples are collected from the pit face, and samples are homogenized for chemical, physical, and mineralogical analyses. The 20- to 75-mm fraction is sieved, weighed, and discarded. The tag on the sample bag is labeled to identify the site, pedon, and soil horizon.

A series of three clods is collected for bulk density and water retention analysis, and an additional clod is taken for micromorphological analysis (when requested). Clods are taken from the same representative areas of the pit as the bulk sample. Clods used for micromorphology studies should have a nail, staple, or other defining object carefully pressed into the top of clod indicating sample orientation. Clods are placed in specific cells of a clod box, and the box is labeled with site, pedon, and horizon information.

Water samples may be collected for laboratory analyses at the same time as pedon sampling. The site for water sampling is dependent on the purpose of the investigation, local conditions, depth, and the frequency of sampling (Velthorst, 1996). Water samples require expedited transport under ice or gel packs and are refrigerated (4 °C) immediately upon arrival at the laboratory.

Biological samples may also be collected in conjunction with pedon sampling or for specific research projects. Use sampling techniques appropriate to the project when obtaining a representative sample for laboratory analyses. Sampling for root biomass includes selecting a representative site, sampling by horizon, and designating and sampling a sub-horizon if root mass and morphology change. The bulk sample collected for soil mineralogical, physical, and chemical analyses during pedon sampling can also be used for some soil biological analyses. Separate bio-bulk sample material can be collected in the field. Surface litter and O horizons are sampled separately, as with pedon sampling. If certain biological analyses, e.g., microbial biomass, are requested, these samples require expedited transport under ice or gel packs and are refrigerated (4 °C) immediately upon arrival at the laboratory to avoid changes in the microbial communities.

USDA–NRCS field procedures and sampling protocols for samples that do not require analysis at the KSSL are not covered in this manual.

3.1 Interferences

Environmental obstacles can include weather, accessibility, steep terrain, wet terrain, insects, vegetation, and large rock fragments.

Hand excavating the pit face where sampling occurs can cause cross-contamination. Preservation of sample integrity, i.e., avoiding changes or introducing contamination, is important during sampling and transport.

Use non-metallic equipment when sampling for trace element analysis. Extreme care and precision are required for samples that have low natural elemental concentrations.

Some soils irreversibly harden upon drying, which affects some laboratory analyses, such as particle size (Kubota, 1972; Espinoza et al., 1975; and Nanzyo et al., 1993). Soils subject to irreversible changes upon drying should be securely sealed and noted on the sample submission sheets. These steps allow moist sample preparations to be prepared in the lab. High temperatures can also alter microbial populations and activity (Wollum, 1994).

The variable nature of a soil or special problems inherent in the soil, e.g., Vertisols, Histosols, or permafrost-affected soils, may result in the need for specific excavation and sampling techniques. For example, the shear failure that forms slickensides in Vertisols also disrupts the soil to the point that conventional soil horizons do not adequately describe the morphology.

Avoid contamination of water samples; do not touch the inner part of the sample container, screw cap, or sample water. Disposable, powderless gloves

may be used. Water samples are affected by microbial activity, resulting in a change in the concentration of some elements (e.g., nitrate, phosphate, and ammonium); the reduction of sulfate to sulfide and chlorine to chloride; and the loss of iron through precipitation or oxidation (Velthorst, 1996). The addition of microbial inhibitors may be necessary.

Biological samples should be double-bagged in zip-lock plastic bags to prevent loss of water. For most biological samples, plastic bags are adequate. They prevent sample drying but are sufficiently permeable to CO_2 and O_2 that aerobic samples will remain aerobic during transport to the laboratory (Wollum, 1994).

The material type and volume of the container used for a water-sample can affect the analytical results. Polyethylene bottles increase the chlorine content over time or adsorb organic material; errors increase with the permeability of the container; glass bottles release sodium and silicon over time; and a small sample has more contact with the surface of a larger bottle than a small bottle (Velthorst, 1996).

Water-sample containers should be acid washed and capped in the laboratory prior to use in the field. Ceramic sample cups may require an acid pretreatment prior to installation in the field. These cups have a small cation exchange capacity, sorbing dissolved organic carbon and releasing aluminum and silica (Velthorst, 1996).

All samples of water, microbial biomass, and acid sulfate soil should be shipped as soon as possible after collection. Do not allow water samples to freeze, which can influence pH and the separation of dissolved organic matter from the water phase.

4. Apparatus

4.1 Plastic bags, for mixed soil samples

4.2 Tags, for bagged samples

4.3 Plastic bags, 8-mL, for bulk samples

4.4 Plastic bags, 1-mL, for bulk density clods and natural fabric thin section clods

4.5 Clod trunk, accommodates six clod boxes

4.6 Equipment trunk, accommodates equipment to be returned

4.7 Shipping boxes, 18” × 18” × 12”, and associated liners for bulk samples

4.8 Clod boxes, cardboard with dividers

4.9 Heavy duty plier-style S-stapler, with staples

4.10 Hair nets

4.11 Rope

4.12 Clothespins

4.13 Sampling pans

4.14 Sampling knives

4.15 Chisel
4.16 Rock hammer
4.17 Golf tees
4.18 Measuring tape
4.19 Photo tape
4.20 Sieves (3-inch and 20-mm)
4.21 Plastic sheets
4.22 Canvas tarp
4.23 Garden clippers
4.24 Pruning shears
4.25 Bucket
4.26 Scale, 100-lb capacity, for rock fragments
4.27 Containers, with screw caps, acid-washed, for water samples
4.28 Gloves, plastic, powderless
4.29 Bulk density equipment, which is available to NRCS employees upon request, is used if natural clods are not appropriate technique. Examples include bulk density frame or ring excavations, compliant cavity, and cores. (The KSSL can be contacted for more information.)
4.30 Frame, 50 cm x 50 cm. Available to NRCS employees upon request. (The KSSL can be contacted for more information.)

5. Chemicals

5.1 Acetone (CH_3COCH_3) (CAS# 67-64-1)
5.2 Tap water, in spray bottle
5.3 Hydrochloric acid (HCl) (CAS# 7647-01-0), diluted by KSSL
5.4 Saran, polyvinyl dichloride (PVDC) resin. Supplied in premeasured amounts by the KSSL.
5.5 Saran plastic lacquer

Components: Acetone (CH_3COCH_3); saran resin (PVDC)

- Saran is prepared in two resin-to-solvent ratios: 1:4 and 1:7 on a weight basis. Resin is provided in pre-weighed bags by the KSSL.
- In a 3.8-L (1-gal) metal paint, add:
  - 2,700 ±200 mL of acetone (fill to the bottom of handle rivet)
- Add appropriate amount of saran resin for the desired ratio:
  - For a 1:4 ratio saran: Add 540 g of saran resin.
  - For a 1:7 ratio saran: Add 305 g of saran resin.
- Stir plastic lacquer with a wooden stick or spoon for 15 min at 25 °C.
- Store plastic lacquer in covered plastic or steel containers.

- Use the 1:4 plastic lacquer for the initial field coatings.
- Use the 1:7 saran ratio only for samples that have low porosity and permeability. This ratio is used to reduce saran imbibition.

5.6 Hydrochloric acid, 1 *N*

Components: Hydrochloric acid (HCl); RODI water

- HCl is supplied by KSSL at appropriate concentration.
- Review safety data sheets (SDS) before using HCl.

6. Health and Safety

Personal Protective Equipment (PPE).—Disposable gloves with appropriate polymer rating for chemical resistance, work gloves, and safety glasses should be used when appropriate. Field hazards include sharp-edged excavation tools, snake bites, skin irritation from surrounding plants (e.g., poison ivy, oak, or parsnip), and falls.

In accordance with U.S. Department of Labor Occupational Safety and Health Administration (OSHA) standards (available at http://www.osha.gov/), sampling pits deeper than 125 cm (5 feet) must be shored or have one side that is open and sloped upward to prevent entrapment. Take precautions when operating machinery or in the proximity of machinery, e.g., backhoe, drill rig, or hydraulic probe, and when lifting sample bags.

Soil survey regional offices may have additional pit and sampling guidelines designed specifically for their region.

Acetone is highly flammable. Do not use near open flame or electrical equipment. Acetone should be used downwind from a site to keep fumes from collecting in the bottom of the pit. Use extra care when storing and transporting acetone. Refer to the safety data sheets (SDS) for information.

7. Sample Preparation

7.1. Sample collection and preparation are dictated by project focus and objectives. The project objectives and analyses requests are used as a basis for categorizing projects and sampling schemes, which include:

7.1.1 Characterization Projects.—These projects are designed to obtain comprehensive soil characterization data for a representative pedon. They are used for research or map refining purposes. A standard suite of laboratory analyses is performed on each horizon; additional analysis can be requested for pedons of special interest. Samples are collected from each horizon, including:

- Bulk samples of approximately 3 kg
- Three clods for bulk density and water retention and one oriented-micromorphology clod (if requested) for each layer.

7.1.2 Reference Projects.—These projects are designed to answer specific questions. A limited number of analyses specific to the

project focus are performed on these samples. Reference samples include:

- Samples collected from specific horizons in three to five locations that either relate to the sampling question or are representative of the map unit.
- Transect samples used to test map unit composition. An appropriate sample from each transect point may be collected for analyses that are critical for distinguishing between map unit components.
- Samples collected as standards for the survey project based on texture, organic carbon, or for calibration of field office analyses, such as base saturation.
- Samples taken in several locations for analysis to determine the range of a specific soil characteristic within the area of interest and to locate a representative location to be sampled for full characterization.

7.1.3 Geomorphology and Stratigraphy Projects.—These are research projects designed to study relationships between soils, landforms, and stratigraphy of parent materials. Site or pedon selection is governed by the objectives of the study but is often intended to represent typical segments of the landform. Sampling and analytical requests are often similar to those for characterization or reference projects. Core samples may be collected to a depth of several meters using a hydraulic probe.

7.2. Pedon Sampling Schemes include horizon, incremental, and fixed-depth sampling types.

7.2.1 Horizon sampling is the most common of the sampling schemes that are used for comprehensive characterization projects in soil survey.

7.2.2 Incremental sampling is generally limited to special projects and may be used when project objectives (e.g., soil genesis or archeological) require within-horizon detail (Schoeneberger et al., 2012). Incremental samples should be taken within horizons, without crossing horizon boundaries. This sampling method provides more detail than horizon sampling but adds time and expense.

7.2.3 Fixed-depth sampling is used when specified objectives (e.g., surface compaction studies, dynamic soil properties) address properties by fixed depths (e.g., 0 to 5 cm or 5 to 10 cm) instead of by horizons (Schoeneberger et al., 2012). Data collected by fixed-depth sampling are comparable within a study and to other studies employing the same depths. This approach is appropriate for certain purposes but precludes data comparison by horizon. Fixed-depth samples may cross horizons that contain contrasting

materials (e.g., sandy over clayey strata). Resulting data do not represent the horizons and are difficult to interpret. Caution is advised when this approach is used (Schoeneberger et al., 2012).

8. Procedure

8.1. Excavating Pits

8.1.1 Pedons are generally excavated either through the solum and into the parent material or to a maximum depth of 2 meters. Excavate a soil pit by hand or with a backhoe.

8.1.2 Hand-digging may be necessary due to specific characteristics of the site location, type of soil material, or equipment availability (backhoe).

8.1.3 If the pit is more than 150 cm deep (5 feet), follow the appropriate procedures to meet OSHA requirements, including shoring or sloping sides of the pit. Understand and comply with any additional local or regional office requirements.

8.1.4 The depth of sampling may be extended by bucket auger or hydraulic probe as appropriate to meet the objectives of the project.

Figure 1A–2.—Excavated pit for pedon sampling.

8.2. Pit Sampling

8.2.1 The sampling procedure is the same for hand-dug and backhoe pits. Refer to the video "How to Sample Bulk Density in the Field" (https://youtu.be/E7BSZrJ-TDw).

8.2.2 Mark the horizons or zones to be sampled. Begin by collecting a bulk sample. Take a representative sample that extends from boundary to boundary of each horizon. The lateral extent should include the observed short-range variability.

Figure 1A–3.—Soil horizons or zones of uniform morphological characteristics are identified for sampling.

8.2.3 For semi-homogenous soils, place 4 to 5 kg soil on the plastic sheet or canvas tarp.

8.2.4 Mix thoroughly by rolling. Place a representative subsample in a plastic bulk sample bag. The subsample should be approximately 2 kg. Soils that have a high content of organic material or fragments require the sample bag to filled until there is only enough room to close the bag securely.

8.2.5 Label a tag with—at a minimum—soil name, soil survey number, horizon (zone), and depth. Double fold the top of the plastic bag (forward and reverse) and staple the top of the tag under the folds. If the soil has rock fragments in one or more horizons, the soil

Figure 1A–4.—Photographs are typically taken of a soil profile after the layers have been identified but before the vertical section by the sampling process. Note scale in metric units.

and coarse fragments must be sieved and weighed as described below.

8.2.6 Collect three clods for bulk density and water retention from each horizon. Collect them from the same vicinity of the pit as the bulk sample. It is important that these clods be as representative of the bulk sample as possible.

- Carve out a working section in the pit wall to remove an undisturbed block.
- Remove a consolidated piece of soil about 250 to 550 cm^3 in volume (roughly the size of a large potato) from the face of sampling pit. From this piece, prepare a clod by gently cutting or breaking off protruded peaks and compacted material until the clod is about 100 to 200 cm^3 in volume (roughly the size of a fist). If roots are present, trim roots with shears.
- If micromorphology analysis is requested, collect a fourth clod. Press a staple into the top of the clod to denote orientation. Label the appropriate cell on the inside of the

lid of the box to identify the soil survey number and horizon (zone) for the clod.

8.2.7 Using the rope, make a clothesline to hang clods after the initial dip in saran. Place clod in a hairnet. If clod is dry, moisten surface with a fine mist of water. Holding the ends of the hairnet, quickly dip entire clod into plastic saran lacquer (fig. 1A–5). Suspend clod from clothesline to dry (fig. 1A–6). Dry clod for 30 min or until odor of solvent dissipates. When the clod is dry (bottom is not sticky to the touch), place the clod in a plastic bag and then into a cell of a clod box.

Figure 1A–5.—Dipping clods with hairnet in plastic lacquer.

8.2.8 Label the appropriate cell on the inside of the lid of the box to identify the soil survey number and horizon (zone) for the clod. Make sure all cells of the clod box are filled with sample or packing material (such as newspaper) to protect clods during shipping.

8.2.9 If soil is friable and not consolidated, do not use clod method. The following confined core cylinder method may be more appropriate.

Figure 1A–6.—After dipping, clods are tied to clothesline to dry.

8.2.9.1 Press or drive a metal cylinder into the soil.

8.2.9.2 Remove the cylinder, extracting a sample of known volume.

8.2.9.3 Collect three confined cores from each horizon in the same vicinity of the pit as the bulk sample. It is important that these cores be as representative of the bulk sample as possible. Cap the ends of the cylinder and core and provide the core volume in the sample-submission information.

8.2.9.4 Compaction of the sample is a common problem. Compression can be observed by comparing the soil elevation inside the cylinder with the original soil surface outside the cylinder. If compression is excessive, the soil core may not be a valid sample for analysis.

8.2.10 Rock fragments in the soil interfere with core collection.

8.2.11 Dry or hard soils often shatter when the cylinder is hammered into the soil. Pressing the cylinder into the soil reduces the risk of shattering the sample.

8.2.12 Core cylinders and caps are available from the KSSL upon request.

8.2.13 An alternative method for obtaining material for unconfined bulk density measurements involves using a known-volume can or an unconfined cylinder and core.

8.2.13.1 Use a can or cylinder of known volume. Sampling is easier if the bottom of the can has a small hole that allows air to escape as the can is inserted.

8.2.13.2 Smooth a planar area in the pit face. Choose an area that appears representative of the horizon.

8.2.13.3 With the palm of your hand, gently push the can into the smoothed area until the bottom of the can is flush with the wall. If resistance stops you before the bottom of the can is flush with the pit wall, lay a board across the bottom of the can and tap lightly with a hammer or geology pick until the can is flush.

8.2.13.4 Dig out the sampling can plus extra sample and, with a knife blade, smooth off the sample flush with the top of the can.

8.2.13.5 Empty the contents of the can into a plastic bag, tie the top of the bag in a single knot. For smaller samples, place sample bag into a cell in a clod box and label box with sample information. For larger samples, attach a tag with sample information and place the sample in a bulk shipping box liner.

8.2.13.6 Label the appropriate cell on the inside of the lid of the box. Identify the soil survey number and horizon (zone) for the sample. Collect three samples per horizon in separate bags and label each bag.

8.2.13.7 It is critical to write the volume of the can or cylinder on the sample cell of the box and in the sampling notes. It is assumed that there is no volume change with water content in sandy soils. Therefore, one density is representative for all water contents in coarse-textured soils.

8.2.14 Once sampling is complete, tape down and label the top of the clod box. Identify type of sample (clod, core, or thin section) and appropriate sample identification information.

8.2.15 Place six clod boxes in a clod trunk for shipment. If less than six boxes of clods have been collected, then assembled, empty clod boxes can be used as filler in the clod trunk to prevent shifting during shipping.

8.3 Hand Probe Sampling

8.3.1 Remove litter from surface if it is not suitable for coring. Core into soil with minimal compression if possible.

8.3.2 Remove core sections and lay them in order on plastic sheet. Mark horizon breaks on the plastic.

8.3.3 Measure core length against depth in hole to determine if the core has been compressed.

8.3.4 Mix the horizon or zone to be sampled. Place sample in a plastic bag and label with soil survey number, horizon (zone), and depth for the core. Samples need to be a minimum of 500 g (1 pint) and are suitable for a limited number of analyses.

8.4 Hydraulic Probe Sampling

8.4.1 Remove litter that is not suitable for coring from the surface.

8.4.2 Remove core sections and lay in order on plastic sheet. With a sharp knife, trim the exterior to remove any oil and contaminating soil material.

8.4.3 Split one core open to mark horizon breaks on the plastic, describe, and then sample.

8.4.4 Measure core length against depth in hole to determine if the core has been compressed. If the core is 3 inches or more in diameter and has not been compressed, samples for bulk density can be taken from a second core.

8.4.5 Mark an 8-cm long segment on an undisturbed section and slice a cylindrical segment.

8.4.6 Measurements of core diameter and length can be used to calculate volume and density at the field-state water content.

8.4.7 Core segments can be placed in a hair net, dipped once briefly in saran mix to coat the clod, hung from a rope with a clothes pin to dry, placed in a plastic bag, and then put into a cell of a clod box.

8.4.8 Note the core diameter and length in the soil description.

8.4.9 Mix the horizon or zone to be sampled. Place sample in a plastic bag and label with soil survey number, horizon (zone), and depth for the core. Obtain a minimum of 500 g (1 pint) for a reference sample or 2 kg (1-2.5 L) for a characterization sample.

8.5 Bucket Auger Sampling

8.5.1 Remove surface if it is not suitable to be augered.

8.5.2 Remove auger loads and lay them in order on plastic sheet. Where horizon breaks are detected, measure depth in hole and mark it on the plastic. Sampling depth in a pit can be extended using an auger in the pit bottom.

8.5.3 Mix the horizon or zone to be sampled. Place sample in a plastic bag and label with soil survey number, horizon (zone), and depth for the sample. Obtain a minimum of 500 g (1 pint) for a reference sample or 2 kg (1-2.5 L) for a characterization sample.

8.6 Exceptional Pedon Sampling Types

8.6.1 Soils with Rock Fragments

8.6.1.1 If coarse fragments up to 75 mm (3 in) in diameter are to be weighed in the field, weigh the excavated sample in a bucket of known weight (tare).

8.6.1.2 Sieve the sample through both a 75-mm and 20-mm sieve (¾ in) onto a canvas tarp that can be suspended from a scale.

8.6.1.3 Estimate the coarse fragment volume percent of both the 75- to 250-mm (10 in) fraction and >250-mm fraction. Record these values in the description or sampling notes.

8.6.1.4 Weigh the 20- to 75-mm and the <20-mm fractions in pounds or kilograms and record these weights. Weights are calculated to an oven-dry base in the laboratory.

8.6.1.5 Place a minimum of 3 kg (2-2.5 L) in a plastic bag, double fold the bag, and staple. The water content of the sample is determined in the laboratory.

8.6.1.6 If the 20- to 75-mm fraction is not weighed in the field, estimate the volume percent and record the estimate in the sampling notes or description. Refer to method 3A2 of this manual on the analysis of particles >2 mm.

8.6.2 Organic Soils

8.6.2.1 If the soils are drained or the natural water table is below the surface, obtain samples of upper layers from a pit.

8.6.2.2 If the hydraulic conductivity is slow enough, dig and remove samples below the water table as far as safely possible. Place on a plastic sheet in grouping in samples describing and bagging.

8.6.2.3 If consolidated blocks can be removed for bulk density, carve out cubes of known dimension with a minimum of 5 cm on a side. Larger samples result in less variability. Place the block in a plastic bag and tie the top in a knot. Place in a second plastic bag if soil is saturated, tie the top in a knot. Submit three replicate samples for each horizon or layer. Put the double bagged samples in a clod box and label the appropriate cell on the inside. Include the sample identification information and horizon information for the sample. Note the sample dimensions on the sample bags and in the sampling notes.

8.6.2.4 Collect samples below the water table using a Macaulay peat sampler. If the samples appear undisturbed, mark 10-cm segments, slice with a knife, and place a single segment in a plastic bag. Tie the top in a knot, place in a second plastic bag, and tie the top of the second bag in a knot. Submit three replicate samples for each horizon

or layer. Put the double-bagged samples in a clod box. Label the appropriate cell on the inside of the lid with the sample identification information. Document the core diameter and length. The sample shape is a half-cylinder.

8.6.2.4.1 As an alternative, carve a block to fit snugly in a tared water can. Place the lid on the can; put the can in a plastic bag; tie the top of the bag; and put the bag in a clod box. Identify the can number, depth, and tare weight in sampling notes. Take replicate samples for the mixed sample, as necessary.

8.6.2.5 Large samples can be taken below the water table by removing the surface mat with a spade and sampling lower layers with a post-hole digger. Place samples of each layer on plastic for examination. Transfer samples to small plastic bags and knead to remove air. Put three small bags of sample into one large plastic bag, fold the top, staple, and tag.

8.6.3 Sulfidic Soil Materials

8.6.3.1 These materials, as defined in the "Keys to Soil Taxonomy" (Soil Survey Staff, 2014a), commonly occur in intra-tidal zones adjacent to oceans and are saturated most or all of the time.

8.6.3.2 Due to the potential for rapidly changing sample conditions, test soil pH at the field site to establish the initial or in-situ pH. Record the initial pH on the pedon information sheet. This measurement is necessary as a reference for QC of chemical analyses. Field tests can be used for determining if samples possess reactive iron sulfide. Monosulfides react very rapidly when exposed to air, even when refrigerated.

8.6.3.3 On sample labels and sample documentation, identify the samples as needing oxidized pH and 1:5 EC. Provide advance notification to the laboratory that sulfidic samples are being submitted. The samples should be analyzed immediately when received to establish the initial pH, which is considered to be the in-situ pH.

8.6.3.4 Use containers with an airtight cover. Completely fill containers with soil and ambient water. Seal the containers with parafilm provided by the Lab.

8.6.3.5 Ship the samples to the KSSL in a cooler immediately after sampling. If containers cannot be shipped immediately, freeze the samples until shipping is possible.

8.6.3.6 Sulfidic soil samples should be analyzed immediately upon arrival at the laboratory. If analysis cannot be started immediately, samples should be frozen.

8.6.4 Permafrost Soils

8.6.4.1 Permafrost is very resistant to excavation, and the cryoturbation disrupts horizon morphology.

8.6.4.2 In many cases, the surface layers are organic materials that can be carved out and removed with a sharp knife or shovel. Save the large chunks, if possible.

8.6.4.3 Test the depth to the frost table with a small (1 to 2 mm) diameter steel rod. Excavate a small pit (about 0.7 by 1.3 m) such that about 10 cm of unfrozen material is over the permafrost. If a cyclic pattern (up to a few meters) is evident in the surface topography, extend the pit through at least one cycle to the depth of sampling. Record the morphology of the unfrozen soil before the permafrost is disturbed. If the soil is disrupted to the extent that lateral horizons do not represent the morphology, impose a grid over the pit face and sketch the morphology on graph paper.

8.6.4.4 Describe the soil down to the frost table. Examine the surface. Designate horizons. When the description of the unfrozen material is complete, remove all unfrozen material to examine the conformation of the frost table. Document on graph paper if necessary and photograph.

8.6.4.5 Frozen earth can be removed in successive steps with a gasoline-powered jackhammer. Place pieces from each step on a separate plastic sheet. Examine pieces and describe the morphology as they are removed. Note thickness of segregated ice lenses and make a visual estimate of relative volume of segregated ice. Place representative pieces into a water-tight container so that the sample can be weighed, dried, and weighed again to calculate the amount of water and volume of ice. Excavate to a depth of 30 to 50 cm below the frost table, if practical. Be ready to photograph immediately and then clean off the pit face. Sample each horizon or zone for mixed sample, bulk density, and thin section as practical.

8.6.5 Vertisols

8.6.5.1 Dig a trench long enough to cover two or three cycles of morphological expression. From the bottom of the trench, remove soil from the nonwork face so it slopes up and away.

8.6.5.1.1 One convention is to sample pedons out of the low and the high areas, which represent extremes in the cyclic morphology. A gilgai surface topography is reflected in the subsurface by bowl-shaped lows and highs.

8.6.5.1.2 The shear failure that forms slickensides in Vertisols also disrupts the soil to the point that conventional horizons do not adequately describe the morphology. To examine morphology and associated soil properties in more spatial detail, use nails and string to create morphological cells for description.

8.6.5.2 Assign a number and a horizon designation to each cell.

8.6.5.3 Construct a level line about 1 meter below the highest point on the surface. Hammer a spike into the wall at one end of the pit. Tie a loop in string, place the loop over the spike, and run the string to the far end of the pit. Place a line level on the string, tie another loop in the string, place a second spike through the loop, pull the string taut, raise or lower the spike until the string is level, and hammer the spike into the pit face.

8.6.5.4 Place a marker at each meter along the string from one end to the other. Transfer the morphology outlined by the string to graph paper by measuring the x-coordinate along the string and the y-coordinate above or below the string. Measure in centimeters.

8.6.5.5 Sample each cell for characterization analysis as described above. The sampling scheme can include traditional pedon sequences by sampling vertical sequences of cells at low, high, and intermediate positions along the cycle.

8.6.6 Subaqueous Soils

8.6.6.1 Detailed instructions for sampling subaqueous soils are provided in chapter 10 of the “Soil Survey Manual” (Soil Science Division Staff, 2017). Soils are described and classified using USDA–NRCS soil survey methods (Soil Survey Staff, 2014a; Schoeneberger et al., 2012).

8.6.6.2 Soils are sampled using a standard bucket auger, Macaulay peat sampler, or vibracorer.

8.6.6.3 Common measurements in a subaqueous soil survey include, but are not limited to, bathymetry, water-quality measurements (e.g., pH, dissolved oxygen, salinity water temperature), and soil-quality measurements

(e.g., reaction to H_2O_2, reaction by oxidized pH, fluidity, electrical conductivity, bulk density satiated).

8.6.6.4 For more information on water column measurements, soil profile descriptions, and soil profile measurements, refer to Schoeneberger et al. (2012). For additional information on subaqueous soils, refer to Demas and Rabenhorst (1999), Bradley and Stolt (2003), and Erich et al. (2010).

8.6.7 Biological Samples

8.6.7.1 Biological samples can be collected for laboratory analysis, either in conjunction with pedon sampling or for specific research projects.

8.6.7.2 The plants at the site at the time of sampling for above-ground biomass should be identified. Identification can be conducted either in the field or later using a plant identification key. Identification is needed to determine which plants are associated with the soil microbial communities.

8.6.7.3 Typically, a 50 cm x 50 cm area is sampled. All above ground biomass vegetation is clipped to the soil surface and separated by genus or species and by live and dead fractions.

8.6.7.4 Each plant fraction is identified, weighed, dried, and reweighed to determine above-ground biomass

8.6.7.5 Sampling for root biomass includes selecting a representative site, sampling by horizon, and designating and sampling a subhorizon if root mass and morphology change. The sampling area is approximately 1 m^2. The samples are weighed, dried, and reweighed to determine root biomass. Typically, the roots are separated by hand sieving at the laboratory.

8.6.7.6 The bulk sample collected during pedon sampling for mineralogical, physical, and chemical analyses can also be used for some soil biological analyses, e.g., particulate organic matter (POM) and total N, C, and S. Alternatively, a separate bio-bulk sample can be collected in the field.

8.6.7.7 As with pedon sampling, surface litter and O horizons are sampled separately for bulk density determinations by cutting out a 50 cm x 50 cm area in a square to a measured depth.

8.6.7.8 Include replicate samples in the sampling plan. The primary purposes of the replicate samples are to identify

and quantify the variability in all or part of the sampling and analysis system.

8.6.7.9 Properly label samples to show important information; e.g., layer identification, soil, depth, and horizon.

8.6.7.10 If certain biological analyses, e.g., microbial biomass, are requested, the samples require expedited transport under ice or gel packs. The samples are refrigerated (4 °C) immediately upon arrival at the laboratory to avoid changes in the microbial communities.

8.6.8 Water Samples

8.6.8.1 Typically, NRCS projects that require collection of water samples are performed in conjunction with pedon sampling or for specific research projects. Choice of a water-sampling site depends not only on the purpose of the investigation but also on local conditions, depth, and frequency of sampling (Velthorst, 1996). Specific recommendations for sample collection are not applicable. Use proper gear and best judgement regarding the sampling site and local conditions.

8.6.8.2 Before collecting the water samples in the field, rinse the containers several times with the sample water. Completely fill the container and screw cap with the sample water. Wear disposable gloves to avoid touching the sample water, the inner part of the container, or the screw cap. Collect a representative sample for use in laboratory analyses.

8.6.8.3 The amount and composition of water samples vary strongly with small changes in location. Preserve samples in the field-state until analysis at the laboratory.

8.6.8.4 Include blank samples in the sampling plan. The primary purpose of blank samples is to identify potential sources of sample contamination and assess the magnitude of contamination with respect to concentration of target analytes.

8.6.8.5 Include replicate samples in the sampling plan. The primary purposes of the replicate samples are to identify and quantify the variability in all or part of the sampling and analysis system.

8.6.8.6 Refer to Wilde et al. (1993) for more detailed descriptions of the purpose and processing procedures for blanks and replicate samples.

8.6.8.7 Properly label sample containers to indicate sample ID, location, depth, and time. Water samples require

expedited transport under ice or gel packs. The samples are refrigerated (4 °C) immediately upon arrival at the laboratory.

8.6.8.8 Some water analyses, e.g., electrical conductivity, total C, and inorganic C, must be performed promptly because optimal preservation is not possible (Velthorst, 1996). Upon completion of carbon and EC analyses, sample filtration (0.45-µm membrane) is used to separate dissolved from suspended material. The sample is then split into two subsamples. One is acidified to pH 2 for cation analyses (e.g., Al, Fe, Mn), and the other is used for anion analyses. These other water analyses also need to be performed as promptly as possible.

9. Calculations

Record information as requested for specific tests or sampling methods. No calculations are required. Laboratory data is calculated and reported according to specific analysis method codes.

10. Quality Assurance/Quality Control

10.1 Assess plausibility of test sample data in context of expected soil profile trends.

10.2 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.3 Assign overall project data to soil data quality specialist.

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Laboratory Sample Collection and Preparation (1B)
Soil (1B1)
Samples (1B1a)

The purpose of any soil sample is to obtain information about a particular soil and its characteristics. Sampling provides a means to estimate the parameters of these soil characteristics with an acceptable accuracy at the lowest possible cost (Petersen and Calvin, 1986). Subsampling also may be used, as it permits the estimation of some characteristics of the larger sampling unit without the necessity of measurement of the entire unit. Subsampling reduces the cost of the investigation, but usually decreases the precision with which the soil characteristics are estimated. Efficient use of subsampling depends on a balance between cost and precision (Petersen and Calvin, 1986).

Soil variability and sample size are interferences to sample collection and preparation. The objective of laboratory preparation is to homogenize the soil samples used in chemical, physical, and mineralogical analyses. At each stage of sampling, an additional component of variability, the variability within the larger units, is added to the sampling error (Petersen and Calvin, 1986). Soil material needs to be adequate in amount and thoroughly mixed to obtain a representative sample.

KSSL receives bulk soil samples from across the United States and internationally for a wide variety of chemical, physical, and mineralogical analyses. KSSL also typically receives natural fabrics, clods, and cores. Undisturbed clods are used to investigate micromorphology and determine some physical properties, e.g., bulk density.

Laboratory Sample Collection and Preparation (1B)
Soil (1B1)
Samples (1B1a)
Bulk Samples (1B1a1)

Laboratory identification numbers and preparation codes are assigned to bulk soil samples. These identification numbers are unique client- and laboratory-assigned numbers that carry important information about the soil sample (e.g., pedon, soil horizon, location, and year sampled). Laboratory preparation codes depend on the properties of the sample and on the requested analyses. These codes carry generalized information about the characteristics of the analyzed fraction, i.e., the water content (e.g., air-dry, field-moist) and the original and final particle-size fraction (e.g., sieved <2-mm fraction processed to 75 µm). By inference, the codes also carry the type of analyses performed. Identification numbers and preparation codes are reported on the KSSL Primary Characterization Data Sheets. Refer to the Soil Survey Investigations Report No. 45, “Soil Survey Laboratory Information Manual” (Soil Survey Staff, 2011), for a

detailed explanation of sample identification numbers. Since the publication of SSIR No. 42, version 3 (1996), these preparation codes have been significantly revised. Detailed information on the current preparation codes as they appear on the Primary Characterization Data Sheets may be obtained from the KSSL upon request.

All soils from quarantined areas are strictly controlled under quarantine regulations 7 CFR 330 of the United States Department of Agriculture, Animal and Plant Health Inspection Service (APHIS). For information regarding preparation methods of soil bulk samples, proceed to 1B1b.

Laboratory Sample Collection and Preparation (1B)
Soil (1B1)
Samples (1B1a)
Clods (1B1a2)

Clod samples are intact sections of soil taken from soil horizons. They are collected with the objectives of retaining the in-situ physical and morphological characteristics of that soil layer and representing the soil layer in physical analyses, including determination of bulk density and water retention. Clod samples are coated with plastic resin in the field to preserve the sample during collection and shipping. Details for collection and preparation of clod samples are described in the respective bulk density and water retention procedures. Oriented clods are marked (usually with a staple or tack on the top side) to indicate their original directional orientation and are used to prepare thin sections for micromorphological examination. Sampling procedures are described in the respective methods.

Laboratory Sample Collection and Preparation (1B)
Soil (1B1)
Samples (1B1a)
Cores (1B1a3)

Soil cores are samples taken with a known-volume cylinder that is pushed or driven into the soil. The cylinder or ring is inserted so that it is filled with minimal disturbance, compacting, or loosening of the soil sample. The ends are smoothed so that the sample volume equals the volume of the cylinder. If the cylinder is not filled completely, the height of the soil sample is measured and used to calculate the actual volume. The mass of the core sample is determined and used to calculate bulk density. Two approaches are available for transporting, drying, and weighing the core sample. (1) The sample is kept in the cylinder. The ends are capped, and the sample is transported to the laboratory to be dried and weighed while still in the cylinder. This is designated as a “soil core” sample. (2) Alternatively, the volume of the sample is recorded, and the sample is removed

from the core or ring and bagged. The bagged sample is transported to the lab, dried, and weighed. The weight is used to calculate the bulk density. The bagged sample is designated as a “field core.”

Laboratory Sample Collection and Preparation (1B)
Soil (1B1)
Samples (1B1a)
Cores (1B1a3)
Soil Cores (1B1a3a)

Soil cores are samples taken with a cylinder or ring and which remain in the sampling cylinder (which is capped). They are transported, dried, and weighed while in the cylinder. The volume or dimensions of the cylinder are submitted with information accompanying the sample. The weight of the empty cylinder is determined and subtracted to calculate the mass of the sample. Soil cores may also be used for water retention analyses. Detailed sampling procedures are described with the respective analytical methods.

Laboratory Sample Collection and Preparation (1B)
Soil (1B1)
Samples (1B1a)
Cores (1B1a3)
Field Cores (1B1a3b)

Field cores are samples taken with a cylinder or ring and then removed from the cylinder before being bagged, transported, dried, and weighed. The volume of the core and sample is recorded and submitted with information accompanying the sample. The weight of the sample is determined and used to calculate the bulk density of the sample. This sample type includes core samples taken with rings, with known-volume cans, or with Giddings, vibracore, Macaulay, or similar tube or probe samplers. Detailed sampling procedures are described with the respective analytical methods or equipment.

Laboratory Sample Collection and Preparation (1B)
Soil (1B1)
Samples (1B1a)
Syringe (1B1a4)

A syringe sample is collected with an open-ended syringe that has a known volume. The volume of the sample is recorded, and the sample is injected into a bag, oven dried, and weighed. The bulk density is calculated from the volume and oven-dry weight. Most commonly, syringe samples are taken as subsamples from saturated subaqueous samples, including those from vibracores and Macaulay

samplers. The subsamples are used to calculate satiated bulk density. Detailed sampling procedures are included with the respective analytical and equipment procedures

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Laboratory Sample Collection and Preparation (1B)
Soil (1B1)
Samples (1B1a)
Compliant Cavity (1B1a5)

The Compliant Cavity method code also applies to Ring Excavation and Frame Excavation. Samples are taken by excavating soil from a horizontal surface. Volume of the sample is determined by filling the lined excavation with a measured volume of water in the compliant cavity method, or by measuring and calculating the elevation of the surface before and after excavation and calculating the volume from the change in elevation (ring and frame methods). The excavated sample is bagged, transported, oven dried, and weighed. The calculated volume is submitted with the sample. If rock fragments are present, the weight and volume of >2-mm material in the sample are corrected and bulk density is computed. Refer to the analytical methods for the detailed procedures. Excavation procedures (e.g., compliant cavity, ring, and frame) have applicability to layers that can be described as cohesionless, that have a high content of rock fragments >5 mm, or thin (<5 cm thick) and for which the clod method is unsuitable (Grossman and Reinsch, 2002).

Laboratory Sample Collection and Preparation (1B)
Soil (1B1)
Samples (1B1a)
Block (1B1a6)

Block samples are undisturbed rectangular sections cut from organic soil material. Block sampling can be applicable in fibrous organic materials. Appropriate tools, including sharp or serrated knives or sawing edges, and careful sampling are required to cut block samples. Such tools are necessary to prevent compressing, loosening, or disturbing the sample and to obtain uniform dimensions. The dimensions of the block are measured, and volume is calculated. If the shapes of blocks are not uniform, multiple measurements and averaging are necessary. (Error in measurement of smaller blocks has a relatively greater effect in calculated bulk density; therefore, blocks should be as large as practicable to minimize error related to measurement.) Dimensions, volume, or both are submitted with the sample for calculation of bulk density. Samples are bagged and transported to the lab. Oven-dried (OD) weight and bulk density (Db) are calculated. Refer to analytical and sampling methods for detailed sampling procedures.

Laboratory Sample Collection and Preparation (1B)
Soil (1B1)
Samples (1B1a)
Hole Saw (1B1a7)

Hole-saw samples are undisturbed sections of organic soil material that are cut with a hole saw or similar cylindrical cutting device. Hole-saw samples are applicable in fibrous organic horizons similarly to block samples. Hole-saw samples are cylinders or discs. The samples are taken from a flat surface so that the sampling surface is the top of the disc. The bottom of the hole-saw sample is cut even with the cutting cylinder to form the bottom of the disc sample. The dimensions that are needed for calculation of the volume of a hole-saw sample are either radius or diameter and either height or thickness. Dimensions, volume, or both are submitted with the sample for calculation of bulk density. Samples are bagged, transported, and oven dried, and bulk density is calculated. Refer to applicable sampling guidelines for detailed sampling procedures.

Laboratory Sample Collection and Preparation (1B)
Soil (1B1)
Samples (1B1a)
Macaulay (1B1a8)

Macaulay samples are sections taken with a Macaulay sampler (which may also be referred to as a peat sampler). The Macaulay sampler includes a partially open tube with a cutting edge. It is inserted into the layer to be sampled and rotated to cut a section equivalent to a core sample. The sampler also has a mechanism that closes the tube around the sample, which allows the sample to remain intact during extraction. The Macaulay sampler obtains intact samples from saturated and submerged horizons consisting of organic or poorly consolidated soil materials. Macauley samples obtained to determine bulk density should be intact and not distorted by the collection procedure. Samples are removed from the sampling tube. Sample volume, dimensions, or both are recorded and submitted with the bagged sample. Care must be taken when measuring the core to account for any distortion of the sample. Refer to applicable sampling guidelines for detailed sampling procedures.

Laboratory Sample Collection and Preparation (1B)
Soil (1B1)
Samples (1B1a)
Undisturbed (1B1a9)

Undisturbed samples are bulk samples that have been taken in a manner that minimizes disturbance of soil aggregates, which are measured in an

aggregate stability procedure (soil aggregates <2 mm). Samples are taken from an undisturbed pit face or other undisturbed source. They are packaged and transported in a box or rigid container. Samples are air dried with no physical processing and are used directly in the aggregate stability procedure. Detailed sampling procedures are described with the analytical procedures.

Laboratory Sample Collection and Preparation (1B)

Soil (1B1)

Soil Sample Preparation (1B1b)

Once samples are received at the laboratory, the pedon ID, field sample number, and sample format are recorded in the Laboratory Information Management System (LIMS). All samples belonging to a specific pedon and layer are recorded in the LIMS. The Pedon ID serves as a heading for the samples collected at that site. Folloing are two examples of project sites and subordinate layers. The first example shows the tiered system for recording Characterization projects (fig. 1B1b–1). The second example illustrates a subaqueous sampling project (fig. 1B1b–2). The sample format is reflected for each sample and layer.

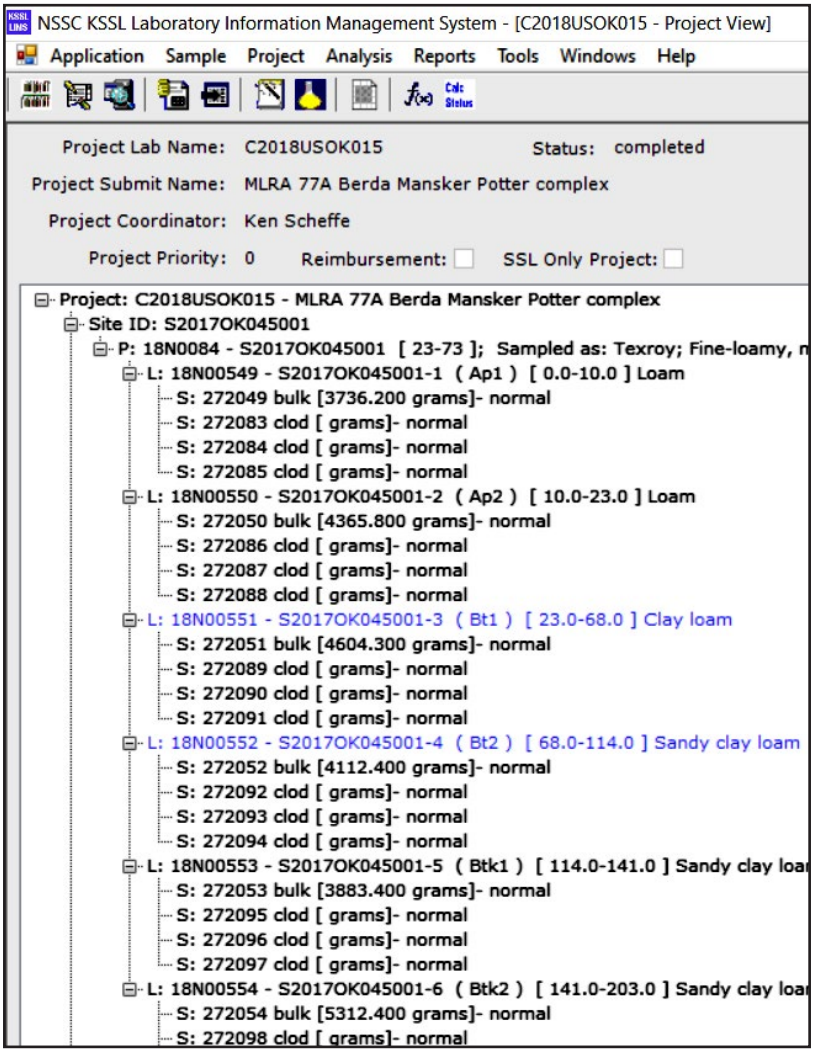

Figure 1B1b–1.—Screen capture showing the tiered system of laboratory sample documentation prior to preparation. Characterization projects include bulk samples and a series of clods for each layer.

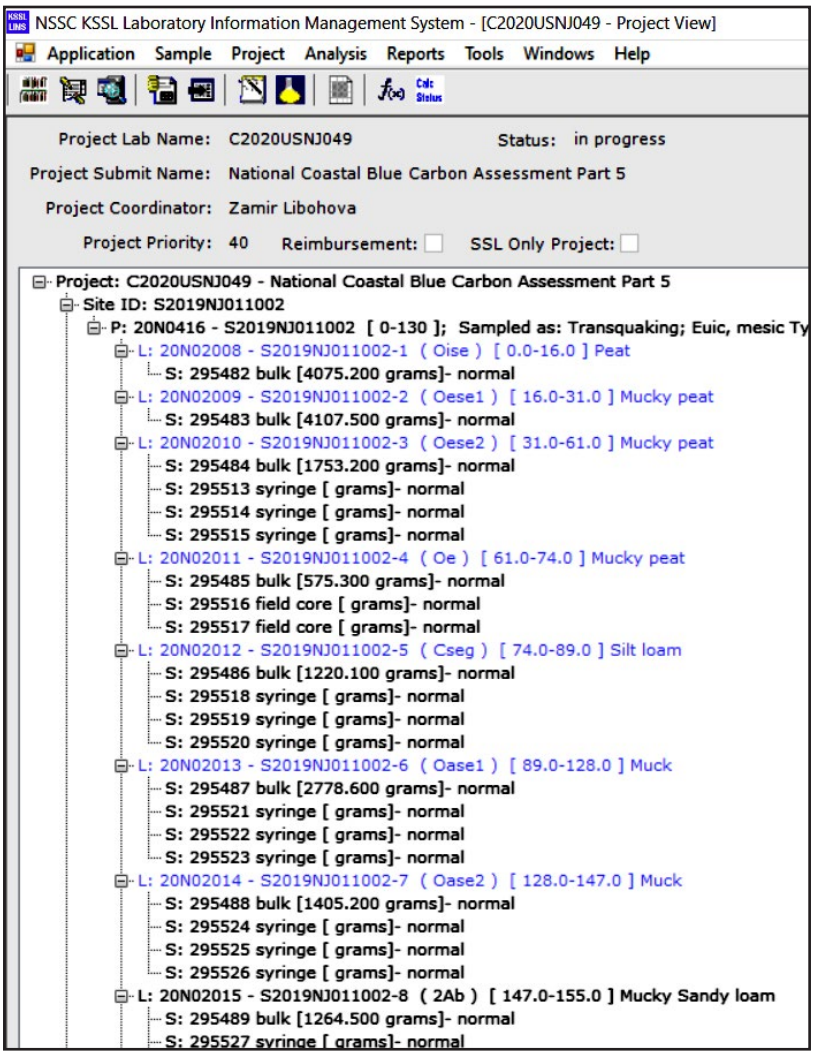

Figure 1B1b–2.—Screen capture illustrating sample documentation of a subaqueous project showing the bulk sample and syringe samples for each layer.

A bulk sample may be processed into four different sample formats to accommodate specific analyses. Preparation codes are recorded for each sample.

All soils from quarantined areas are strictly controlled under quarantine regulations 7 CFR 330 of the United States Department of Agriculture, Animal and Plant Health Inspection Service (APHIS). For preparation methods for soil bulk samples, proceed to 1B1b.

Laboratory Sample Collection and Preparation (1B)
Soil (1B1)
Soil Sample Preparation (1B1b)
Standard Chemical, Physical, and Mineralogical Analysis (1B1b2b)

1. Introduction to Soil Sample Collection and Preparation

A soil sample received from the field undergoes several laboratory subsample preparations based on analytical requests and type of materials. This method focuses on the <2-mm sample processing, the most common preparation procedure requested for laboratory analyses.

2. Scope and Field of Application

For routine soil analyses, most U.S. and Canadian laboratories homogenize and process samples to pass a 2-mm sieve (Bates, 1993). Knowing the quantity of fragments >2 mm in a sample is necessary for such applications as available water capacity and linear extensibility. However, laboratory analyses of soil samples are generally performed on the air-dry, fine-earth (<2-mm) fraction. This fraction possesses the optimum water content for handling and processing soil.

3. Principle

A field-state, whole-soil sample is prepared in the laboratory based on the analyses that are requested and the properties of the sample. For most standard chemical, physical, and mineralogical analyses, the field sample is air-dried, crushed, and sieved to <2 mm.

The >2-mm material is sieved from the fine-earth fraction, and weights are recorded for the 20- to 75-mm, 5- to 20-mm, and 2- to 5-mm fractions. Fragments >2 mm are excluded from most chemical, physical, and mineralogical analyses. Exceptions include samples containing carbonate- or gypsum-indurated coarse fragments or material from Cr and R layers.

3.1 Interferences

Soil material needs to be thoroughly mixed to obtain a representative sample, particularly in samples that have limited size and large soil variability.

At each stage of sampling, an additional component of variability, the variability among smaller elements within the larger units, is added to the sampling error (Petersen and Calvin, 1986).

To ensure a representative sample, collect three times the amount of organic sample in relation to mineral soils.

4. Apparatus

4.1 Electronic Balance, ±1-g sensitivity and 15-kg capacity

4.2 Cardboard sample boxes for sample storage and working pint samples

4.3 Trays, fiberglass or heat-resistant plastic, tared

4.4 Sieves, square-hole, stainless steel

- **4.4.1** 80 mesh, 180 µm
- **4.4.2** 10 mesh, 2 mm
- **4.4.3** 4 mesh, 4.75 mm
- **4.4.4** 19 mm, ¾ in
- **4.4.5** 76 mm, 3 in

4.5 Wooden roller, 25 cm long x 15 cm diameter, custom made. (The KSSL can be contacted for more information.) See fig. 1B1b2b–1.

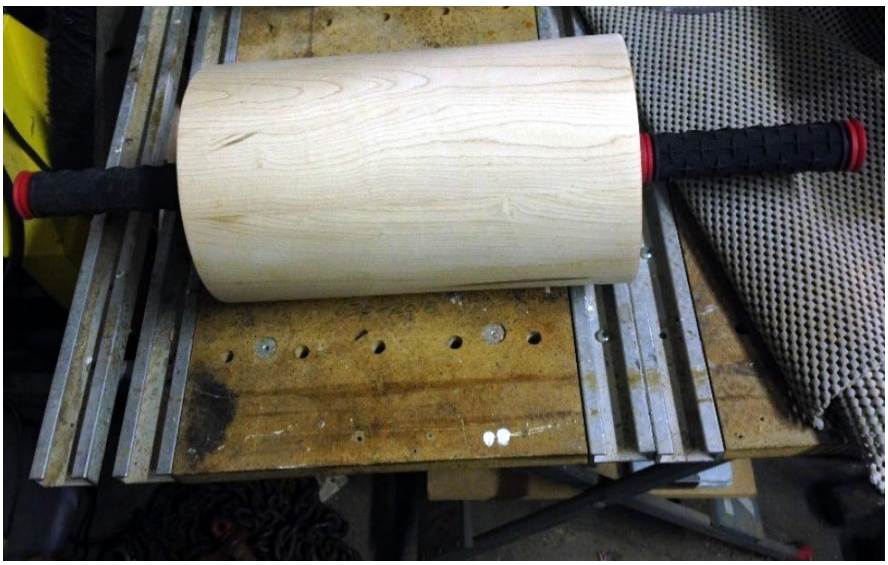

Figure 1B1b2b–1.—Wooden sample roller, custom made for KSSL.

4.6 Rubber rollers, soft and hard polymer, 3 cm long x 10 cm diameter and 5 cm long x 10 cm diameter, custom made (fig. 1B1b2b–2). (The KSSL can be contacted for more information.)

4.7 3–5 lb drilling or club hammer (fig. 1B1b2b–2)

4.8 Laboratory jaw crusher, floor model, adjustable plate

4.9 Downdraft table grinding bench, 3 ft x 6 ft (0.91 m x 1.8 m)

4.10 Metal plate for grinding bench, 76 cm x 76 cm x 0.5 cm

4.11 Containers, paper, 12-oz, with lids

4.12 Containers, plastic, 1-pint, 1-oz, 4-oz, 8-oz, with tops

4.13 Scintillation glass vials, 20-mL

Figure 1B1b2b–2.—Hammer and rubber rollers, custom made for KSSL.

4.14 Metal weighing cans, 2-oz

4.15 Brown kraft paper

4.16 Flat-bottom sample scoop, stainless steel

4.17 Air compressor

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Sodium hexametaphosphate solution

Components: Sodium carbonate (Na_2CO_3) (CAS# 497-9-8); sodium hexametaphosphate $(NaPO_3)_6$ (CAS# 68915-31-1), reagent grade; RO water

- In a 1-L polyethylene bottle, add the following in order:
  - 1 L of RO water
  - 35.7 g of $(NaPO_3)_6$
  - 7.94 g of Na_2CO_3
- Invert to mix.

6. Health and Safety

Personal Protective Equipment (PPE).—ANSI approved safety glasses are provided and must be worn when processing samples. Use disposable gloves with appropriate polymer rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling

reagents or samples. Keep clothing and hands away from the crusher and mill when these machines are in use.

Dust from the sample processing can irritate sinuses, lungs, and eyes. Engineering measures are provided in the sample processing area to keep dust levels below OSHA established limits. When samples are processed, the overhead ventilation canopy and the flexible arm filter boxes must be on and adjusted closely to the actual working area at all times. NIOSH N95 half masks are optional but if used should be fitted and worn properly. Draw-down tables are also installed for optional use in processing areas.

7. Sample Preparation

This method describes the procedures for <2-mm air-dry samples. The weight of air-dry soil remains relatively constant. Biological activity is low during storage. Refer to subordinate methods for finer size fraction, moist soil, and whole soil.

8. Procedure

8.1 Initial sample weights are entered into the Laboratory Information Management System (LIMS) when projects are logged in.

8.2 Organize samples according to sample number.

8.3 Record bagged sample weight in whole grams.

8.4 Remove soil sample from sample bag and distribute on a fiberglass tray. Record the tared tray number. Place sample tag on tray with moist sample. (fig. 1B1b2b–3)

Figure 1B1b2b–3.—Sample prepared for drying with tared tray and sample tag.

8.5 If moist samples are required for project analysis, refer to appropriate method below before proceeding.

8.5.1 Field-Moist Whole-Soil method: 1B1b1a

8.5.2 Moist Chemical and Selected Physical Analysis: 1B1b1b1

8.5.3 Moist Atterberg Limits: 1B1b1c1

8.6 Air dry the bulk sample on tared tray in an oven at 35 °C for 2 to 4 days. Additional drying time may be required depending on sample moisture content and composition.

8.7 Create labeled containers for each requested <2-mm air-dried sample preparation and for any subsamples that require smaller size fractions.

8.8 Remove sample from drying oven and record weight of sample and tared tray.

8.9 Collect bulk archive storage sample by selecting sample from several areas of the tray to collect a representative subsample. Store soil sample in 12-oz paper container.

8.10 If >2-mm sample is required for project analysis, refer to appropriate method below before proceeding.

8.10.1 2–20 mm carbonate and/or gypsum indurated fragments: 1B1b2f1a1a

8.10.2 2–20 mm lithic fragments or pararock: 1B1b2f1a2a

8.10.3 Analysis for materials from Cr horizon or R layer: 1B1b2f1b1a

8.11 Process sample to <2 mm by placing a large piece of folded brown kraft paper over metal grinding plate on a downdraft grinding table (fig. 1B1b2b–4).

Figure 1B1b2b–4.—Unprocessed sample on downdraft table.

8.12 Place sample on top of brown kraft paper; the fiberglass tray is no longer needed. Use kraft paper as a sling and pour sample through sieve stack. Shake sieve stack to distribute sample through the stack. Rock fragments retained on each sieve should be placed in a pan for that sieve size fraction and set aside (fig. 1B1b2b–5). Place soil aggregates retained on sieves back onto brown paper.

Figure 1B1b2b–5.—Rock fragments collected during sieving; collect weight of each size fraction after grinding soil sample is complete.

8.13 Disaggregate soil sample on flat, metal plate covered with brown kraft paper using rollers or hammers. Tips for sample processing:

- Use least aggressive method possible for disaggregating. Use a hammer only if samples are resistant to rolling.
- Use floor model adjustable plate jaw crusher for hard clay samples that do not possess rock fragments.
- Try not to break rock fragments or concretions/nodules when rolling samples. For samples that have easily crushed coarse fragments, use the softest roller available.
- Roll and sieve until only the coarse fragments that do not slake in sodium hexametaphosphate solution remain on 2-mm sieve.
- Roll and sieve frequently. The <2-mm material can act as a cushion making it more difficult to break apart aggregates.

8.14 Process samples until all soil aggregates are <2-mm or remaining material on 2–5-mm sieve is a candidate for slaking.

8.15 Record weight of fragments retained on 20- to 75-mm, 5- to 20-mm, and 2- to 5-mm sieves.

8.15.1 Method codes for recording fragment weights are as follows:

- Particle-size analysis: 1B1b2f1
- Particle-size analysis, fragments recorded: 1B1b2f1a
- Particle-size analysis, fragments not recorded: 1B1b2f1b. Method is specifically requested if only the <2-mm soil is of concern for the project focus.

8.15.2 All analytical results are reported on a <2-mm basis.

8.16 Thoroughly mix <2-mm sample retained in bottom pan of sieve stack by moving the soil from the corners to the middle of the kraft paper, homogenizing the sample (fig. 1B1b2b–6).

Figure 1B1b2b–6.—Homogenized <2-mm processed soil sample ready for subsampling.

8.17 Analyses that use <2-mm air-dried sample and subsample information are as follows:

8.17.1 <2-mm working pint. Ensure the processed sample is well mixed. Use flat-bottomed stainless-steel scoop to fill 12-oz lidded paper container. Subsamples from this pint are used for most <2-mm laboratory analyses. Examples include cation exchange capacity, particle size distribution analysis, and Mehlich-3 phosphorus.

8.17.2 Air-dry/oven-dry (AD/OD) ratio. Ensure the processed sample is well mixed. Select a representative subsample and scoop ≈20 g of sample into a stamped, tared, 2-oz metal weighing can. AD/OD ratio is required for most sample analysis calculations. Only projects that do not use air-dried samples are exempt.

8.17.3 Saturated paste salt analysis. Ensure the processed sample is well mixed. Select a representative subsample and scoop ≈250 g of sample into a lidded plastic container. Leave space for water during sample preparation.

8.17.4 Visible and near-infrared diffuse reflectance spectroscopy (VNIR–DRS). Ensure the processed sample is well mixed. Select a representative subsample and scoop sample into a labeled 1-oz plastic cup.

8.18 For analyses requiring smaller size fractions, collect <2-mm sample in a glass scintillation vial and refer to the following methods.

8.18.1 Method 1B1b2c1, processing to 40 mesh. Example analysis: Atterberg limits.

8.18.2 Method 1B1b2d, processing to 80 mesh (≈180 µm). Example analyses: total carbon, nitrogen, and sulfur (CNS); mid-infrared diffuse reflectance Fourier transform spectroscopy (MIR–DRIFTS); and calcium carbonate equivalent (CCE).

8.18.3 Method 1B1b2e1, processing to 200 mesh. Example analyses: total major elements and trace elements.

8.19 Record weights of fragments collected on the 20- to 75-mm, 5- to 20-mm, and 2- to 5-mm fractions.

8.20 If slaking is required to determine 2- to 5-mm rock fragments from soil aggregates:

8.20.1 Weigh 100 g of 2- to 5-mm sample into water-resistant container. Add enough sodium hexametaphosphate solution to saturate the sample.

8.20.2 Add RO water until the sample is submerged under 1 cm of solution (clay-rich samples absorb solution), leave overnight (fig. 1B1b2b–7).

8.20.3 The following day, rinse sample with RO water through 2-mm sieve, return to pan, dry retained fragments in ambient lab conditions or oven, and record weight of retained fragments.

8.21 Once subsamples are collected in the appropriate containers and >2-mm fragment weights have been recorded, excess sample can be discarded according to laboratory protocols for health, safety, and environmental standards.

8.22 Vacuum kraft paper clean between samples. Replace paper if it tears or if holes retain material.

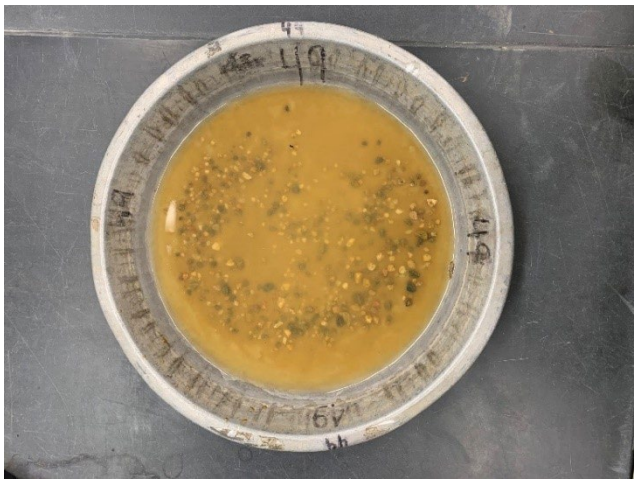

Figure 1B1b2b–7.—Slaking subsample to determine rock fragments from crush-resistant aggregates.

9. Calculations

9.1 Calculations for coarse fragments are reported in method 3A2.

9.2 Reported data include, but are not limited to, the following:

- **9.2.1** Weight (g) of field-moist soil sample
- **9.2.2** Weight (g) of air-dry soil sample
- **9.2.3** Weights (g) of processed air-dry soil
- **9.2.4** Weight (g) of 20- to 75-mm fraction
- **9.2.5** Weight (g) of 5- to 20-mm fraction
- **9.2.6** Weight (g) of 2- to 5-mm fraction
- **9.2.7** Weight (g) of subsample of 2- to 5-mm fraction before slaking
- **9.2.8** Weight (g) of subsample of 2- to 5-mm fraction after slaking

10. Quality Assurance/Quality Control

10.1 Assess plausibility of test sample data in context of expected soil profile trends.

10.2 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.3 Assign overall project data to soil data quality specialist.

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Laboratory Sample Collection and Preparation (1B)
Soil (1B1)
Soil Sample Preparation (1B1b)
Atterberg Limits (1B1b1c1)
<2-mm Fraction Processed to ≈425 µm (1B1b2c1)

1. Introduction to Soil Sample Collection and Preparation

Routine laboratory analysis is commonly performed using samples processed to <2 mm. Capturing certain physical soil properties, however, requires finer size fractions.

This method is a continuation of method 1B1b2b, Standard Chemical, Physical, and Mineralogical Analysis, and should be used in conjunction with the standard soil preparation method.

2. Scope and Field of Application

For routine soil analyses, most U.S. and Canadian laboratories homogenize and process samples to pass a 2-mm sieve (Bates, 1993). Laboratory analyses of soil samples are generally performed on the air-dry, fine-earth (<2-mm) fraction, which possesses the optimum water content for handling and processing soil.

Samples are further processed to 40 mesh (≈425 µm) for analyses capturing Atterberg limits, such as liquid limit (performed on field-moist sample) and plasticity index (performed on air-dried soil sample).

3. Principle

A field-state, whole-soil sample is air dried and processed to <2 mm according to method 1B1b2b. Samples are then processed from <2 mm to 40 mesh (≈425 µm) using sieves, rollers, and rubber stoppers.

3.1 Interferences

Sample sizes are determined by weight for most analyses. Samples that have a high content of organic matter can have relatively low bulk densities. To ensure an adequate amount of sample is available, process two to three times the amount of organic soil sample relative to mineral soils.

Soil material must be thoroughly mixed to obtain a representative sample, particularly in samples that have limited size and large soil variability.

At each stage of sampling, an additional component of variability—the variability among smaller elements within the larger units—is added to the sampling error (Petersen and Calvin, 1986).

4. Apparatus

4.1 Electronic Balance, ±1-g sensitivity and 15-kg capacity

4.2 Cardboard sample boxes for sample storage and working pint samples

4.3 Trays, fiberglass or heat-resistant plastic, tared

4.4 10-mesh sieve, 2-mm square-hole, stainless steel

4.5 40-mesh sieve, 0.42 5-mm square-hole, stainless steel

4.6 Wooden roller, 25 cm long x 15 cm diameter, custom made (fig. 1B1b1-2c1–1). (The KSSL can be contacted for more information.)

4.7 Rubber rollers, soft and hard polymer, 3 cm long x 10 cm diameter and 5 cm long x 10 cm diameter, custom made (fig. 1B1b1-2c1–2). (The KSSL can be contacted for more information.)

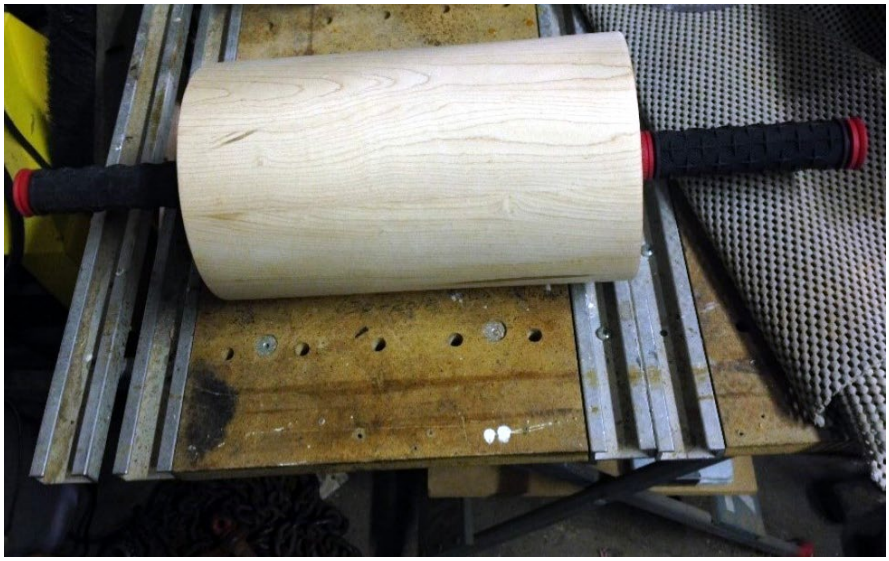

Figure 1B1b2c–1.—Wooden sample roller, custom made for KSSL.

Figure 1B1b2c–2.—Hammer and rubber rollers, custom made for KSSL.

4.8 Large rubber stopper for moist samples
4.9 Downdraft table grinding bench, 3 ft x 6 ft
4.10 Metal plate for grinding bench, 76 cm x 76 cm x 0.5 cm
4.11 Containers, paper, 12-oz, with lids
4.12 Containers, plastic, 1-pint, 1-, 4-, and 8-oz with tops
4.13 Brown kraft paper
4.14 Flat-bottom sample scoop, stainless steel
4.15 Air compressor

5. Chemicals

No chemicals are required for 40 mesh processing.

6. Health and Safety

Personal Protective Equipment (PPE).—ANSI approved safety glasses must be worn when processing samples. Use disposable gloves with appropriate polymer rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents or samples. Keep clothing and hands away from the crusher and mill when these machines are in use.

Dust from the sample processing can irritate sinuses, lungs, and eyes. Engineering measures are provided in the sample processing area to keep dust levels below OSHA established limits. When processing samples, use mechanical and procedural dust management measures, including properly adjusted ventilation and filtering devices as specified in the KSSL Dust Management Procedure document. NIOSH N95 half masks are optional but if used should be fitted and worn properly.

7. Sample Preparation

Air-dried samples are processed to <2 mm (method 1B1b2b1). Subsamples are further pressed, crushed, and sieved to <425 µm for some analyses, including Atterberg limits. The weight of air-dry soil remains relatively constant, and biological and chemical activity is low during storage. Moist samples are used for certain analyses and for samples from some permanently-moist areas. Moist samples are refrigerated until analysis.

8. Procedure

8.1 For field-moist 40-mesh sample preparation:

8.1.1 After obtaining an initial sample weight on a tared fiberglass tray, select a representative subsample of field-moist, whole-soil sample (fig. 1B1b2c–3).

Figure 1B1b2c–3.—Sample prepared for drying with tared tray and sample tag.

8.1.2 Press whole soil through a <2-mm sieve with a large rubber stopper or by hand. Place this sieved material in a labeled, plastic, lidded, 1-pint container. Reserve ≈50 g for further processing.

8.1.3 Press ≈50 g of <2-mm field-moist sample through a 40-mesh sieve using a rubber stopper or by hand. Discard any rock or organic fragments left on the sieve.

8.1.4 Place sample in a plastic bag. Place the bag in a labeled, plastic, lidded, 4-oz container. Place container in refrigerator until analysis.

8.2 For air-dried 40-mesh sample preparation:

8.2.1 Air dried <2-mm soil is processed on a metal plate and brown kraft paper (fig. 1B1b2c1–4).

8.2.2 Collect <2-mm subsamples in appropriate containers. Reserve ≈50 g of <2-mm sample.

8.2.3 Using wooden or rubber rollers, grind <2-mm sample until it passes through 40-mesh sieve. Discard any rock or fibrous fragments left on the sieve.

8.2.4 Place 40-mesh sample in a labeled, 12-oz paper container with a lid.

8.3 40-mesh samples are used in Atterberg testing.

8.3.1 Liquid limit uses moist or air-dried preparations, method 3H1.

8.3.2 Plasticity index uses moist or air-dry preparations, method 3H2.

8.4 Vacuum kraft paper, sieves, and rollers between samples to avoid cross contamination. Replace paper if it tears or if holes retain material.

Figure 1B1b2c–4.—Homogenized <2-mm processed soil sample ready for subsampling.

9. Calculations

There are no calculations for this preparation.

10. Quality Assurance/Quality Control

10.1 Assess plausibility of test sample data in context of expected soil profile trends.

10.2 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.3 Assign overall project data to soil data quality specialist.

11. References

American Society for Testing and Materials (ASTM). 2012. Standard practice for description and identification of soils (visual-manual procedure). D 2488. Annual book of ASTM standards. Construction. Section 4. Soil and rock; dimension stone; geosynthesis. Vol. 04.08. ASTM, Philadelphia, PA.

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Soil Survey Staff. 2014. Keys to soil taxonomy. 12th ed. USDA–NRCS.

Laboratory Sample Collection and Preparation (1B)
Soil (1B1)
Soil Sample Preparation (1B1b)
Standard Chemical, Physical, and Mineralogical Analysis (1B1b2b)
<2-mm Fraction Processed to ≈180 µm (1B1b2d)

1. Introduction to Soil Sample Collection and Preparation

Routine laboratory analysis is commonly performed using samples processed to <2 mm. Capturing certain chemical reactions and quantifying elemental data, however, require finer size fractions.

This method is a continuation of method 1B1b2b and should be used in conjunction with the standard soil preparation method.

2. Scope and Field of Application

For routine soil analyses, most U.S. and Canadian laboratories homogenize and process samples to pass a 2-mm sieve (Bates, 1993). Laboratory analyses of soil samples are generally performed on the air-dry, fine-earth (<2-mm) fraction, which possesses the optimum water content for handling and processing soil. Further processing of samples to 80 mesh (≈180 µm) is required for analyses that capture chemical reactions or elemental composition, such as total carbon, nitrogen, and sulfur analysis (CNS), mid-infrared diffuse reflectance Fourier transform spectroscopy (MIR–DRIFTS), and calcium carbonate equivalent (CCE).

3. Principle

A field-state, whole-soil sample is air dried and processed to <2 mm according to method 1B1b2b. Organic and mineral samples are further processed from <2 mm to 80 mesh (≈180 µm) through mechanical processing using a planetary ball mill, cross beater mill, or Stein mill. The 80-mesh sample is placed in a labeled glass scintillation vial for lab subsampling.

3.1 Interferences

Sample sizes are determined by weight for most analyses. Samples that have a high content of organic matter can have relatively low bulk densities. To ensure an adequate amount of sample is available, process two to three times the amount of organic soil sample relative to mineral soils.

Soil material needs to be thoroughly mixed to obtain a representative sample, particularly in samples that have limited sample and large soil variability.

At each stage of sampling, an additional component of variability, the variability among smaller elements within the larger units, is added to the sampling error (Petersen and Calvin, 1986).

4. Apparatus

4.1 Electronic Balance, ±1-g sensitivity and 15-kg capacity
4.2 Cardboard sample boxes for sample storage
4.3 Downdraft table grinding bench, 3 ft x 6 ft (0.91 m x 1.8 m)
4.4 Metal plate for grinding bench, 76 cm x 76 cm x 0.5 cm
4.5 Scintillation glass vials, 20-mL
4.6 Brown kraft paper
4.7 Flat-bottom sample scoop, stainless steel
4.8 Air compressor
4.9 Planetary ball mill (fig. 1B1b2d–1)
4.10 Planetary ball mill silicon nitride balls, 15-mm; bowls, 80-mL (fig. 1B1b2d–2)
4.11 Cross beater mill for organic samples (fig. 1B1b2d–3)
4.12 Stein mill (fig. 1B1b2d–4)

Figure 1B1b2d–1.—Planetary ball mill.

Figure 1B1b2d–2.—Bowls, balls, and sample vial used with planetary ball mill.

Figure 1B1b2d–3.—Cross beater mill with exchangeable mesh size plates.

Figure 1B1b2d–4.—Stein mill.

5. Chemicals

No chemicals are required for 80 mesh processing.

6. Health and Safety

Personal Protective Equipment (PPE).—ANSI approved safety glasses are provided and must be worn when processing samples. Use disposable gloves with appropriate polymer rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents or samples. Keep clothing and hands away from the crusher and mill when these machines are in use.

Dust from the sample processing can irritate sinuses, lungs, and eyes. Engineering measures in the sample processing area keep dust levels below OSHA established limits. When processing samples, use mechanical and procedural dust management measures, including properly adjusted ventilation and filtering devices, as specified in the KSSL Dust Management Procedure document. NIOSH N95 half masks are optional but if used should be fitted and worn properly.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. Subsamples are further processed via planetary ball mill to 80-mesh. The weight of air-dry soil remains relatively constant. Biological and chemical activity is low during storage.

8. Procedure

8.1 Air dried <2-mm soil is processed on a metal plate and brown kraft paper (fig. 1B1b2b–5).

8.2 Collect a subsample in a labeled, glass scintillation vial and place ordinally in storage box.

8.3 Samples are processed to 80 mesh (180 µm) using a planetary ball mill.

8.3.1 For <2-mm mineral soils, ≈15 cm^3 of sample and 8 silicon-nitride grinding balls are added to a planetary ball mill bowl (fig. 1B1b2d–2). The sample is milled at 360 rpm for 2 minutes. Samples are stored in 20-mL glass vials.

8.3.2 Note: Mill parameters were optimized and qualified for this specific piece of equipment by grinding variously textured soil materials to demonstrate method adequacy.

Figure 1B1b2b–5.—Homogenized <2-mm processed soil sample ready for subsampling.

8.3.3 Examples of common analyses that use 80-mesh (180-µm) sample include:

8.3.3.1 Total carbon, nitrogen, sulfur analysis

8.3.3.2 Mid-infrared diffuse reflectance Fourier transform spectroscopy (MIR–DRIFTS) analysis

8.3.3.3 Calcium carbonate equivalent

8.3.3.4 Equivalent gypsum content analysis

8.3.3.5 Effervescence predictive test

8.4 Samples from O horizons may include constituents such as pine thatch, fibrous roots, and large seeds or cones that do not crush to <2 mm by rolling. If O horizon material does not pass through the <2-mm sieve during conventional sample preparation, use mechanical milling.

8.4.1 Using a cross-beater mill (fig. 1B1b2d–3), add the <2-mm screen in the base of the grinding chamber.

8.4.2 Slowly add sample through the top chute. Avoid adding too much material at once to prevent mill from jamming.

8.4.3 Once all sample has been milled to <2 mm, sample can be processed to 80 mesh using the cross-beater mill or planetary ball mill.

8.4.3.1 For cross-beater mill, replace <2-mm screen with 80 mesh screen in the base of the grinding chamber, add sample slowly to avoid jamming mill and 80-mesh screen. Place 80-mesh sample in 20-mL glass vial.

8.4.3.2 For planetary ball mill, add ≈15 cm^3 of sample and 8 silicon-nitride grinding balls to planetary ball mill bowl (fig. 1B1b2d–2). The sample is milled at 360 rpm for 2 minutes. Samples are stored in a 20-mL glass vial.

8.5 Vacuum kraft paper and processing mills between samples to avoid cross contamination. Replace paper if it tears or if holes retain material.

9. Calculations

Calculations are not recorded or reported for this preparation.

10. Quality Assurance/Quality Control

10.1 Use ASTM or ISO approved mesh sieves.

10.3 Assign overall project data to soil data quality specialist.

11. References

American Society for Testing and Materials (ASTM). 2012. Standard practice for description and identification of soils (visual-manual procedure). D 2488. Annual book of ASTM standards. Construction. Section 4. Soil and rock; dimension stone; geosynthesis. Vol. 04.08. ASTM, Philadelphia, PA.

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Laboratory Sample Collection and Preparation (1B)
Soil (1B1)
Soil Sample Preparation (1B1b)
Standard Chemical, Physical, and Mineralogical Analysis (1B1b2b)
<2-mm Fraction Processed to ≈75 µm/200 mesh (1B1b2e1)

1. Introduction to Soil Sample Collection and Preparation

Routine laboratory analysis is commonly performed using samples processed to <2 mm. Finer size fractions are required for elemental quantification.

This method is a continuation of method 1B1b2b and should be used in conjunction with the standard soil preparation method.

2. Scope and Field of Application

For routine soil analyses, most U.S. and Canadian laboratories homogenize and process samples to pass a 2-mm sieve (Bates, 1993). Laboratory analyses of soil samples are generally performed on the air-dry, fine-earth (<2-mm) fraction, which possesses the optimum water content for handling and processing soil. Further processing of samples to 200 mesh (≈75 µm) is critical for samples analyzed for total major or trace elements using inductively coupled plasma mass spectrometry (ICP–MS). Air-dry, <75-µm subsamples that are used for major and trace elements are processed metal-free.

3. Principle

A field-state, whole-soil sample is air dried and processed to <2 mm. Organic and mineral samples are further processed from <2 mm to 200 mesh (≈75 µm) through mechanical processing using a planetary ball mill. The 200-mesh sample is placed in a labeled glass scintillation vial for lab subsampling.

3.1 Interferences

To ensure a representative sample of adequate weight, process two to three times the amount of organic soil sample relative to mineral soil samples.

Soil material needs to be thoroughly mixed to obtain a representative sample, particularly in samples that have limited size and large soil variability.

At each stage of sampling, an additional component of variability, the variability among smaller elements within the larger units, is added to the sampling error (Petersen and Calvin, 1986).

4. Apparatus

4.1 Cardboard sample boxes for sample storage

4.2 Downdraft table grinding bench, 3 ft x 6 ft (0.91 m x 1.8 m)

4.3 Metal plate for grinding bench, 76 cm x 76 cm x 0.5 cm
4.4 Scintillation glass vials, 20-mL
4.5 Brown kraft paper
4.6 Air compressor
4.7 Planetary ball mill (fig. 1B1b2e1–1)
4.8 Planetary ball mill silicon nitride balls, 15-mm; bowls, 80-mL (fig. 1B1b2e1–2)
4.9 200-mesh, 75-µm, nylon cloth sieve

Figure 1B1b2e1–1.—Planetary ball mill.

Figure 1B1b2e–2.—Bowls, balls, and sample vial used with planetary ball mill.

5. Chemicals

No chemicals are required for 200 mesh processing.

6. Health and Safety

Personal Protective Equipment (PPE).—ANSI approved safety glasses are provided and must be worn when processing samples. Use disposable gloves with appropriate polymer rating for chemical resistance; safety glasses, face

shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents or samples. Keep clothing and hands away from the crusher and mill when these machines are in use.

Dust from the sample processing can irritate sinuses, lungs, and eyes. Engineering measures are provided in the sample processing area to keep dust levels below OSHA established limits. When processing samples, use mechanical and procedural dust management measures, including properly adjusted ventilation and filtering devices as specified in the KSSL Dust Management Procedure document. NIOSH N95 half masks are optional but if used should be fitted and worn properly.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. Subsamples are further processed via planetary ball mill to 200-mesh. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Air-dried soil sample is processed to <2 mm at a downdraft table. Use a cross-beater mill if necessary. Grind the sample on a metal plate covered with brown kraft paper (fig. 1B1b2e1–3).

Figure 1B1b2e1–3.—Homogenized <2-mm processed soil sample ready for subsampling.

8.2 Collect a subsample in a labeled, glass scintillation vial and place ordinally in storage box.

8.3 Place ≈15 cm^3 of sample and 8 silicon-nitride grinding balls in a planetary ball mill bowl (fig. 1B1b2e1–2).

8.4 Mill sample at 360 rpm for 2 minutes.

8.4.1 Note: Mill parameters were optimized and qualified for this specific piece of equipment by grinding variously textured soil materials to demonstrate method adequacy.

8.5 Sieve the milled sample through 200-mesh (75-µm) nylon sieve. Do not use metal sieves, which may contaminate samples.

8.6 Place any sample remaining on 200-mesh sieve back into ball mill bowl and add nitride grinding balls. Repeat milling process until all sample has passed through the 200-mesh nylon sieve.

8.7 Vacuum kraft paper and processing mill, bowl, and milling balls between samples to avoid cross contamination. Replace paper if it tears or if holes retain material.

8.8 200-mesh (75-µm) sample is used primarily for method 4H1a1b1-21 Inductively Coupled Plasma Mass Spectrophotometer: antimony, arsenic, barium, beryllium, cadmium, cobalt, chromium, copper, lead, manganese, mercury, molybdenum, nickel, phosphorus, selenium, silver, strontium, tin, tungsten, vanadium, and zinc.

9. Calculations

There are no calculations for this preparation.

10. Quality Assurance/Quality Control

10.1 Assess plausibility of test sample data in context of expected soil profile trends.

10.2 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.3 Assign overall project data to soil data quality specialist.

11. References

American Society for Testing and Materials (ASTM). 2012. Standard practice for description and identification of soils (visual-manual procedure). D 2488. Annual book of ASTM standards. Construction. Section 4. Soil and rock; dimension stone; geosynthesis. Vol. 04.08. ASTM, Philadelphia, PA.

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Laboratory Sample Collection and Preparation (1B)
Soil (1B1)
Soil Bulk Sample Preparation (1B1b)
Air-Dry Preparation (1B1b2)
>2-mm Fractions (1B1b2f)
Particle-Size Analysis (1B1b2f1)
Particle-Size Analysis, Recorded (1B1b2f1a)
Proportion and Particle-Size of Air-Dry Rock Fragments that Resist Abrupt Immersion in Tap Water (1B1b2f1a3)

1. Introduction to Abrupt Immersion of Air-Dry Rock Fragments >2 mm

It is widely accepted that the mechanical preparation of soil for laboratory analysis is difficult to standardize for samples that contain >2-mm particles having rupture resistance intermediate between earthy bodies and fragments of highly resistant rock (Grossman, 2004). A procedure is needed that is both reproducible and that subjects the >2-mm fraction to an intermediate stress less than standard mechanical preparation. Abrupt immersion in tap water of the initially air-dry >2-mm fraction has been chosen to apply the stress.

2. Scope and Field of Application

This method provides a comparison to mechanical preparation methods and should aid in the development of a more precise mechanical preparation that is dependent on sample properties (Grossman, 2004). Certain analyses can be run on the >2-mm fraction after separation by the water-immersion method. The resulting values can be subtracted from analyses on the whole ground sample to obtain estimates for the <2-mm fraction removed by the water immersion treatment. In some situations, comparison of the results to the use of a dispersing agent might be valuable, but another procedure would need to be established.

3. Principle

A representative subsample of the air-dry field sample is weighed and passed through a no.10 sieve. The >2-mm fraction is placed abruptly in tap water, left overnight, gently agitated, and passed through a no. 10 sieve. The wet >2-mm material is passed through a nest of sieves: no. 10, no. 4, 9.5-mm (nominally 10 mm), and 20-mm.

3.1 Interferences

There are no known interferences.

4. Apparatus

4.1 Buckets, plastic, 10-L with 1-L marks

4.2 Bucket, plastic, in which 20-cm diameter sieve fits snugly

4.3 Bucket, 19-L (5-gal), straight-sided, with 30-cm diameter

4.4 Drying trays, fiberglass, 35 x 48 cm

4.5 Cake pans, aluminum, 20 x 20 x 4 cm

4.6 Sieves: 30-cm diameter no. 10, 20-mm diameter no. 4, 9.5- and 20-mm, plus bottom pan

4.7 Top loading balance, 1-g sensitivity and >10,000-g capacity, with pan large enough to mount the drying trays listed above as apparatus item 4.4.

4.8 Pan, plastic, 60 x 40 x 15 cm

4.9 Plastic sheet, 8-mm, large enough to line plastic container

4.10 Plastic beads, 9 x 6 mm, separated by color

4.11 Teaspoon and tablespoon

5. Chemicals

5.1 Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) (CAS# 10035-04-8)

5.2 Tap water of acceptable dispersibility (Zone A in Flanagan and Holmgren, 1977)

6. Health and Safety

Personal Protective Equipment (PPE).—Disposable gloves, safety glasses, and lab coat or apron should be used. Thoroughly wash hands after handling reagents or samples.

Use a dust mask and eye protection. Dust from the sample processing can irritate sinuses, lungs, and eyes.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C. The whole soil is used in this method.

8. Procedure

8.1 From the tray of air-dried field sample, remove and weigh a representative subsample that is roughly one-fourth of the sample and inclusive of the >20-mm fraction.

8.2 Pass subsample through a no. 10 sieve. Weigh the >2-mm particles and discard the <2-mm fraction.

8.3 In a 10-L bucket, add 1 L of tap water for about every 500 g of >2-mm sample.

8.4 Immerse the >2-mm fraction abruptly in the bucket of tap water. Leave the sample overnight.

8.5 Insert your hand to the bottom of the bucket and rotate the mass at 1 rotation per second 20 times.

8.5.1 If strength measurements are not taken: Quantitatively transfer from the 30-cm diameter sieve to a tray. Air-dry the sample on the tray at 30 to 35 °C. Pass through a nest of sieves: 20-mm, no. 4, and no. 10.

8.5.2 Weigh each separate to the nearest g and report. Subtract the >20-mm weight from the initial >2-mm weight. Obtain the 2- to 5-mm, 5- to 20-mm, and 2- to 20-mm particles as a percent of the <20-mm fraction.

8.6 In the sink, place the 30-cm diameter no. 10 sieve over the top of a 19-L bucket. Quantitatively transfer the >2-mm particles into the No.10 sieve and wash with a water stream to remove the material that is not resistant to the immersion treatment. Use a minimum amount of water.

8.7 After the 19-L bucket is full, add about 30 g of $CaCl_2$. Allow to stand until settled out. Pour off as much of the water as possible without transferring solids to the sink. Dry the sediment in the bucket by evaporation, followed by disposal as a solid.

8.8 Quantitatively transfer from the 30-cm diameter sieve to a tray. Air-dry the sample on the tray at 30 to 35 °C. Pass through a nest of 20-mm, no. 4 and no. 10 sieves.

8.9 Weigh each separate to the nearest gram and report. Subtract the >20-mm weight from the initial >2-mm weight. Obtain the 2- to 5-mm, 5- to 20-mm, and 2- to 20-mm particles as a percent of the <20-mm fraction.

9. Calculations

9.1 $A = [B / (C - D)] \times 100$

9.2 $E = [F / (C - D)] \times 100$

9.3 $G = A + E$

A = Weight percentage 2- to 5-mm fraction on <20-mm basis (%)

B = Air-dry weight of 2- to 5-mm fraction after water immersion (g)

C = Air-dry total weight of whole-soil subsample (g)

D = Air-dry weight of >20-mm fraction after water immersion (g)

E = Weight percentage of 5- to 20-mm fraction on <20-mm basis (%)

F = Air-dry weight of 5- to 20-mm fraction after water immersion (g)

G = Weight percentage 2- to 20-mm fraction on <20-mm basis (%)

9.4 Report the 2- to 5-mm, 5- to 20-mm, and 2- to 20-mm fractions as weight percentages of the <20-mm fraction.

10. Quality Assurance/Quality Control

10.1 Assess plausibility of test sample data in context of expected soil profile trends.

10.2 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.3 Assign overall project data to soil data quality specialist.

11. References

Flanagan, C.P., and G.G.S. Holmgren. 1977. p. 121–134. Field methods for determination of soluble salts and percent sodium from extract for identifying dispersive clay soils. *In* J.L. Sherard and R.S. Decker (eds.) Dispersive clays, related piping, and erosion in geotechnical projects, ASTM STP 623. American Society of Testing Materials, West Conshohocken, PA.

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Laboratory Sample Collection and Preparation (1B)
Water (1B2)
Samples (1B2a)

Just as for soil samples, laboratory identification numbers and preparation codes are assigned to water samples. Refer to 1B1a1 for information on these numbers and codes.

Laboratory Sample Collection and Preparation (1B)
Water (1B2)
Water Sample Preparation (1B2b)

Avoid long periods between collection and laboratory analysis of water. To prevent significant changes (e.g., degradation, volatilization), water samples require expedited transport under ice or gel packs. The samples are refrigerated (4 °C) immediately upon arrival at the laboratory. Do not allow water samples to freeze, which can influence pH and the separation of dissolved organic matter from the water phase.

Some water analyses (e.g., electrical conductivity, total C, inorganic C) must be performed promptly because optimal preservation is not possible (Velthorst, 1996). Upon completion of these analyses, sample filtration (0.45-µm membrane) is used to separate dissolved from suspended material. The sample is then split into two subsamples. One subsample is acidified to pH 2 for cation analyses (e.g., Al, Fe, Mn), and the other is used for anion analyses. These analyses also need to be performed as promptly as possible.

Laboratory Sample Collection and Preparation (1B)
Biological Materials (1B3)
Samples (1B3a)
Biology Bulk Sample (1B3a1)
Microbial Biomass Sample (1B3a2)

Biological samples require ice or gel packs and expedited shipping to the KSSL from the field. Samples are refrigerated (4 °C) immediately upon arrival at the laboratory. Whether part of the bulk sample or separate sampling unit, all biological samples are given specific preparation codes and identification numbers.

Biology samples may be subsampled from the bulk sample for specific testing, or they many consist of individual samples collected from sampling units that are separate from the bulk sample units.

Microbial biomass samples are specific sample units from soil bulk or other biology samples. These samples have preparation codes that reflect the specific analysis required.

Laboratory Sample Collection and Preparation (1B)
Biological Materials (1B3)
Biological Material Preparation (1B3b)

Avoid long periods between collection and laboratory analysis of biological samples to prevent significant changes (e.g., in the microbial community). Store biology samples in the refrigerator (4 °C) for future analysis.

Laboratory Sample Collection and Preparation (1B)
Biological Materials (1B3)
Biological Material Preparation (1B3b)
Field-Moist Preparation (1B3b1)
<2-mm Fraction (1B3b1a)
Microbial Biomass (1B3b1a1)

Refer to section 6 of this method manual for more information about analysis of biological samples.

Laboratory Sample Collection and Preparation (1B)
Biological Materials (1B3)
Biological Material Preparation (1B3b)
Air-Dry Preparation (1B3b2)
<2-mm Fraction Sieved to <53 µm, with ≥53 µm (Particulate Organic Matter) and <53 µm Processed to ≈180 µm (1B3b2a)
Total Carbon, Nitrogen, and Sulfur (1B3b2a1)

Refer to section 6 of this method manual for more information about analysis of biological samples.

Laboratory Sample Collection and Preparation (1B)
Biological Materials (1B3)
Biological Material Preparation (1B3b)
Air-Dry Preparation (1B3b2)
<2-mm Fraction (1B3b2b)
Other Biological Analyses (1B3b2b1)

Refer to section 6 of this method manual for more information about analysis of biological samples.

Laboratory Sample Collection and Preparation (1B)
Biological Materials (1B3)
Biological Material Preparation (1B3b)
Dry (50 °C) Preparation (1B3b3)
Roots (1B3b3a)
Root Biomass (1B3b3a1)
Roots Processed to ≈180 µm (1B3b3a1a)
Total Carbon, Nitrogen, and Sulfur (1B3b3a1a1)
Plants (1B3b3b)
Plant Biomass (1B3b3b1)
Plants Processed to ≈180 µm (1B3b3b1a)
Total Carbon, Nitrogen, and Sulfur (1B3b3b1a1)

Refer to section 6 of this method manual for more information about analysis of biological samples.

11. References

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CONVENTIONS (2)

Methods and Codes (2A)

The KSSL ensures continuity in its analytical measurements with the use of standard operating procedures (SOPs) referred to as methods. Methods are written in a standard format designed for repetitive use and to ensure quality assurance, quality control, and reproducibility. They are described in enough detail to be performed in many laboratories; however, brands of laboratory equipment, suppliers, and vendors are at the discretion of the laboratories. All KSSL methods are appropriate for their specific purpose, specific measurements, or sampling operation. The methods are peer-recognized, KSSL-developed, and/or specified in "Keys to Soil Taxonomy" (Soil Survey Staff, 2014).

KSSL method codes are in hierarchical and alphanumerical format. They are linked to specific suites and individual analyses, which are included on reports issued by the KSSL. Method codes were expanded to include more characters after 1996. The expansion allows for more information to be conveyed about the method and accommodates the significant increase in the number and kinds of methods performed at the KSSL. This volume of the method manual, Part1, contains current method codes. The reader may use Part 2 to cross reference information from older, obsolete method codes related to KSSL data sheets and scientific publications. The links between current and obsolete codes provide a means of technical criticism and of traceability, which becomes important if data are questioned in the future. Not all obsolete methods and procedures presented in Part 2 are described in the same detail as the current methods.

Only those data assigned method codes with a reproducible standard operating procedure are reported in Primary Characterization Data Sheets. Data on the Supplementary Characterization Data Sheets and the Taxonomy Characterization Data Sheets are derived data using analytical data as a basis for calculations. "Pedon Calculations," e.g., Weighted Average Clay, are also derived data. These data do not carry method codes and are not described in this manual.

For detailed information about the calculation and application of derived values and the application of KSSL data, refer to Soil Survey Investigations Report (SSIR) 45, "Soil Survey Laboratory Information Manual" (Soil Survey Staff, 2011), and to "Keys to Soil Taxonomy" (Soil Survey Staff, 2014).

SSIR No. 42, "Soil Survey Laboratory Methods Manual," version 6.0, replaces previous versions of SSIR No. 42 (1989, 1992, 1996, 2004, and 2014) and SSIR No. 1, "Procedures for Collecting Soil Samples and Methods of Analysis for Soil Survey" (1972, 1982, and 1984).

Reports and data are available via the NRCS Soils website at http://soils.usda.gov/ or directly from the National Cooperative Soil Survey Soil Characterization Data website at https://ncsslabdatamart.sc.egov.usda.gov/.

Data Types (2B)

The methods described herein provide analytical, quantitative, or semiquantitative measurements and include physical, chemical, mineralogical, and biological analyses. Sample collection and preparation in the field and the laboratory are also described. SSIR No. 42 also describes some derived values, e.g., coefficient of linear extensibility (COLE) and water retention difference (WRD), that are reported along with the analytical data on the Primary Characterization Data Sheets. For more detailed information about the calculation and application of derived values that have method codes, refer to SSIR No. 45 (Soil Survey Staff, 2011) and "Keys to Soil Taxonomy" (Soil Survey Staff, 2014).

Particle-Size Fraction Base for Reporting Data (2C)

Particles <2 mm (2C1)

Particles >2 mm (2C2)

Unless otherwise specified, all data are reported on the basis of the <2-mm material. Other size fractions reported on the Primary Characterization Data Sheets include, but are not limited to, the <0.4, <20, <75 mm, and whole-soil bases.

The maximum coarse-fragment size for the >2-mm base varies. The base usually includes those fragments as large as 75 mm (3 in) present in the soil. The maximum size for fragments >75 mm, commonly termed "whole soil," includes cobbles with maximum horizontal dimensions less than those of the pedon. The maximum particle-size set is recorded in the parentheses in the column heading of the data sheet. The base with which to calculate the reported >2-mm percentages includes all material in the sample smaller than the particle size recorded in the column heading. The reporting conventions for particle-size fractions for the <2-mm and >2-mm fractions are designated as 2C1 and 2C2, respectively.

Sample Weight Base for Reporting Data (2D)

Air-Dry/Oven-Dry (2D1)

Field-Moist/Oven-Dry (2D2)

Correction for Crystal Water (2D3)

Unless otherwise specified, all data are reported on an oven-dry weight or volume basis for the designated particle-size faction. Air-dried (AD) and oven-dried (OD) weights are defined herein as constant sample weights obtained after drying at 30 ±5 °C (≈3 to 7 days) and at 110 ±5 °C (≈12 to 16 h). As a rule of thumb, air-dry soils contain about 1 to 2 percent water and are drier than soils at 1,500-kPa water content.

The AD/OD ratio, unless otherwise specified, is determined on a <2-mm sieved sample described in method 3D1. Tests requiring smaller grain-size fractions

use the <2-mm AD/OD results in the calculations. Smaller sample preparations include the following.

- "Fine grind" preparation <180 µm (80 mesh) for total C
- <75 µm for trace elements
- 2- to 0.5-mm fraction for aggregate stability
- ≥0.53- and <0.53-µm fractions for hyper-particulate organic matter

The calculation of the air-dry/oven-dry (AD/OD) ratio is used to adjust air-dried results to an oven-dried weight basis. Field-moist (FM) weight is defined herein as the sample weight obtained without drying prior to laboratory analysis. The AD/OD ratio can also be used to calculate the sample weight that is equivalent to the required OD soil weight. For the methods of analysis and calculations of the AD/OD and FM/OD ratios, refer to methods 3D1 and 3D2. For correction of crystal water, refer to method 2D3.

Significant Figures and Rounding (2E)

Unless otherwise specified, the KSSL uses the procedure of significant figures to report analytical data. Historically, significant figures are said to be all digits that are certain plus one, which contains some uncertainty. If a value is reported as 19.4 units, the 0.4 is not certain; i.e., repeated analyses of the same sample would vary more than one-tenth but generally less than a whole unit.

Data Sheet Symbols (2F)

The analytical result of "zero" is not reported by the KSSL. The following symbols are used or have been used for trace or zero quantities and for samples not tested.

Symbol	Explanation
tr, Tr, TR	Trace, either is not measurable by quantitative procedure used or is less than reported amount.
tr(s)	Trace, detected only by qualitative procedure more sensitive than quantitative procedure used.
-	Analysis run but none detected.
--	Analysis run but none detected.
-(s)	None detected by sensitive qualitative test.
blank	Analysis not performed.
nd	Not determined, analysis not run.
<	Either none is present, or amount is less than reported amount, e.g., <0.1 is in fact <0.05 since 0.05 to 0.1 is reported as 0.1.

Obsolete Methods, SSIR No. 42, Part 2 (2G)

Obsolete and legacy methods are included in a companion volume, SSIR No. 42, Part 2. Part 2 is dedicated to methods that are no longer used at the Kellogg Soil Survey Laboratory (KSSL) and were described in earlier versions of Soil Survey Investigations Report (SSIR) No. 42 and in SSIR No. 1, "Procedures for Collecting Soil Samples and Methods of Analysis for Soil Survey" (1972, 1982, and 1984). Documentation and archiving of these obsolete methods create an important reference. Older lab characterization data may have been produced using some of these methods, and many older SSIRs and scientific publications report these methods. The intent of this documentation is to provide a historical linkage for the KSSL principal methods. Some of these procedures are in the original format and are not described in the same detail as current methods.

References

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SOIL PHYSICAL AND FABRIC RELATED ANALYSES (3)

Particle-Size Distribution Analysis (3A)

Particles <2 mm (3A1)

Pipette Analysis (3A1a)

Standard KSSL PSDA (3A1a1)

<2-mm Air-Dry (3A1a1a)

1. Introduction to Particle Size Distribution Analysis via Pipette Method

Particle Size Distribution Analysis (PSDA) quantifies the size distribution of individual mineral particles in a soil sample and is a key component of the KSSL characterization reports. It is used as a tool to explain soil genesis and soil classification and to help define soil texture. Most soil physical properties and many chemical properties are influenced by presence and relative abundance of the particle-size distribution classes.

In this method, sand, silt, and clay are isolated into discrete grain-size fractions by chemical, mechanical, or ultrasonic means. The amount of each size-fraction is gravimetrically measured as a percent of the total sample weight on an oven-dry basis. The KSSL is working towards implementing an additional method that includes laser particle-size distribution analysis.

2. Scope and Field of Application

PSDA uses the principles of Stokes' Law, which takes the following assumptions into account for soil sedimentation measurements.

- Terminal velocity is attained as soon as settling of particles begins.
- Settling and resistance of particles are entirely due to the viscosity of the fluid.
- Particles are smooth and spherical.
- There is no interaction between individual particles in the solution (Gee and Bauder, 1986; Gee and Or, 2002).

Because soil particles are neither smooth nor spherical, the radius of the particle is considered an equivalent rather than an actual radius and particle density is assumed to be 2.65 g cc^{-1}; the density of quartz.

Additional analysis, such as fine-clay size-fraction percentage determinations, are used to determine the presence of argillic horizons or as a tool to help explain soil genesis.

Samples may need treatment to disperse individual grains aggregated by cementing agents, such as silica, iron oxides, or carbonates. These treatments are conducted in conjunction with this standard PSDA method and are outlined in this section.

- Carbonate Removal: Method 3A1a2a
- Iron Removal: Method 3A1a3a
- Silica Removal: Method 3A1a4a
- Ultrasonic Dispersion: Method 3A1a5a
- Water Dispersible: Method 3A1a6a
- Gypsum Removal: Method 3A1a7a
- Field-Moist PSDA: Methods 3A1a1b–3A1a6b

3. Principle

A 10 g <2-mm air-dry sample is treated with hydrogen peroxide to remove organic matter and is filtered to remove soluble salts. The sample is dried in an oven to obtain the initial weight, dispersed with a sodium hexametaphosphate solution, and mechanically shaken. The sand-separates are removed from the suspension by wet sieving, are dried, are fractionated through a sieve stack, and are weighed. The fine silt- to clay-sized separates are determined by extracting aliquots of sample from sedimentation cylinders at specific time and depth intervals. The samples are dried at 110 °C and weighed. The fine-clay fraction is obtained from the sedimentation cylinder soil suspension. This suspension is stirred, poured into a centrifuge bottle, and centrifuged at 1,500 rpm. An aliquot is extracted, dried, and weighed.

Coarse silt is determined as the difference between 100 percent and the sum of the sand, clay, and fine silt percentages. The percentage of fine clay is calculated based on the total sample weight.

3.1 Interferences

Cementing agents, such as carbonates, iron oxides, and silica, may inhibit complete dispersion. Special treatment and dispersion methods 3A1a2a–6b should be used in conjunction with this method as appropriate.

Gypsum interferes with particle distribution by causing flocculation of particles and is removed by stirring and washing the soil with reverse osmosis water. Samples containing >25% gypsum require additional treatments with NaCl.

Partial flocculation may occur in some soils if excess salt or hydrogen peroxide is not removed from the soil after its use in organic matter oxidation.

Treatment of micaceous soils with H_2O_2 causes exfoliation of the mica plates and a matting of particles when dried in the oven. Because of exfoliation in these soils, a true measurement of fractions is uncertain (Drosdoff and Miles, 1938).

The removal of carbonates with 1 *N* sodium acetate (pH 5) (method 3A1a2) results in sample acidification. This treatment can destroy the primary mineral structure of clay (Gee and Bauder, 1986).

If the temperature of the water bath exceeds 80 °C during iron removal (method 3A1a3), elemental sulphur can precipitate (Mehra and Jackson, 1960).

This treatment can destroy primary mineral grains in the clay fraction (El-Swaify, 1980).

The use of 0.1 *N* sodium hydroxide to remove silica (method 3A1a4) may damage 2:1 phyllosilicate clays or semi-amorphous clays.

Ultrasonic dispersion (method 3A1a5) has been reported to destroy primary soil particles (Watson, 1971). Studies have reported the destruction of biotite and breakdown of microaggregates by ultrasonic dispersion. However, Saly (1967) reported that ultrasonic vibration did not cause the destruction of the clay crystalline lattice or the breakdown of primary grains. The samples studied ranged from sandy to clayey soils. The cementing agents represented humus, carbonates, and hydroxides of iron and aluminum.

Soils that irreversibly harden when dried are difficult to disperse. The PSDA for these soils can be performed on moist samples (method 3A1a1b) upon the request of the project coordinator. Ultrasonic dispersion can also be requested.

4. Apparatus

4.1 KIMAX 250-mL GL-45 bottle, tared to 1 mg. Wash and tare bottles every 6 months.

4.2 Ceramic filter, 0.3-µm absolute retention

4.3 Rack to hold ceramic filters and sample containers

4.4 Mechanical shaker, horizontal, 120 oscillations min^{-1}, 1½-in strokes

4.5 Cylinders, 1-L, white line fused onto glass at 1-L mark

4.6 Oven, 110 °C

4.7 Hot plate, 100 °C

4.8 Vacuum, capable of 0.8 bar (80 kPa)

4.9 Thermometer, 0 to 150 °C

4.10 Desiccator

4.11 Motor driven stirrer. (The KSSL can be contacted for more information.)

4.12 Cyclonic dampening hand stirrer that has a brass rod threaded at one end and a perforated plexiglass disk fastened to the threaded end to reduce sample vortex from mechanical stirrer. The rod should be slightly longer than the height of the settling cylinders. The plexiglass disk should be ½" narrower than inside diameter of the cylinders.

4.13 Adjustable pipette rack (figs. 3A1a1–1, 3A1a1–2, and 3A1a1–3; Shaw, 1932)

4.14 Lowy pipettes, 25-mL, with overflow bulb. (The KSSL can be contacted for more information.)

4.15 Polyurethane foam pipe insulation that fits snugly around cylinder

4.16 Sieve shaker with 12.7-mm (½ in) vertical and lateral movement at 500 oscillations min^{-1}, accommodates nesting 2-⅜ inch sieves

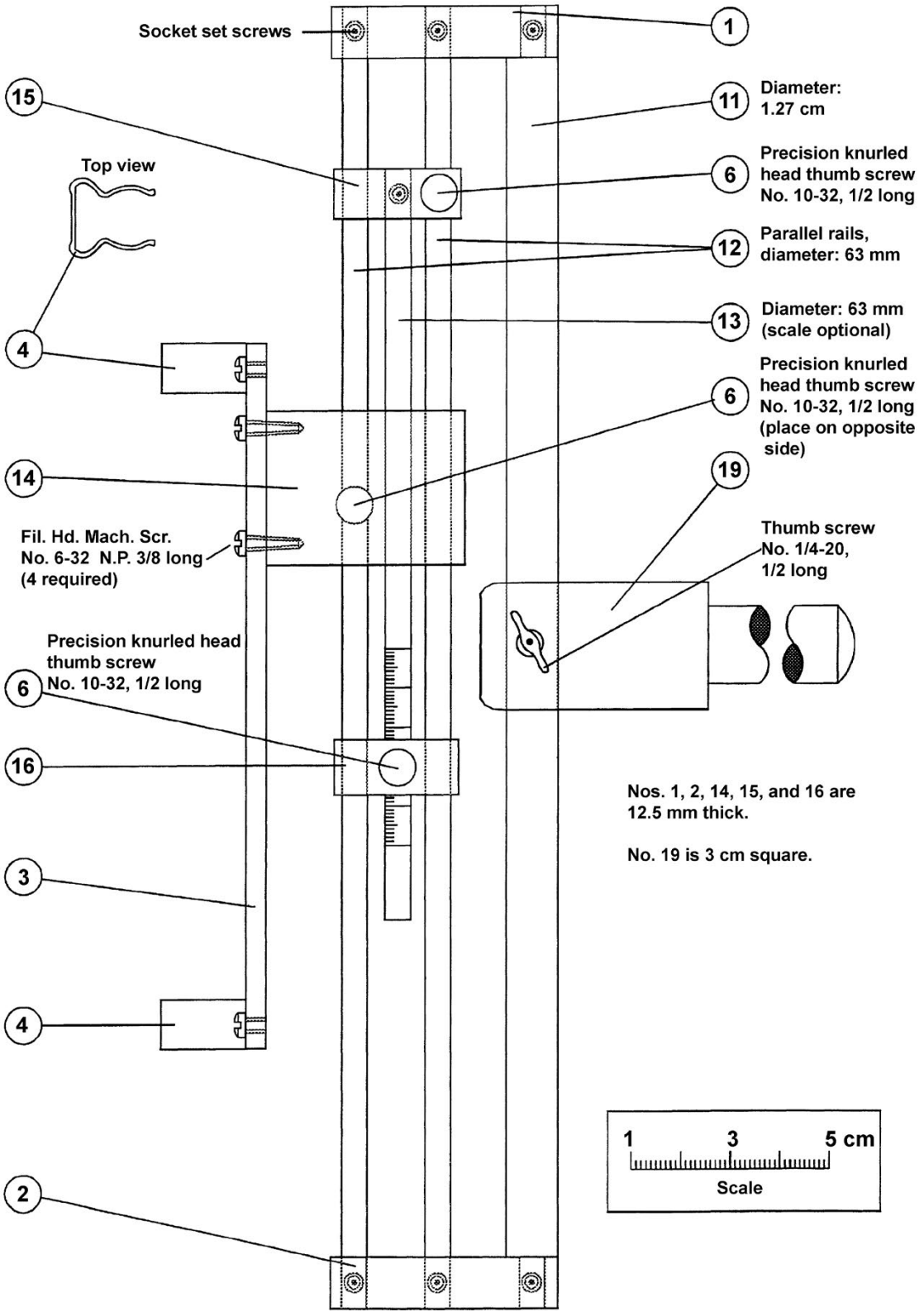

Figure 3A1a1–1.—Shaw Pipette apparatus (Shaw, 1932).

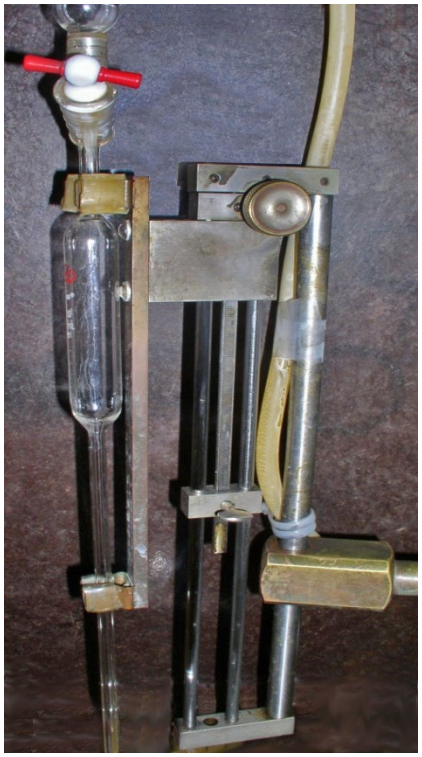

Figure 3A1a1–2.—Close-up of the Shaw Pipette apparatus. The apparatus holds a Lowy Pipette (left).

Figure 3A1a1–3.—Shaw Pipette apparatus and Lowy Pipettes used for particle-size analysis at the USDA–NRCS Kellogg Soil Survey Laboratory.

4.17 Weighing bottles, 90-mL, tared to 0.0001 g
4.18 Drying dishes, aluminum
4.19 Lab timer
4.20 Electronic balance, ±0.10-mg sensitivity
4.21 Electronic balance, ±1.0-mg sensitivity
4.22 Watch glass, 65-mm diameter
4.23 Evaporating dish, porcelain, 80-mm diameter, 32-mm height, with lip
4.24 Centrifuge, floor model capable of 1,500 rpm
4.25 Centrifuge bottles, 500-mL
4.26 Torsion balance
4.27 Manometer, hand-held, gauge and differential pressure, capable of 1,000 psi
4.28 Gelatin capsules, 5-mL
4.29 Machined PVC caps for threaded 90-mL weighing bottles, 3.2-cm (1¼ in) diameter with 1.1-cm (7⁄16 in) diameter hole drilled in center, O-ring seal

4.30 O-rings, 3.2 x 38.1 mm (⅛ x 1½ in)

4.31 Septa, rubber, 7.9-mm (5⁄16 in) diameter. Place in machined cap.

4.32 Hypodermic needle, 25.4-mm (1-in), 23-gauge

4.33 Mortar and pestle

4.34 Stir rod with rubber policeman

4.35 Set of 60-mm (2-⅜ in) sieves, square-weave phosphor bronze wire cloth (except 300 mesh, which is twilled weave). U.S. series and Tyler Screen Scale equivalent designations are as follows:

Sand Size	Opening	U.S. No.	Tyler Mesh Size
	(mm)		
Very coarse sand (VCS)	1.0	18	16
Coarse sand (CS)	0.5	35	32
Medium sand (MS)	0.25	60	60
Fine sand (FS)	0.105	140	150
Very fine sand (VFS)	0.047	300	300

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Sodium hexametaphosphate $(NaPO_3)_6$ (CAS# 68915-31-1)

5.3 Sodium carbonate (Na_2CO_3) (CAS# 497-9-8)

5.4 Sodium chloride (NaCl) (CAS# 7647-14-5), granular

5.5 Hydrochloric acid (HCl) (CAS# 7647-01-0), concentrated, technical grade

5.6 Ethanol 95%, U.S.P. (CH_3CH_2OH) (CAS# 64-17-5)

5.7 Hydrogen peroxide, 30 to 35% (H_2O_2) (CAS# 7722-84-1)

5.8 Calcium sulfate ($CaSO_4$) (anhydrous) (CAS# 7778-18-9) or equivalent desiccant (example: Drierite)

5.9 Sodium hexametaphosphate solution

Components: Sodium hexametaphosphate $(NaPO_3)_6$; sodium carbonate (Na_2CO_3); RO water

- To a 1-L polyethylene bottle, add the following in order:
  - 1 L of RO water
  - 35.7 g of $(NaPO_3)_6$
  - 7.94 g of Na_2CO_3
- Invert to mix.

5.9.1 Standardize each new batch of hexametaphosphate solution. Use only designated weighing bottles for standardization. Wash and tare these bottles after each standardization.

5.9.2 Standards are run in duplicate. Add sodium hexametaphosphate solution to numbered, tared, 90-mL weighing bottles. Aliquots are: 8.5, 9.0, 9.3, 9.6, 10.0, 10.3, 10.6, and 11.0 mL.

5.9.3 Place the 16 weighing bottles and aliquots in the oven overnight and record the dry residue weight of sodium hexametaphosphate.

5.9.4 Determine the exact volume of solution needed to add 0.4408 g of sodium hexametaphosphate into each sample by regressing the volume of sodium hexametaphosphate solution against the dry residue weight of sodium hexametaphosphate.

5.10 Hydrochloric acid solution, 6 *N*

Components: Hydrochloric acid (HCl); RO water

- To a 2-L polyethylene bottle, add the following in order:
  - 1 L of RO water
  - 1 L of concentrated HCl
- Invert to mix.

5.11 Sodium carbonate solution

Components: Sodium carbonate (Na_2CO_3); RO water

- To a 1-L polyethylene bottle, add the following in order:
  - 1 L of RO water
  - 10.6 g Na_2CO_3
- Invert to mix.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids. Dispense concentrated acids and bases in fume hood.

Users should be familiar with operation of a centrifuge. Balance the centrifuge bottles.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Weigh 10 g of <2-mm, air-dry soil to nearest mg on an electronic balance. Place sample into a numbered, tared vessel. A quality-control standard

sample is included in each batch (≤24 samples). If the sample is composed of a large percent organic material, split sample between two 500- or 1,000-mL beakers.

8.2 Add ≈50 mL of RO water and 7.5 mL of H_2O_2 to the soil sample.

8.3 Place the sample on a hot plate and heat to 90 °C. Add additional H_2O_2 in four increments of 7.5 mL at 30-min intervals. If oxidation of organic matter is incomplete, add additional H_2O_2 until oxidation is complete. Record any unusual sample reactions. If the reaction is violent, try:

8.3.1 Adding small increments of ethanol to the sample to lower surface tension of the bubbles and thereby dissipate any foaming; or

8.3.2 Transferring sample to a larger beaker or split the sample into multiple beakers to better contain and control the reaction.

8.4 Place the sample vessel on the filter rack. Add RO water up to the 150-mL mark on the vessel. Place a ceramic filter in the sample, connect to the vacuum trap assembly with tubing, and turn on the vacuum. Filter until liquid is removed and approximately 5 mL remain in the bottom of the vessel.

8.5 Wash the sample from the filter and add ≈150 mL of RO water. Repeat filtering and adding water until sample has been rinsed five times total. Stir the sample with the filter after filling with water each time to ensure all soil particles will be rinsed.

8.5.1 During aspiration, it may be necessary to occasionally apply back-pressure to the filter to remove soil obstructing the pores in the ceramic.

8.5.2 Samples that contain gypsum require additional treatment and filtering.

- 1–5% gypsum: Stir the sample with a magnetic stirrer for 5 min and rinse five times with ≈250 mL of RO water each time.
- 5–10% gypsum: Place the sample in a 1,000-mL beaker, add ≈800 mL of RO water, stir the sample with a magnetic stirrer for 5 min, and then rinse with ≈800 mL five times.
- 10–20% gypsum: Place the sample in a 1,000-mL beaker, add ≈800 mL of RO water, add 100 g sodium chloride (NaCl), and stir the sample with a magnetic stirrer for 10 minutes. Rinse the sample with ≈800 mL of RO water five times.
- 20–40% gypsum: Place the sample in a 1,000-mL beaker, add ≈800 mL of RO water, add 100 g sodium chloride (NaCl), stir the sample with a magnetic stirrer for 10 minutes, and filter once. Remove sample from the rack, repeat sodium chloride treatment, and return sample to the rack. Rinse the sample with ≈800 mL of RO water five times.

- 40–60% gypsum: Repeat sodium chloride treatment and single filtering three times. Rinse the sample with ≈800 mL of RO water five times.
- 60–80% gypsum: Repeat sodium chloride treatment four times. Rinse the sample with ≈800 mL of RO water five times.
- >80% gypsum: Repeat sodium chloride treatment five times and rinse five times.

8.6 Upon completion of filtering, place the sample in the oven. Dry the sample overnight at 110 °C. Remove the sample from the oven, place in a desiccator, and cool to ambient temperature.

8.7 Record the total weight (TW) of the sample to the nearest mg.

8.8 Add the exact volume of sodium hexametaphosphate solution (≈10 mL) needed to add 0.4408 g of sodium hexametaphosphate to each sample. Let stand approximately 1 hour or until sample is completely moistened by sodium hexametaphosphate. If sample imbibes hexametaphosphate, add RO water until sample is slightly damp. For samples that are hydrophobic, add a few of drops of ethanol. For samples that do not appear to become disaggregated, use a rubber policeman to break these apart; gentle rubbing with a mortar and pestle also helps. Add RO water to the 175-mL mark on the vessel.

8.9 Place the sample in a horizontal shaker at 120 oscillations min^{-1} and shake for 15 h (overnight).

8.10 Remove the sample from the shaker. Place a 300-mesh (0.047-mm) sieve in a ring stand. Place a funnel in a 1-L cylinder. Place funnel and cylinder under sieve to collect the silt and clay. Pour sample through the sieve, rinsing all <20-µm particles into the cylinder. Continue to wash until the suspension volume in the cylinder is ≈800 mL. Fill the cylinder to 1 L with RO water and cover with a 65-mm watch glass.

8.11 Wash sand and coarse silt from the sieve into an evaporation dish and dry at 110 °C overnight. Record weight.

8.12 Place cylinders on stable bench top and apply pipe insulation around sample cylinders. The insulation moderates temperature changes and settling rates. Prepare an RO-water blank cylinder to measure temperature fluctuations. Allow the cylinders to stand overnight to equilibrate the suspension with the room temperature.

8.13 Transfer the dried sand to a nest of sieves. Shake on sieve shaker for 3 minutes. Record the weight of each separate sand fraction (SWi) to the nearest mg.

8.13.1 If optical analysis is requested, place the very fine sand and fine sand fractions in gelatin capsules together with the remaining loose sand fractions in a labeled vial.

8.14 Stir the silt and clay suspension with the mechanical stirrer for at least 5 minutes. Place the cylinder on a stable lab bench. With the cyclonic dampener, draw the rod up-and-down through the length of the cylinder for 30 s to eliminate swirling action caused by the mechanical stirrer.

8.15 Acquire fine silt and clay separates gravimetrically by using a Lowy 25-mL pipette mounted on an adjustable pipette rack (figs. 3A1a1–1, 3A1a1–2, and 3A1a1–3). Obtain an aliquot of <20-µm fraction sample from the cylinder based on the temperature of the blank and table 3A1a1a–1. Withdraw an aliquot at the calculated time in the table. Slowly lower the closed pipette to a depth of 10 cm below the surface of the suspension in the cylinder. Regulate the vacuum such that the pipette fills in ≈12 s.

8.16 Dispense the aliquot into a tared and numbered, 90-mL weighing bottle. Rinse the pipette twice with RO water, placing the rinse water into the tared weighing bottle.

8.17 Wash and tare <2-µm employed bottles after every use. Wash and tare <20-µm bottles after every fourth use.

8.18 Record temperature of the sample (T1) and the blank (T2). Use the average of T1 and T2 to adjust the pipette depth in the suspension as indicated in table 3A1a1a–2 for the <2-µm fraction pipetting. To obtain an aliquot of <2-µm size fraction, pipette after one of the following time intervals: 4.5, 5, 5.5, 6, or 6.5 h according to table 3A1a1a–2.

8.19 Perform the aliquot withdrawal for the <2-µm size fraction the same as described for the <20-µm fraction. Regulate the vacuum such that the pipette fills in ≈12 s.

8.20 Retain sample cylinder if optical mineralogy or fine-clay determinations are requested. Dry the aliquots at 110 °C overnight and cool in a desiccator. Record the weight of the residue (RW) to the nearest 0.1 mg.

8.21 If optical mineralogy is requested, decant remaining sample suspension and transfer the sediment to a 400-mL beaker.

8.22 Fill the beaker to a height of 5.5 cm. Stir the sediment and allow it to settle for 5 minutes. Discard the supernatant. Refill the beaker to a height of 5.5 cm. Stir again, allow to settle for 3 min, and then decant. Fill, stir, and decant after 2-minute settling. Repeat filling, stirring, and decanting until the top half of suspension is clear after the 2-minute settling time.

8.23 Transfer the sediment to a labeled drying dish. Pour off excess water. Air dry. Save in the drying dish for optical mineralogy. Sediment is ≈20 to 50 µm.

Table 3A1a1a–1.—Sampling Times at 10-cm Depth for 0.4408 g L^{-1} Sodium Hexametaphosphate Solution, Assuming 2.65 g cc^{-1} Particle Density.

Temp	20 µm		5 µm		Temp	20 µm		5 µm	
(°C)	*(min)*	*(s)*	*(min)*	*(s)*	*(°C)*	*(min)*	*(s)*	*(min)*	*(s)*
15.00	5	17	84	--	24.25	4	12	67	13
16.00	5	9	82	--	24.50	4	11	66	50
17.00	5	1	80	--	24.75	4	9	66	27
18.00	4	53	78	--	25.00	4	8	66	4
18.50	4	50	77	--	25.25	4	6	65	42
19.00	4	46	76	--	25.50	4	5	65	19
19.50	4	42	75	--	25.75	4	4	64	57
20.00	4	39	74	--	26.00	4	2	64	35
20.25	4	37	73	--	26.25	4	1	64	13
20.50	4	36	73	--	26.50	3	59	63	52
20.75	4	34	73	--	26.75	3	58	63	30
21.00	4	32	72	--	27.00	3	57	63	9
21.25	4	31	72	--	27.25	3	56	62	48
21.50	4	29	71	--	27.50	3	54	62	27
21.75	4	27	71	--	27.75	3	53	62	7
22.00	4	26	70	--	28.00	3	52	61	46
22.25	4	24	70	27	28.25	3	50	61	26
22.50	4	23	70	2	28.50	3	49	61	6
22.75	4	21	69	37	28.75	3	48	60	46
23.00	4	20	69	13	29.00	3	47	60	26
23.25	4	18	68	48	29.25	3	45	60	6
23.50	4	17	68	24	29.50	3	44	59	47
23.75	4	15	68	0	29.75	3	43	59	28
24.00	4	14	67	37	30.00	3	42	59	9

Table 3A1a1a–2.—Sampling Depths (cm) for 2-micron Pipetting of 0.4408 g L^{-1} Sodium Hexametaphosphate Solution, Assuming 2.65 g cc^{-1} Particle Density.

Temp	Sampling Depth at Specified Times					Temp	Sampling Depth at Specified Times				
	4.5 h	5.0 h	5.5 h	6.0 h	6.5 h		4.5 h	5.0 h	5.5 h	6.0 h	6.5 h
(°C)	*(cm)*	*(cm)*	*(cm)*	*(cm)*	*(cm)*	*(°C)*	*(cm)*	*(cm)*	*(cm)*	*(cm)*	*(cm)*
15.00	5.11	5.67	6.24	6.81	7.38	24.25	6.43	7.14	7.85	8.57	9.28
16.00	5.25	5.83	6.41	6.99	7.58	24.50	6.46	7.18	7.90	8.62	9.34
17.00	5.38	5.98	6.58	7.18	7.77	24.75	6.50	7.22	7.95	8.67	9.39
18.00	5.52	6.14	6.75	7.37	7.98	25.00	6.54	7.26	7.99	8.72	9.44
18.50	5.59	6.22	6.84	7.46	8.08	25.25	6.58	7.31	8.04	8.77	9.50
19.00	5.66	6.29	6.92	7.55	8.18	25.50	6.61	7.35	8.08	8.82	9.55
19.50	5.74	6.37	7.01	7.65	8.29	25.75	6.65	7.39	8.13	8.87	9.61
20.00	5.81	6.45	7.10	7.74	8.39	26.00	6.69	7.43	8.18	8.92	9.66
20.25	5.84	6.49	7.14	7.79	8.44	26.25	6.73	7.47	8.22	8.97	9.72
20.50	5.88	6.53	7.19	7.84	8.49	26.50	6.76	7.52	8.27	9.02	9.77
20.75	5.92	6.57	7.23	7.89	8.54	26.75	6.80	7.56	8.31	9.07	9.83
21.00	5.95	6.61	7.27	7.93	8.60	27.00	6.84	7.60	8.36	9.12	9.88
21.25	5.99	6.65	7.32	7.98	8.65	27.25	6.88	7.64	8.41	9.17	9.94
21.50	6.02	6.69	7.36	8.03	8.70	27.50	6.92	7.69	8.45	9.22	9.99
21.75	6.06	6.73	7.41	8.08	8.75	27.75	6.96	7.73	8.50	9.27	10.05
22.00	6.10	6.77	7.45	8.13	8.81	28.00	6.99	7.77	8.55	9.32	10.10
22.25	6.13	6.81	7.49	8.18	8.86	28.25	7.03	7.81	8.59	9.38	10.16
22.50	6.17	6.85	7.54	8.22	8.91	28.50	7.07	7.86	8.64	9.43	10.21
22.75	6.21	6.89	7.58	8.27	8.96	28.75	7.11	7.90	8.69	9.48	10.27
23.00	6.24	6.94	7.63	8.32	9.02	29.00	7.15	7.94	8.74	9.53	10.33
23.25	6.28	6.98	7.67	8.37	9.07	29.25	7.19	7.99	8.78	9.58	10.38
23.50	6.32	7.02	7.72	8.42	9.12	29.50	7.23	8.03	8.83	9.63	10.44
23.75	6.35	7.06	7.76	8.47	9.18	29.75	7.27	8.07	8.88	9.69	10.49
24.00	6.39	7.10	7.81	8.52	9.23	30.00	7.30	8.12	8.93	9.74	10.55

8.24 Fine Clay Determination (<0.2 µm)

8.24.1 In the fine-clay determination, the distance from the center of rotation to the surface of the suspension must be constant for each centrifuge bottle. The particle density (ρp) of the fine clay is assumed to be 2.5 g cc^{-1} (Jackson, 1969). The suspension temperature must be known before the correct liquid viscosity can be entered in the equation.

8.24.2 After taking the <2-µm aliquot, stir the silt and clay suspension with the mechanical stirrer for 5 minutes. Remove sample from the stirrer and place on the lab bench. With the cyclonic dampener, draw the rod up-and-down through the length of the cylinder for 30 s to eliminate swirling action caused by the mechanical stirrer. Allow the suspension to settle for 15 minutes.

8.24.3 Pour the suspension slowly into a centrifuge bottle and fill to the 13 cm line (distance from the center of rotation to the surface of the suspension) marked on the bottle. Stopper the bottle and shake well to mix the suspension.

8.24.4 Centrifuge at 1,500 rpm. Time varies according to temperature of the suspension. Refer to table 3A1a1a–3 below for proper centrifuging time.

Table 3A1a1a–3.—Centrifuge Times for <0.2 micron Pipetting (Based on Stokes' Law with s=15 cm, r=18 cm, $N_{m=}$1,500 rpm, and ρ_p=2.5 g cc^{-1}).

Temp	Viscosity	Delta-Density	Time
(°C)	*(η)*	*(Δρ)*	*(Min)*
18	0.01055	1.501	39.0
19	0.01029	1.501	38.0
20	0.01004	1.502	37.1
21	0.00980	1.502	36.2
22	0.00957	1.502	35.3
23	0.00934	1.502	34.5
24	0.00913	1.502	33.7
25	0.00892	1.503	32.9
26	0.00872	1.503	32.2
27	0.00853	1.503	31.4
28	0.00834	1.503	30.8
29	0.00816	1.504	30.1
30	0.00799	1.504	29.4

8.24.5 After centrifuging, lower the pipette to a 3-cm depth in the suspension. Withdraw a 25-mL aliquot at a rate of ≈12 s. Avoid turbulence. Transfer the aliquot to a weighing bottle.

8.24.6 Place weighing bottle with aliquot in oven. Dry overnight at 110 °C. Remove sample from oven, place in desiccator, and cool to ambient temperature.

8.24.7 Weigh residue weight (RW) to nearest 0.1 mg.

8.25 Carbonate Clay (<2 µm): Manometer Calibration

8.25.1 Before analyzing samples for carbonate clay, a sodium carbonate solution is used to establish a slope and intercept curve for sample analytes and equipment calibration. Calibrate every 6 months or when equipment changes.

8.25.2 Add Na_2CO_3 solution into numbered, tared, 90-mL weighing bottles. Aliquots are: 0.0, 0.5, 1.0, 3.0, 5.0, 7.5, 10.0, 15.0, and 20.0 mL.

8.25.3 Weigh samples in duplicate. Dry the standard samples in the oven overnight at 110 °C. Remove samples from oven, place in desiccator, and cool to ambient temperature. Record the weight of the standard samples to nearest 0.1 mg.

8.25.4 Lay a thin bead of glycerin along lip of the bottle lid.

8.25.5 Fill gelatin capsules with 3 mL of 6 *N* HCl. If HCl leaks from the capsule, discard the capsule. Place the capsule into the glass bottle and immediately cap the bottle. Release any pressure in the bottle by piercing the septa with a hypodermic needle that is not connected to the manometer. Allow 3 to 5 seconds for pressure in bottle to equalize with outside air pressure. Remove needle.

8.25.6 After the gelatin capsule has dissolved, slowly swirl the bottle to saturate the sample adhering to the sides of the bottle. Handle the bottle by the cap to avoid changing the temperature of the container. Allow sample to stand for at least 30 minutes to ensure full reaction of acid with the sample.

8.25.7 Adjust the manometer to zero before taking measurements. Insert the manometer's hypodermic needle in the septa stopper. Measure the pressure inside the weighing bottle and record the manometer readings (mm Hg) to the nearest whole number. Begin readings with the blank.

8.25.8 Calculate the linear regression equation. The dependent variable is the weight of Na_2CO_3 (regressed or predicted values) and the independent variable is the corresponding manometer readings.

8.26 Carbonate Clay (<2 µm) Analysis

8.26.1 If effervescence test results are not available for PSDA samples, perform the effervescence test prior to analyzing for carbonate clay. Samples qualify for carbonate clay analysis if the soil yields

an effervescence reading (method 4E3a1a1) of "slight" or greater. Use the bottle containing the <2-µm dried aliquot (clay) for analysis.

8.26.2 Lay a thin bead of glycerin along O-ring of the bottle lid.

8.26.3 Dispense 3 mL of 6 *N* HCl into a gelatin capsule and place the top on the capsule. If HCl leaks from the capsule, discard the capsule. Place the capsule into the bottle and immediately cap the bottle. Release any pressure in the bottle by piercing the septa with a hypodermic needle that is not connected to the manometer. Allow 3 to 5 seconds for pressure in bottle to equalize with outside air pressure. Remove needle.

8.26.4 Include three blanks for each set of samples (≤24 samples). The average of these blanks is needed for final calculations.

8.26.5 After the gelatin capsule has dissolved, slowly swirl the bottle to saturate the clay adhering to the sides of the bottle. Handle the bottle by the cap to avoid changing the temperature of the container. Allow sample to stand for at least 30 minutes to ensure full reaction of acid with the sample.

8.26.6 Adjust the manometer to zero before taking measurements. Insert the manometer's hypodermic needle in the septa stopper. Measure the pressure inside the weighing bottle and record the manometer readings (MR) to the nearest whole number (mm Hg). Begin readings with the blanks (BR).

8.26.7 Compare the sample readings with those of the standard curve established with the slope and intercept $NaCO_3$ standards.

9. Calculations

9.1 Clay % = 100 x [(RW2 – DW) x (CF / TW)]

RW2 = Residue weight (g), <2-µm fraction

DW = Dispersing agent weight (g) = (0.4408 / CF)

CF = 1,000 mL / DV

DV = Dispensed pipette volume

TW = Total weight (g), H_2O_2-treated, oven-dry sample

9.2 Fine Silt % = 100 x [(RW20 – DW) x (CF / TW)] – Clay %

RW20 = Residue weight (g) of <20-µm fraction

9.3 Sand % = $\sum$ (Swi / TW) x 100

Swi = Weight of sand fractions (1.0, 0.5, 0.25, 0.1, and 0.047 mm)

9.4 Coarse silt % = 100 − (Clay % + Fine silt % + Sand %)

% = weight percent

9.5 Fine Clay (%) = 100 x [(RW − DW) x (CF / TW)]

RW = Residue weight (g) of <0.2-µm fraction

DW = Dispersing agent weight (g) = (0.4364 / CF)

CF = 1,000 mL / DV

DV = Dispensed pipette volume

TW = Total weight of H_2O_2-treated, oven-dry sample

9.6 Calculate carbonate clay percentage. Establish corrected (CR) linear regression equations to estimate the g of $CaCO_3$ in the sample. Correct the manometer reading as follows:

CR = (MR − BR)

CR = Corrected reading

MR = Manometer reading

BR = Average of three blank readings run with each batch (≤24 samples).

9.7 Calculate two regression equations; i.e., one for corrected manometer readings <100 and another for corrected readings ≥100. Use the Na_2CO_3 weights as the dependent variable (regressed or predicted values) and the corresponding manometer readings as the independent variable.

9.8 Carbonate Clay Equivalent (<2 µm) (%) = [(g $CaCO_3$) x 100 x CF] / TW

CF = 1,000 mL / dispensed pipette volume (mL)

TW = Total weight of H_2O_2-treated oven-dry sample

9.9 Noncarbonate Clay (<2 µm) (%) = Total Clay (%) − Carbonate Clay Equivalent (%)

9.10 The time of centrifugation is determined from the following equation modified from Stokes' law (Jackson, 1969).

$Tm = [63.0 \times 10^8 \eta \log (r\ s^{-1})]\ (Nm^2\ D\mu^2\ \Delta\rho)^{-1}$

tm = Time in minutes

η = Viscosity in poises

r = Radius in cm from center of rotation to sampling depth (3 cm + s)

s = Radius in cm from center of rotation to surface of suspension

Nm = rpm (1,500)

Dµ = Particle diameter in microns (0.2 µm)

Δρ = Difference in specific gravity between solvated particles and suspension liquid

63.0×10^8 = Combination of conversion factors for convenient units of time in minutes, t_{min}, Nm as rpm, and particle diameter in microns, Dµ.

9.11 The sedimentation equation that is used to measure the settling rates of particles of different sizes is as follows:

$\nu = 2\ r^2\ g\ (\rho_s - \rho_l) / (9\ \eta)$

ν = Velocity of fall

r = Particle radius

g = Acceleration due to gravity

ρ_s = Particle density

ρ_l = Liquid density

η = Fluid viscosity

9.12 Report each particle-size fraction to the nearest 0.1 percent.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

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Particle-Size Distribution Analysis (3A)
Particles <2 mm (3A1)
Pipette Analysis (3A1a)
Carbonate Removal (3A1a2)
<2-mm Air-Dry (3A1a2a)

1. Introduction to PSDA Carbonate Removal

This method is performed in conjunction with the standard analysis for PSDA (method 3A1a1a) and is not appropriate for all samples.

2. Scope and Field of Application

Soils that have a high carbonate content do not readily disperse. Treatment of these soils with acid removes the carbonates (Grossman and Millet, 1961; Jackson, 1969; Gee and Bauder, 1986; Gee and Or, 2002). The determination of particle-size distribution after the removal of carbonates is used primarily for studies of soil genesis and parent material.

3. Principle

Carbonates are destroyed with a 1 *N* sodium acetate (NaOAc) solution buffered to pH 5. The NaOAc solution is added to the sample until carbonate bubbles no longer evolve. The supernatant is then decanted or filtered from the sample solution. Samples are analyzed according to method 3A1a1, which is the standard KSSL method for PSDA.

3.1 Interferences

The removal of carbonates with 1 *N* NaOAc (pH 5) results in sample acidification. This treatment can destroy the primary mineral structure of clay (Gee and Bauder, 1986).

4. Apparatus

4.1 KIMAX 250-mL GL-45 bottle, tared to 1 mg. Wash and tare bottles every 6 months.

4.2 Ceramic filters, .3-µm absolute retention. (The KSSL can be contacted for more information.)

4.3 Rack to hold ceramic filters and sample containers

4.4 Hot plate capable of 90 °C

4.5 Vacuum, 0.8-bar (80-kPa)

4.6 Thermometer, 0 to 150 °C

4.7 Glass stirring rod

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Sodium acetate solution, 1 *N,* buffered to pH 5

Components: Sodium acetate ($C_2H_3NaO_2$) (CAS# 127-09-3) anhydrous; acetic acid (CH_3CO_2H) (CAS# 64-19-7); RO water

- To a 5-L glass carboy, add the following in order:
  - 4 L of RO water
  - 680 g of sodium acetate
  - ≈250 mL of acetic acid
  - Fill to volume with RO water.
  - Buffer solution to pH 5
- Swirl to mix.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Dispense concentrated acids and bases in fume hood. Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Weigh enough sample to result in a 10 g sample size of <2-mm, air-dry soil after carbonates are removed (e.g., if the sample contains 50% carbonates, weigh 20 g of soil). Place the <2-mm, air-dry sample into a numbered, tared vessel.

8.2 Add ≈200 mL of 1 *N* sodium acetate solution to the sample, mix with a stirring rod, and cover with a watch glass. Allow the sample to stand overnight.

8.3 Place the sample on the hot plate and heat to ≈90 °C. Continue heating until bubbles are no longer visible. Do not boil. Decant the solution, taking care not to pour off any sample. Add another 200 mL of sodium acetate solution. If a reaction occurs, repeat with further additions of sodium acetate solution, heating and decanting until no effervescence is observed.

8.4 When effervescence has stopped, place the vessel on the filter rack and place a ceramic filter in the vessel. Apply vacuum and filter the sample until <5 mL of solution remains. Rinse once with 200 mL of RO water and filter until <5 mL of solution remains.

8.5 Proceed to PSDA standard analysis method (3A1a1a) for filtering. Complete this analysis by following the PSDA standard analysis method beginning at the filtering step (8.5).

9. Calculations

Report the calculations for PSDA standard analysis method 3A1a1a.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Refer to PSDA standard analysis method 3A1a1a.

Particle-Size Distribution Analysis (3A)
Particles <2 mm (3A1)
Pipette Analysis (3A1a)
Iron Removal (3A1a3)
<2-mm Air-Dry (3A1a3a)

1. Introduction to PSDA Iron Removal

This method is performed in conjunction with the standard analysis for PSDA (method 3A1a1a) and is not appropriate for all samples.

2. Scope and Field of Application

Iron oxides (Fe_2O_3) are some of the most common oxides that coat and bind particles of sand, silt, and clay to form aggregates. Soils with iron cementation do not readily disperse. The iron oxides are removed using bicarbonate-buffered, sodium dithionite-citrate solution (Mehra and Jackson, 1960; Gee and Bauder, 1986; Gee and Or, 2002).

3. Principle

Soil samples are treated with H_2O_2 to remove organic matter. Samples are treated with bicarbonate-buffered, sodium dithionite-citrate solution and heated until the sample changes to a grayish color. The suspension is flocculated with saturated NaCl solution and filtered to remove soluble salts. After removal of iron oxides, continue with method 3A1a1, which is the standard KSSL method for PSDA.

3.1 Interferences

If the temperature of the water bath exceeds 80 °C during iron removal, elemental sulphur can precipitate (Mehra and Jackson, 1960). This treatment can destroy primary mineral grains in the clay fraction (El-Swaify, 1980).

4. Apparatus

4.1 KIMAX 250-mL GL-45 bottle, tared to 1 mg. Wash and tare bottles every 6 months.

4.2 Ceramic filters, 0.3-µm absolute retention. (The KSSL can be contacted for more information.)

4.3 Rack to hold ceramic filters and sample containers

4.4 Hot plate capable of 90 °C

4.5 Vacuum, 0.8-bar (80-kPa)

4.6 Thermometer, 0 to 150 °C

4.7 Glass stirring rod

4.8 Water bath

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Hydrogen peroxide, 30 to 35% (H_2O_2) (CAS# 7722-84-1)

5.3 Ethanol (CH_3CH_2OH) (CAS# 64-17-5), 95%, U.S.P.

5.4 Sodium bicarbonate ($NaHCO_3$) (CAS# 144-55-8)

5.5 Sodium chloride (NaCl) (CAS# 7647-14-5)

5.6 Sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) (CAS# 6132-04-3)

5.7 Sodium dithionite ($Na_2S_2O_4$, hydrosulphite) (CAS# 7775-14-6)

5.8 Sodium citrate solution, 0.3 M

Components: Sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$); RO water

- Place a magnetic stir bar in a 1-L glass beaker and add the following in order:
  - 800 mL of RO water
  - 88.4 g of sodium citrate
- Stir until dissolved.
- Fill to volume with RO water.

5.9 Sodium bicarbonate buffer solution, 1 M

Components: Sodium bicarbonate ($NaHCO_3$); RO water

- Place a magnetic stir bar in a 1-L glass beaker and add the following in order:
  - 800 mL of RO water
  - 84.0 g of sodium bicarbonate
- Stir until dissolved.
- Fill to volume with RO water.

5.10 Saturated NaCl solution

Components: Sodium chloride (NaCl); RO water

- Place a magnetic stir bar in a 1-L glass beaker and add the following in order:
  - 800 mL of RO water
  - 360.0 g of sodium chloride
- Stir until dissolved.
- Fill to volume with RO water.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Dispense concentrated acids and bases in fume hood. Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Weigh 10 g samples of <2-mm soil to nearest mg and place into numbered, tared vessels. Since a maximum of ≈0.5 g of Fe_2O_3 can be dissolved in 40 mL of the citrate solution, adjust the weight of the samples so that no single vessel contains more than 0.5 g of Fe_2O_3. Split samples into multiple vessels if necessary. Total sample weight after dissolution should be ≈10 g.

8.2 Add ≈50 mL of RO water and 7.5 mL of hydrogen peroxide to the soil sample at ambient temperature. Allow initial oxidation of organic matter and then place sample on hot plate. If the froth from the reaction exceeds the capacity of the vessel, transfer the sample to a larger beaker.

8.3 Place the sample on a hot plate and heat to 90 °C. Add additional H_2O_2 in increments of 7.5 mL at 30-min intervals until oxidation has completed. Add a total minimum of 30 mL of H_2O_2. If oxidation of organic matter is incomplete, add additional H_2O_2 until oxidation is complete. Heat the sample for an additional 45 min to decompose excess peroxide. If the reaction is violent, add small increments of ethanol to the sample to lower surface tension of the bubbles and thereby dissipate any foaming, or split the sample into multiple beakers for digestion. After oxidation of organic matter is complete, filter the sample once to remove any remaining peroxide.

8.4 In a fume hood, add 40 mL of sodium citrate solution and 5 mL of sodium bicarbonate solution to the sample.

8.5 Place sample in a water bath and heat sample to 80 °C. Do not exceed this temperature.

8.6 Add ≈1 g of sodium dithionite powder. Stir constantly with a glass rod for 1 min and then occasionally for 15 minutes. Add 10 mL of saturated NaCl solution and mix.

8.7 If the sample contains <0.5 g of Fe_2O_3, repeat the dissolution treatment—steps 8.4 and 8.5—one additional time. If the sample contains >0.5 g of Fe_2O_3, repeat the dissolution treatment two more times.

8.8 Combine samples that have been split into separate vessels and proceed to PSDA standard analysis method 3A1a1a for filtering. Complete this analysis by following the PSDA standard analysis method (3A1a1a) beginning at the filtering step (8.5).

9. Calculations

Report the calculations for PSDA standard analysis method 3A1a1a.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Refer to PSDA standard analysis method 3A1a1a.

Particle-Size Distribution Analysis (3A)

Particles <2 mm (3A1)

Pipette Analysis (3A1a)

Silica Removal (3A1a4)

<2-mm Air-Dry (3A1a4a)

1. Introduction to PSDA Silica Removal

This method is performed in conjunction with PSDA standard analysis method (3A1a1a) and is not appropriate for all samples.

2. Scope and Field of Application

Soils that are cemented by silica do not completely disperse with hydrogen peroxide treatment and sodium hexametaphosphate. Treatment with a weak base dissolves the silica bridges and coatings and increases the soil dispersion. This determination is used for studies of parent material and soil genesis.

3. Principle

Soils are pretreated with H_2O_2 to remove organic matter. Soils with silica cementation or coatings are pretreated with a weak NaOH solution overnight. After removal of siliceous cementing agents, analysis continues with method 3A1a1, which is the standard KSSL method for PSDA.

3.1 Interferences

The effects of silica removal by 0.1 *N* NaOH on the clay fraction and particle-size distribution are unknown.

4. Apparatus

4.1 KIMAX 250-mL GL-45 bottle, tared to 1 mg. Wash and tare bottles every 6 months.

4.2 Hot plate capable of 90 °C

4.3 Glass stir rod

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Hydrogen peroxide, 30 to 35% (H_2O_2) (CAS# 7722-84-1)

5.3 Ethanol (CH_3CH_2OH) (CAS# 64-17-5), 95%, U.S.P.

5.4 Sodium hydroxide solution, 0.1 N

Components: Sodium hydroxide (NaOH) (CAS# 1310-73-2); RO water

- To a 1-L glass beaker, add the following in order:

  - 1 L of RO water
  - 4 g NaOH pellets
- Stir with glass rod to combine

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Dispense concentrated acids and bases in fume hood. Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Weigh 10 g of <2-mm, air-dry soil to nearest mg on an electronic balance and place in a numbered, tared vessel.

8.2 Add ≈50 mL of RO water and 7.5 mL of H_2O_2 to soil sample at ambient temperature. Allow initial oxidation of organic matter and then place sample on hot plate. If the froth from the reaction exceeds the capacity of the vessel, transfer the sample to a larger beaker.

8.3 Place the sample on a hot plate and heat to 90 °C. Add three additional 7.5 mL increments of H_2O_2 at 30-min intervals. If oxidation is incomplete, add additional H_2O_2 until organic matter oxidation is complete. Record any unusual sample reactions. If the reaction is violent, try:

8.3.1 Adding small increments of ethanol to the sample to lower surface tension of the bubbles and thereby dissipate any foaming; or

8.3.2 Transferring sample to a 1,000-mL beaker to better contain and control the reaction.

8.4 Remove the sample vessel from the hot plate and place on the filter rack. Add RO water to the 150-mL mark and filter once. Remove sample vessel from filter rack.

8.5 Soak the sample overnight in 100 mL of 0.1 *N* NaOH.

8.6 Proceed to PSDA standard analysis method (3A1a1a) for filtering. Complete this analysis by following the PSDA standard analysis method beginning at the filtering step (8.5).

9. Calculations

Report the calculations for PSDA standard analysis method 3A1a1a.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Refer to PSDA standard analysis method 3A1a1a.

Particle-Size Distribution Analysis (3A)
Particles <2 mm (3A1)
Pipette Analysis (3A1a)
Ultrasonic Dispersion (3A1a5)
<2-mm Air-Dry (3A1a5a)

1. Introduction to PSDA Ultrasonic Dispersion

This method is performed in conjunction with the standard analysis for PSDA (method 3A1a1a) and is not appropriate for all samples.

2. Scope and Field of Application

Soils that are not completely dispersed by standard PSDA may be more thoroughly dispersed using ultrasonic dispersion (Gee and Bauder, 1986; Gee and Or, 2002). Treatments performed with ultrasonic dispersion yield maximum clay concentrations (Mikhail and Briner, 1978).

3. Principle

A soil sample is treated to remove organic matter and soluble salts. The sample is dried in an oven and weighed to obtain the initial weight. Sodium hexametaphosphate solution is added to the sample, which is then made to 100 mL with RO water. The sample is subjected to ultrasonic energy for 5 minutes. After dispersion with the ultrasonic probe, the analysis continues with method 3A1a1, which is the standard KSSL method for PSDA.

3.1 Interferences

Ultrasonic dispersion has been reported to destroy primary soil particles. Watson (1971) summarized studies that reported the destruction of biotite and breakdown of microaggregates by ultrasonic dispersion. However, Saly (1967) reported that ultrasonic vibration did not cause the destruction of the clay crystalline lattice or the breakdown of primary grains. The samples ranged from sandy to clayey soils. The cementing agents represented humus, carbonates, and hydroxides of iron and aluminum.

4. Apparatus

4.1 KIMAX 250-mL GL-45 bottles, tared to 1 mg. Wash and tare bottles every 6 months.

4.2 Beakers, 500-mL or 1,000-mL

4.3 Electronic balance, ±0.10-mg sensitivity

4.4 Hot plate, capable of 100 °C

4.5 Ceramic filters, .3-µm absolute retention. (The KSSL can be contacted for more information.)

4.6 Rack to hold ceramic filters and sample containers

4.7 Watch glasses, 65-mm diameter

4.8 Ultrasonic probe, 19-mm (¾ in) horn, 20 kHz, 600 watts

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Calcium sulfate ($CaSO_4$) (CAS# 7778-18-9), anhydrous, or equivalent desiccant (Reagent example: Drierite)

5.3 Ethanol (CH_3CH_2OH) (CAS# 64-17-5), 95%, U.S.P.

5.4 Hydrogen peroxide, 30 to 35% (H_2O_2) (CAS# 7722-84-1)

5.5 Sodium hexametaphosphate solution

Components: Sodium hexametaphosphate $(NaPO_3)_6$ (CAS# 68915-31-1), reagent grade; sodium carbonate (Na_2CO_3) (CAS# 497-9-8); RO water

- To a 1-L polyethylene bottle, add the following in order:
  - 1 L of RO water
  - 35.7 g of $(NaPO_3)_6$
  - 7.94 g of Na_2CO_3
- Invert to mix.

5.5.1 Standardize each new batch of hexametaphosphate solution. Use only designated weighing bottles for standardization. Wash and tare these bottles after each standardization.

5.5.2 Standards are run in duplicate. Add sodium hexametaphosphate solution to numbered, tared, 90-mL weighing bottles. Aliquots are: 8.5, 9.0, 9.3, 9.6, 10.0, 10.3, 10.6, and 11.0 mL

5.5.3 Place the 16 weighing bottles and aliquots in the oven overnight and record dry residue weight of sodium hexametaphosphate.

5.5.4 Determine the exact volume of solution needed to add 0.4408 g of sodium hexametaphosphate into each sample by regressing the volume of sodium hexametaphosphate solution against the dry residue weight of sodium hexametaphosphate.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Dispense concentrated acids and bases in fume hood. Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Weigh 10 g of <2-mm, air-dry soil to nearest mg on an electronic balance and place into a numbered, tared vessel. A quality control sample is included in each batch (≤24 samples).

8.2 Add ≈50 mL of RO water and 7.5 mL of H_2O_2 to the soil sample at ambient temperature. Allow initial oxidation of organic matter and then place sample on hot plate. If the froth from the reaction exceeds the capacity of the vessel, transfer the sample to a larger beaker.

8.3 Place the sample on a hot plate and heat to 90 °C. Add three additional 7.5 mL increments of H_2O_2 at 30-min intervals. If oxidation is incomplete, add additional H_2O_2 until organic matter oxidation is complete. Record any unusual sample reactions. If the reaction is violent, try:

8.3.1 Adding small increments of ethanol to the sample to lower surface tension of the bubbles and thereby dissipate any foaming; or

8.3.2 Transferring sample to a 1,000-mL beaker to better contain and control the reaction.

8.4 Place the sample vessel on the filter rack. Add RO water up to the 150-mL mark. Place ceramic filter in sample, connect to the vacuum trap assembly with tubing, and turn on the vacuum. Filter until liquid is removed and approximately 5 mL remain in the bottom of the vessel.

8.5 Wash the sample from the filter, add ≈150 mL of RO water four additional times. Stir the sample with the filter to ensure all soil particles will be rinsed. Steps for filtering are as follows:

8.5.1 During aspiration, it may be necessary to occasionally apply back-pressure to the filter to remove soil obstructing the pores in the ceramic.

8.5.2 Samples that contain gypsum require additional treatment and filtering.

- 1–5% gypsum: Stir the sample with a magnetic stirrer for 5 min and rinse five times with ≈250 mL of RO water each time.
- 5–10% gypsum: Place the sample in a 1,000-mL beaker, add ≈800 mL of RO water, stir the sample with a magnetic stirrer for 5 min, and then rinse with ≈800 mL five times.
- 10–20% gypsum: Place the sample in a 1,000-mL beaker, add ≈800 mL of RO water, add 100 g sodium chloride (NaCl), and stir the sample with a magnetic stirrer for 10 minutes. Rinse the sample with ≈800 mL of RO water five times.

- 20–40% gypsum: Place the sample in a 1,000-mL beaker, add ≈800 mL of RO water, add 100 g sodium chloride (NaCl), stir the sample with a magnetic stirrer for 10 minutes, and filter once. Remove sample from the rack, repeat sodium chloride treatment, and return sample to rack. Rinse the sample with ≈800 mL of RO water five times
- 40–60% gypsum: Repeat sodium chloride treatment and single filtering three times. Rinse the sample with ≈800 mL of RO water five times.
- 60–80% gypsum: Repeat sodium chloride treatment four times. Rinse the sample with ≈800 mL of RO water five times.
- >80% gypsum: Repeat sodium chloride treatment five times and rinse five times.

8.6 Place sample in oven. Dry the sample overnight at 110 °C. Remove the sample from the oven, place in a desiccator, and cool to ambient temperature.

8.7 Record the total weight (TW) of the sample to the nearest mg.

8.8 Add the exact volume of sodium hexametaphosphate solution (≈10 mL) needed to add 0.4408 g of sodium hexametaphosphate to sample. Let stand approximately 1 hour or until sample has slightly dispersed by sodium hexametaphosphate and can be transferred to a 50-mm diameter beaker for sonication. If sample imbibes hexametaphosphate, add RO water until sample is slightly damp. After 1 hour, swirl sample to loosen it from vessel and pour into a 50-mm diameter beaker using a minimum of water to rinse sample from one vessel to the other. Use a rubber policeman to remove any residue adhering to the vessel. Try to keep the volume of suspension under 100 mL.

8.9 Disperse the suspension with ultrasonic vibrations. Consult the instruction manual to ensure the power supply is properly tuned. Immerse the probe in the suspension to ≈½ inch above bottom of the beaker. Adjust output control as required. Sonicate for 5 minutes. Between samples, clean the probe by placing it in water or alcohol and energizing it for a few seconds if needed.

8.10 Place a 300-mesh (0.047-mm) sieve above a funnel in a ring stand. Place a 1-L cylinder below the funnel. After ultrasonic dispersion, pour the suspension through the sieve. Collect the silt and clay in the 1-L cylinder by rinsing all <20-µm particles into the cylinder. Use a rubber policeman or finger to expedite filtering. Continue to wash until the suspension volume in the cylinder is ≈800 mL. Fill the cylinder to 1 L with RO water and cover with a 65-mm watch glass.

8.11 Sand and coarse silt may remain on the sieve. If so, wash the sand into an evaporation dish and dry the sand at 110 °C overnight. Record weight.

8.12 Place cylinders on stable bench top and apply pipe insulation around sample cylinders. Prepare an RO-water blank cylinder to measure

temperature fluctuations. Allow the cylinders to stand overnight to equilibrate the suspension with the room temperature.

8.13 Proceed to PSDA standard analysis method (3A1a1a) for sieving sand fractions and sample extraction. Complete this analysis by following the PSDA standard analysis method beginning at the filtering step (8.5).

9. Calculations

Report the calculations for PSDA standard analysis method 3A1a1a.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Refer to PSDA standard analysis method 3A1a1a.

Particle-Size Distribution Analysis (3A)

Particles <2 mm (3A1)

Pipette Analysis (3A1a)

Water Dispersible PSDA (3A1a6)

<2-mm Air-Dry (3A1a6a)

1. Introduction to PSDA Water Dispersion

This method is performed in conjunction with the standard analysis for PSDA (method 3A1a1a) and is not appropriate for all samples.

2. Scope and Field of Application

This method provides a means of evaluating the susceptibility of a soil to water erosion. The degree to which a soil disperses without the oxidation of organic matter, the removal of soluble salts, or the addition of a chemical dispersant may be compared with results from chemical dispersion (Bouyoucos, 1929).

3. Principle

Water dispersible particle-size distribution analysis may also be determined from a soil suspension without the removal of organic matter or soluble salts or without the use of a chemical dispersant. Results from this analysis are compared to results from standard PSDA. In the standard PSDA, salts and cementing agents have been removed and grains are thoroughly dispersed.

3.1 Interferences

No interferences are known.

4. Apparatus

4.1 KIMAX 250-mL GL-45 bottles, tared to 1 mg. Wash and tare bottles every 6 months.

4.2 Electronic balance, ±0.10-mg sensitivity

4.3 Desiccator

4.4 Cylinders, 1-L, white line fused onto glass at 1-L mark

4.5 Oven, 110 °C

4.6 Mechanical shaker, horizontal, 120 oscillations min^{-1}, 1½-in strokes

4.7 Motor driven stirrer (Equipment example: Kilmer and Mullins)

4.8 Cyclonic dampening hand stirrer that has a brass rod threaded at one end and a perforated plexiglass disk fastened to the threaded end to reduce sample vortex from mechanical stirrer. The rod should be slightly longer than the height of the settling cylinders. The plexiglass disk should be ½" narrower than inside diameter of the cylinders.

4.9 Adjustable pipette rack (figs. 3A1a1–1, 3A1a1–2, 3A1a1–3; Shaw, 1932)

4.10 Lowy pipettes, 25-mL, with overflow bulb. (The KSSL can be contacted for more information.)

4.11 Polyurethane foam pipe insulation that fits snugly around cylinder

4.12 Sieve shaker with 12.7-mm (½ in) vertical and lateral movement at 500 oscillations min^{-1}, accommodates nesting 2-⅜ inch sieves

4.13 Watch glasses, 65-mm diameter

4.14 Evaporating dishes, porcelain, 80-mm diameter, 32-mm height, with lip

4.15 Set of 60-mm (2-⅜ in) sieves, square-weave phosphor bronze wire cloth, except 300 mesh, which is twilled weave. U.S. series and Tyler Screen Scale equivalent designations are as follows:

Sand Size	Opening	U.S. No.	Tyler Mesh Size
	(mm)		
Very coarse sand (VCS)	1.0	18	16
Coarse sand (CS)	0.5	35	32
Medium sand (MS)	0.25	60	60
Fine sand (FS)	0.105	140	150
Very fine sand (VFS)	0.047	300	300

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Calcium sulfate ($CaSO_4$) (anhydrous) (CAS# 7778-18-9) or equivalent desiccant (Reagent example: Drierite)

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Weigh 10 g of <2-mm, air-dry soil to nearest mg on an electronic balance and place into a numbered, tared vessel. A quality control sample is included in each batch (≤24 samples).

8.2 Dry the sample in an oven at 110 °C overnight. Remove the sample from the oven, place in a desiccator, and cool to ambient temperature.

8.3 Record the total weight (TW) of the sample to the nearest mg.

8.4 Add ≈175 mL of RO water to sample. Place the sample in a horizontal shaker at 120 oscillations min^{-1} for 15 h (overnight).

8.5 Proceed to PSDA standard analysis method (3A1a1a) for collecting silt and clay in the cylinder. Complete this analysis by following the PSDA standard analysis method beginning at the filtering step (8.5). Reference table 3A1a6a–1 and table 3A1a6a–2 for time and sampling depths.

Table 3A1a6a–1.—Sampling Times for 20-micron and 5-micron Pipetting at 10-cm depth, Using RO Water and Assuming 2.65 g cc−1 Particle Density. (Use this table with methods 3A1a6a and 3A1a6b.)

Temp	20 µm		5 µm		Temp	20 µm		5 µm	
(°C)	*(min)*	*(s)*	*(min)*	*(s)*	*(°C)*	*(min)*	*(s)*	*(min)*	*(s)*
15.00	5	17	84	26	24.25	4	12	67	5
16.00	5	8	82	12	24.50	4	10	66	42
17.00	5	0	80	7	24.75	4	9	66	19
18.00	4	53	78	3	25.00	4	7	65	56
18.50	4	49	77	4	25.25	4	6	65	34
19.00	4	45	76	8	25.50	4	4	65	11
19.50	4	42	75	9	25.75	4	3	64	49
20.00	4	38	74	14	26.00	4	2	64	27
20.25	4	37	73	47	26.25	4	0	64	6
20.50	4	35	73	20	26.50	3	59	63	44
20.75	4	33	72	53	26.75	3	58	63	23
21.00	4	32	72	27	27.00	3	56	63	1
21.25	4	30	72	0	27.25	3	55	62	40
21.50	4	28	71	35	27.50	3	54	62	20
21.75	4	27	71	9	27.75	3	52	61	59
22.00	4	25	70	43	28.00	3	51	61	39
22.25	4	24	70	18	28.25	3	50	61	18
22.50	4	22	69	53	28.50	3	39	60	58
22.75	4	21	69	29	28.75	3	47	60	38
23.00	4	19	69	4	29.00	3	46	60	19
23.25	4	17	68	40	29.25	3	45	59	59
23.50	4	16	68	16	29.50	3	44	59	40
23.75	4	15	67	52	29.75	3	43	59	21
24.00	4	13	67	28	30.00	3	41	59	1

Table 3A1a6a–2.—Sampling Depths (cm) for 2-micron Pipetting, Using RO Water and Assuming 2.65 g cc^{-1} Particle Density. (Use this table with methods 3A1a6a and 3A1a6b.)

Temp	Sampling depth in cm at specified times				
(°C)	*4.5 (h)*	*5.0 (h)*	*5.5 (h)*	*6.0 (h)*	*6.5 (h)*
15.00	5.12	5.69	6.25	6.82	7.39
16.00	5.26	5.84	6.42	7.01	7.59
17.00	5.39	5.99	6.59	7.19	7.79
18.00	5.54	6.15	6.77	7.38	8.00
18.50	5.61	6.23	6.85	7.47	8.10
19.00	5.67	6.31	6.94	7.57	8.20
19.50	5.75	6.39	7.03	7.66	8.30
20.00	5.82	6.47	7.11	7.76	8.41
20.25	5.86	6.51	7.16	7.81	8.46
20.50	5.89	6.55	7.20	7.86	8.51
20.75	5.93	6.59	7.24	7.90	8.56
21.00	5.96	6.63	7.29	7.95	8.61
21.25	6.00	6.67	7.33	8.00	8.67
21.50	6.04	6.71	7.38	8.05	8.72
21.75	6.07	6.75	7.42	8.10	8.77
22.00	6.11	6.79	7.47	8.14	8.82
22.25	6.14	6.83	7.51	8.19	8.88
22.50	6.18	6.87	7.55	8.24	8.93
22.75	6.22	6.91	7.60	8.29	8.98
23.00	6.25	6.95	7.64	8.34	9.03
23.25	6.29	6.99	7.69	8.39	9.09
23.50	6.33	7.03	7.73	8.44	9.14
23.75	6.37	7.07	7.78	8.49	9.19
24.00	6.40	7.11	7.83	8.54	9.25

Temp	Sampling depth in cm at specified times				
(°C)	*4.5 (h)*	*5.0 (h)*	*5.5 (h)*	*6.0 (h)*	*6.5 (h)*
24.25	6.44	7.16	7.87	8.59	9.30
24.50	6.48	7.20	7.92	8.64	9.36
24.75	6.51	7.24	7.96	8.69	9.41
25.00	6.55	7.28	8.01	8.74	9.46
25.25	6.59	7.32	8.05	8.79	9.52
25.50	6.63	7.36	8.10	8.84	9.57
25.75	6.66	7.41	8.15	8.89	9.63
26.00	6.70	7.45	8.19	8.94	9.68
26.25	6.74	7.49	8.24	8.99	9.74
26.50	6.78	7.53	8.28	9.04	9.79
26.75	6.82	7.57	8.33	9.09	9.85
27.00	6.85	7.62	8.38	9.14	9.90
27.25	6.89	7.66	8.42	9.19	9.96
27.50	6.93	7.70	8.47	9.24	10.01
27.75	6.97	7.74	8.52	9.29	10.07
28.00	7.01	7.79	8.57	9.34	10.12
28.25	7.05	7.83	8.61	9.40	10.18
28.50	7.09	7.87	8.66	9.45	10.23
28.75	7.12	7.92	8.71	9.50	10.29
29.00	7.16	7.96	8.75	9.55	10.35
29.25	7.20	8.00	8.80	9.60	10.40
29.50	7.24	8.05	8.85	9.65	10.46
29.75	7.28	8.09	8.90	9.71	10.52
30.00	7.32	8.13	8.95	9.76	10.57

9. Calculations

9.1 Clay % = 100 x [(RW_2 x CF) / TW]

RW_2 = Residue weight (g), <2-µm fraction

CF = 1,000 mL / DV

DV = Dispensed pipette volume

TW = Total weight (g), oven-dry sample

9.2 Fine Silt % = [(100 x RW_{20} x CF) / TW] – Clay %

RW_{20} = Residue weight (g) of <20-µm fraction

9.3 Sand % = ∑(Swi / TW) x 100

Swi = Weight of sand fractions (1.0, 0.5, 0.25, 0.1, and 0.047 mm)

9.4 Coarse silt % = 100 – (Clay % + Fine silt % + Sand %)

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Refer to PSDA standard analysis method 3A1a1a.

Particle-Size Distribution Analysis (3A)
Particles <2 mm (3A1)
Pipette Analysis (3A1a)
Gypseous PSDA (3A1a7)
<2-mm Air-Dry (3A1a7a)

1. Introduction to PSDA for Gypseous Samples

This method is performed in conjunction with the standard analysis for PSDA (method 3A1a1a) and is not appropriate for all samples.

2. Scope and Field of Application

Soil taxonomy was amended in 2014 to comprehensively recognize properties of gypseous soils (Soil Survey Staff, 2014). Among the revisions was the addition of substitute particle-size classes (family level of classification) for soils with ≥40% gypsum in the <20 mm size fraction (gypseous soils) (Soil Survey Staff, 2014). The added substitute particle-size classes were “gypseous-skeletal” for gypseous soils that have ≥35% coarse fragments and two classes for gypseous soils that have <35% coarse fragments: “coarse-gypseous” (≥50% particles 0.1 to 2.0 mm diameter) and “fine-gypseous” (<50% particles 0.1 to 2.0 mm diameter).

These taxa were established to enable better interpretations of soils with high amounts of gypsum, especially interpretations of those properties related to water retention and movement. These definitions apply to “particles” with any mineralogy, including gypsum (Soil Survey Staff, 2014).

3. Principle

This PSDA method is intended for soils that have ≥40% gypsum but can be applied to samples with lesser amounts of gypsum. Clay percentages are determined using the standard KSSL PSDA in which gypsum is removed. These clay percentages are then recalculated on a <2-mm “gypsum-intact” basis. Sand fractions are determined on a separate 10-g sample using sonication in 50 mL of 70/30 ethanol-aqueous solution. Sands are wet-sieved through a 300-mesh screen (0.047-mm opening), rinsed with 800 mL of 70/30 ethanol-aqueous solution, and collected. Sands are then dried at 35 ºC, dry sieved, and weighed by fraction. Silt percentages are calculated as the difference between 100% and the combined recalculated clay plus sand percentages.

3.1 Interferences

Gypsum interferes with particle distribution by causing flocculation of particles.

4. Apparatus

4.1 KIMAX 250-mL GL-45 bottles, tared to 1 mg. Wash and tare bottles every 6 months.

4.2 50-mm diameter beakers

4.3 Oven, capable of 110 °C

4.4 Desiccator

4.5 Electronic balance, ±0.10-mg sensitivity

4.6 Evaporating dishes, porcelain, 80-mm diameter, 32-mm height, with lip

4.7 Ultrasonic probe, 19-mm (¾ in) horn, 20 kHz, 600 watts

4.8 Set of 60-mm (2-⅜ in) sieves, square-weave phosphor bronze wire cloth, except 300 mesh, which is twilled weave. U.S. series and Tyler Screen Scale equivalent designations are as follows:

Sand Size	Opening	U.S. No.	Tyler Mesh Size
	(mm)		
Very coarse sand (VCS)	1.0	18	16
Coarse sand (CS)	0.5	35	32
Medium sand (MS)	0.25	60	60
Fine sand (FS)	0.105	140	150
Very fine sand (VFS)	0.047	300	300

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Calcium sulfate ($CaSO_4$) (CAS# 7778-18-9) anhydrous, or equivalent desiccant (Reagent example: Drierite)

5.3 Ethanol (CH_3CH_2OH), (CAS# 64-17-5), 95%, U.S.P.

5.4 **Ethanol-aqueous solution, 70/30, 70% ethanol solution**

Components: Ethanol (CH_3CH_2OH), RO water

- To a 1-L glass graduated cylinder or beaker, add the following in order:
  - 700 mL of ethanol
  - 300 mL of RO water

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Weigh two 10 g samples of <2-mm, air-dry soil to nearest mg. Place one sample into a numbered, tared vessel. Place the vessel in the oven. Place the other 10 g sample into numbered, tared, 50-mm diameter beaker. A quality control standard sample is included in each batch (≤24 samples).

8.2 To the 10 g sample placed in the 50 mm diameter beaker, add 50 mL of 70/30 ethanol-aqueous solution. Allow solution to stand for 5 minutes.

8.3 Insert ultrasonic probe ≈20 mm below the surface of solution and apply energy for 5 minutes.

8.4 Pass solution through the 300-mesh screen (0.047-mm opening), rinsing with ≈800 mL of 70/30 ethanol-aqueous solution.

8.5 Wash the sand into an evaporating dish and dry the sand at 35 °C overnight. (Do not allow a higher temperature as the solution is 70% ethanol.)

8.6 Transfer the dried sand to the nest of sieves. Shake on sieve shaker for 3 minutes. Record the weight of each separate sand fraction (SWi) to the nearest mg.

8.6.1 If optical analysis is requested, place the very fine sand and fine sand fractions in gelatin capsules together with the remaining loose sand fractions in a labeled vial.

8.7 For the 10 g sample placed in the tared vessel, proceed to standard analysis method 3A1a1a for organic matter removal. Complete this analysis by following the PSDA standard analysis method (3A1a1a) beginning at the filtering step (8.5). Results from this analysis are required for calculations.

9. Calculations

9.1 Calculate the percent clay with gypsum removed.

$$Clay_{GR}\ \% = 100 \times [(RW_2 - DW) \times (CF / TW)]$$

$Clay_{GR}$ = Clay (%) with gypsum removed

RW_2 = Residue weight (g), <2-µm fraction

DW = Dispersing agent weight (g) = (0.4408 / CF)

CF = 1,000 mL / DV

DV = Dispensed pipette volume

TW = Total weight (g), H_2O_2-treated, oven-dry sample

9.2 Calculate percent clay with gypsum intact.

$$Clay_{GI}\ \% = Clay_{GRA1} \times Clay_{GRA2}$$

$Clay_{GI}$ % = Clay (%) with gypsum intact

$Clay_{GRA1}$ = Clay with gypsum removed, adjusted to g clay / 100 g insoluble soil basis

$Clay_{GRA2}$ = Clay with gypsum removed, adjusted to g insoluble soil / 10 g <2-mm intact soil basis

9.3 Sand % = $\sum$ (SWi / TW) x 100

SWi = Weight of sand fractions (1.0, 0.5, 0.25, 0.1, and 0.047 mm)

9.4 Total Silt % = 100 − (Total $Clay_{GI}$ % + Total Sand %)

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Refer to PSDA standard analysis method 3A1a1a.

Particle-Size Distribution Analysis (3A)
Particles <2 mm (3A1)
Pipette Analysis (3A1a)
Field-Moist PSDA (3A1a1b)

1. Introduction to Field-Moist PSDA

The standard KSSL procedure for particles with <2-mm diameter is the air-dry method (3A1a1a). Although a homogenized sample is more easily obtained from air-dry material than from moist material, some soils irreversibly harden when dried. In such cases, Field-Moist PSDA may be used.

2. Scope and Field of Application

The phenomenon of aggregation through oven- or air-drying is an important example of irreversibility of colloidal behavior in the soil-water system (Kubota, 1972; Espinoza et al., 1975). Drying such soils decreases the measured clay content. This decrease can be attributed to the cementation upon drying (Maeda et al., 1977). The magnitude of the effect varies with the particular soil (Maeda et al., 1977).

PSDA uses the principles of Stokes' Law, which takes the following assumptions into account for soil sedimentation measurements:

- Terminal velocity is attained as soon as settling of particles begins.
- Settling and resistance of particles are entirely due to the viscosity of the fluid.
- Particles are smooth and spherical.
- There is no interaction between individual particles in the solution (Gee and Bauder, 1986; Gee and Or, 2002).

Since soil particles are neither smooth nor spherical, the radius of the particle is considered an equivalent rather than an actual radius. In this method, particle density is assumed to be 2.65 g cc^{-1}, which is the density of quartz. Special treatment of samples may be needed to disperse individual grains aggregated by cementing agents, such as silica, iron oxides, or carbonates. Several treatments can be conducted in conjunction with the field-moist PSDA method and are outlined in this section.

- Carbonate Removal: Method 3A1a2b
- Iron Removal: Method 3A1a3b
- Silica Removal: Method 3A1a4b
- Ultrasonic Dispersion: Method 3A1a5b
- Water Dispersible: Method 3A1a6b
- Gypsum Removal: Method 3A1a7b

3. Principle

Samples for the field-moist PSDA are analyzed in tandem. Ten grams of <2-mm field-moist sample is treated with hydrogen peroxide and any additional method for the removal of iron oxides, carbonates, or silica. Samples are filtered to remove any treatment solution and soluble salts. Samples are then weighed in tandem, each undergo different treatments. One sample is oven-dried and its weight is recorded.

The second sample is treated with sodium hexametaphosphate to improve dispersion by removing cementing agents, rehydrating clays, and separating individual soil particles. The sample is dried in an oven to obtain the initial weight, dispersed with a sodium hexametaphosphate solution, and mechanically shaken. The sand fraction is removed from the suspension by wet sieving and then is fractionated by dry sieving. The clay and fine silt fractions are determined by extracting aliquots of sample from sedimentation cylinders at specific time and depth intervals. The samples are dried at 110 °C and weighed. Coarse silt is the difference between 100% and the sum of the sand, clay, and fine silt percentages.

The soil suspension from the sedimentation cylinder is used to determine the fine-clay fraction. This suspension is stirred, poured into a centrifuge bottle, and centrifuged at 1,500 rpm. A 25-mL aliquot is withdrawn with a pipette. The aliquot is dried in an oven and weighed, and the percentage of fine clay is calculated based on the total sample weight. Both the air-dry and moist PSDA data are determined as percent of the <2-mm fraction on an oven-dry basis.

3.1 Interferences

Cementing agents, such as carbonates, iron oxides, and silica, can inhibit complete dispersion. Special treatment and dispersion methods are presented later in this section and should be used in conjunction with this method.

Gypsum interferes with particle distribution by causing flocculation of particles and is removed by stirring and washing the soil with reverse osmosis water or sodium chloride solution.

Partial flocculation may occur in some soils if excess H_2O_2 is not removed from the soil after its use in organic matter oxidation.

Treatment of micaceous soils with H_2O_2 causes exfoliation of the mica plates and a matting of particles when dried in the oven. Because of exfoliation in these soils, a true measurement of fractions is uncertain (Drosdoff and Miles, 1938).

The removal of carbonates with 1 *N* sodium acetate (pH 5) (method 3A1a2) results in sample acidification. This treatment can destroy the primary mineral structure of clay (Gee and Bauder, 1986).

If the temperature of the water bath exceeds 80 °C during iron removal (method 3A1a3), elemental sulphur can precipitate (Mehra and Jackson, 1960). This treatment can destroy primary mineral grains in the clay fraction (El-Swaify, 1980).

The effects of silica removal with 0.1 *N* sodium hydroxide (method 3A1a4) on the clay fraction and particle-size distribution are unknown.

Ultrasonic dispersion (method 3A1a5) has been reported to destroy primary soil particles (Watson, 1971). Studies have reported the destruction of biotite and breakdown of microaggregates by ultrasonic dispersion. However, Saly (1967) reported that ultrasonic vibration did not cause the destruction of the clay crystalline lattice or the breakdown of primary grains. The samples ranged from sandy to clayey soils. The cementing agents represented humus, carbonates, and hydroxides of iron and aluminum. No standard procedures have been adopted using ultrasonic dispersion.

4. Apparatus

4.1 KIMAX 250-mL GL-45 bottles, tared to 1 mg. Wash and tare bottles every 6 months.

4.2 Ceramic filters, .3-µm absolute retention. (The KSSL can be contacted for more information.)

4.3 Rack to hold ceramic filters and sample containers

4.4 Mechanical shaker, horizontal, 120 oscillations min^{-1}, 1½-in strokes. (The KSSL can be contacted for more information.)

4.5 Cylinders, 1-L, white line fused onto glass at 1-L mark

4.6 Oven, 110 °C

4.7 Hot plate, 100 °C

4.8 Vacuum, 0.8 bar (80 kPa)

4.9 Thermometer, 0 to 150 °C

4.10 Desiccator

4.11 Motor driven stirrer. (The KSSL can be contacted for more information.)

4.12 Cyclonic dampening hand stirrer that has a brass rod threaded at one end and a perforated plexiglass disk fastened to the threaded end to reduce sample vortex from mechanical stirrer. The rod should be slightly longer than the height of the settling cylinders. The plexiglass disk should be ½" narrower than inside diameter of the cylinders.

4.13 Adjustable pipette rack (figs. 3A1a1–1, 3A1a1–2, and 3A1a1–3; Shaw, 1932)

4.14 Lowy pipettes, 25-mL, with overflow bulb. (The KSSL can be contacted for more information.)

4.15 Polyurethane foam pipe insulation that fits snugly around cylinder

4.16 Sieve shaker with 12.7-mm (½ in) vertical and lateral movement at 500 oscillations min^{-1}, accommodates nesting 2-⅜ inch sieves

4.17 Weighing bottles, 90-mL, threaded, tared to 0.1 mg

4.18 Drying dishes, aluminum

4.19 Lab timer
4.20 Electronic balance, ±0.10-mg sensitivity
4.21 Electronic balance, ±1.0-mg sensitivity
4.22 Watch glasses, 65-mm diameter
4.23 Evaporating dish, porcelain, 80-mm diameter, 32-mm height, with lip
4.24 Centrifuge, floor model capable of 1,500 rpm
4.25 Centrifuge bottles, 500-mL
4.26 Torsion balance
4.27 Manometer, hand-held, gauge and differential pressure, capable of 1,000 psi
4.28 Gelatin capsules, 5-mL
4.29 Machined PVC caps for threaded 90-mL weighing bottles, 3.2-cm (1¼ in) diameter with 1.1-cm (7⁄16 in) diameter hole drilled in center, O-ring seal
4.30 O-rings, 3.2 x 38.1 mm (⅛ x 1½ in)
4.31 Septas, rubber, 7.9-mm (5⁄16 in) diameter. Place in machined cap.
4.32 Hypodermic needle, 25.4-mm (1 in), 23 gauge
4.33 Stir rods with rubber policemen
4.34 Mortar and pestle
4.35 Set of 60-mm (2-⅜ in) sieves, square-weave phosphor bronze wire cloth, except 300 mesh, which is twilled weave. U.S. series and Tyler Screen Scale equivalent designations are as follows:

Sand Size	Opening	U.S. No.	Tyler Mesh Size
	(mm)		
Very coarse sand (VCS)	1.0	18	16
Coarse sand (CS)	0.5	35	32
Medium sand (MS)	0.25	60	60
Fine sand (FS)	0.105	140	150
Very fine sand (VFS)	0.047	300	300

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water
5.2 Sodium hexametaphosphate $(NaPO_3)_6$ (CAS# 68915-31-1)
5.3 Sodium carbonate (Na_2CO_3) (CAS# 497-9-8)
5.4 Sodium chloride (NaCl) (CAS# 7647-14-5), granular
5.5 Hydrochloric acid (HCl) (CAS# 7647-01-0) concentrated technical grade
5.6 Calcium sulfate $(CaSO_4)$ (anhydrous) (CAS# 7778-18-9) or equivalent desiccant (Reagent example: Drierite)

5.7 Ethanol (CH_3CH_2OH) (CAS# 64-17-5), 95%, U.S.P.

5.8 Hydrogen peroxide, 30 to 35% (H_2O_2) (CAS# 7722-84-1)

5.9 Sodium hexametaphosphate solution

Components: Sodium hexametaphosphate [$(NaPO_3)_6$], sodium carbonate (Na_2CO_3), RO water

- To a 1-L polyethylene bottle, add the following in order:
  - 1 L of RO water
  - 35.7 g of $(NaPO_3)_6$
  - 7.94 g of Na_2CO_3
- Invert to mix.

5.9.1 Standardize each new batch of hexametaphosphate solution. Use only designated weighing bottles for standardization. Wash and tare these bottles after each standardization.

5.9.2 Standards are run in duplicate. Add sodium hexametaphosphate solution to numbered, tared, 90-mL weighing bottles. Aliquots are: 8.5, 9.0, 9.3, 9.6, 10.0, 10.3, 10.6, and 11.0 mL.

5.9.3 Place the 16 weighing bottles and aliquots in oven overnight and record dry residue weight of sodium hexametaphosphate.

5.9.4 Determine the exact volume of solution needed to add 0.4408 g of sodium hexametaphosphate into each sample by regressing the volume of sodium hexametaphosphate solution against the dry residue weight of sodium hexametaphosphate.

5.10 Hydrochloric acid solution, 6 *N*

Components: Hydrochloric acid (HCl), RO water

- To a 2-L polyethylene bottle, add the following in order:
  - 1 L of RO water
  - 1 L of concentrated HCl
- Invert to mix.

5.11 Sodium carbonate solution

Components: Sodium carbonate (Na_2CO_3), RO water

- To a 1-L polyethylene bottle, add the following in order:
  - 1 L of RO water
  - 10.6 g Na_2CO_3
- Invert to mix.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or

apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Dispense concentrated acids and bases in fume hood. Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids.

Users should be familiar with operation of a centrifuge. Balance the centrifuge bottles.

7. Sample Preparation

Samples are representative, field-state, and whole-soil and should be kept in the refrigerator until testing. If the soil is dry at the time of testing, add water and let stand to saturate.

8. Procedure

8.1 Weigh enough <2-mm moist soil to achieve two duplicate samples that are ≈10 g after the soil is air-dry. Each of the two duplicates should have the exact same moist weight. Place the samples into numbered, tared vessels. A quality control standard sample is included in each batch (≤24 samples).

8.2 Add ≈50 mL of RO water and 7.5 mL of H_2O_2 to each sample and allow initial oxidation of organic matter.

8.3 Place the samples on a hot plate and heat to 90 °C. Add H_2O_2 in three additional increments of 7.5 mL at 30-min intervals. If oxidation is incomplete, add additional H_2O_2 until oxidation is complete. Record any unusual sample reactions. If the reaction is violent, try:

8.3.1 Adding small increments of ethanol to the sample to lower surface tension of the bubbles and thereby dissipate any foaming; or

8.3.2 Transferring sample to a 1,000-mL beaker to better contain and control the reaction.

8.4 Place the sample vessels on the filter rack. Add RO water up to the 150-mL mark. Place the filters in the samples, connect to the vacuum trap assembly with tubing, and turn on the vacuum. Filter until liquid is removed and approximately 5 mL remain in the bottom of the vessels.

8.5 Wash the sample from the filter and add ≈150 mL of RO water. Repeat filtering and adding water until sample has been rinsed five times total. Stir the sample with the filter after filling with water each time to ensure all soil particles will be rinsed.

8.5.1 During aspiration, it may be necessary to occasionally apply back-pressure to the filter to remove soil obstructing the pores in the ceramic.

8.5.2 Samples that contain gypsum require additional treatment and filtering.

- 1–5% gypsum: Stir the sample with a magnetic stirrer for 5 min and rinse five times with ≈250 mL of RO water each time.

- 5–10% gypsum: Place the sample in a 1,000-mL beaker, add ≈800 mL of RO water, stir the sample with a magnetic stirrer for 5 min, and then rinse with ≈800 mL five times.
- 10–20% gypsum: Place the sample in a 1,000-mL beaker, add ≈800 mL of RO water, add 100 g sodium chloride (NaCl), and stir the sample with a magnetic stirrer for 10 minutes. Rinse the sample with ≈800 mL of RO water five times.
- 20–40% gypsum: Place the sample in a 1,000-mL beaker, add ≈800 mL of RO water, add 100 g sodium chloride (NaCl), stir the sample with a magnetic stirrer for 10 minutes, and filter once. Remove sample from the rack, repeat sodium chloride treatment, and return sample to rack. Rinse the sample with ≈800 mL of RO water five times.
- 40–60% gypsum: Repeat sodium chloride treatment and single filtering three times. Rinse the sample with ≈800 mL of RO water five times.
- 60–80% gypsum: Repeat sodium chloride treatment four times. Rinse the sample with ≈800 mL of RO water five times.
- >80% gypsum: Repeat sodium chloride treatment five times and rinse five times.

8.6 Once filtered, the samples take separate analytical paths. Place the first sample in the oven and dry overnight at 110 °C.

8.6.1 Remove the sample from the oven, place in a desiccator, and cool to ambient temperature. Record the total weight (TW) of the sample to the nearest mg. Sample can be disposed of after weight is recorded.

8.7 To the second sample, add the exact volume of sodium hexametaphosphate solution (≈10 mL) needed to add 0.4408 g of sodium hexametaphosphate (as determined in step 5.9.4) to the non-oven-dried sample. Let stand approximately 1 hour or until sample is completely moistened by sodium hexametaphosphate. If sample imbibes hexametaphosphate, add RO water until sample is slightly damp. For samples that are hydrophobic, add a few of drops of ethanol. For samples that do not appear to become disaggregated, use a rubber policeman to break these apart; gentle rubbing with a mortar and pestle also helps. Add RO water to the 175-mL mark on the vessel.

8.8 Place the sample in a horizontal shaker at 120 oscillations min^{-1} for 15 h (overnight).

8.9 Remove the sample from the shaker. Place a 300-mesh (0.047-mm) sieve above a funnel in a ring stand. Place a 1-L cylinder below the funnel. Pour the sample through the sieve. Collect the silt and clay in the 1 L cylinder by

rinsing all <20-µm particles into the cylinder. Continue to wash sample until the suspension volume in the cylinder is ≈800 mL. Fill the cylinder to 1 L with RO water and cover with a 65-mm watch glass.

8.10 Wash sand and coarse silt from sieve into an evaporation dish and dry the sand at 110 °C overnight. Record weight.

8.11 Place cylinders on stable bench top and apply pipe insulation around sample cylinders. Prepare an RO-water blank cylinder to measure temperature fluctuations. Allow the cylinders to stand overnight to equilibrate the suspension with the room temperature.

8.12 Transfer the dried sand to a nest of sieves. Shake on sieve shaker for 3 minutes. Record the weight of each separate sand fraction (SWi) to the nearest mg.

8.12.1 If optical analysis is requested, place the very fine sand and fine sand fractions in gelatin capsules together with the remaining loose sand fractions in a labeled vial.

8.13 Stir the silt and clay suspension with mechanical stirrer for at least 5 minutes. Place the cylinder on a stable lab bench. With the cyclonic dampener, draw the rod up-and-down through the length of the cylinder for 30 s to eliminate swirling action caused by the mechanical stirrer.

8.14 Determine the percentage of fine silt and clay gravimetrically by using a Lowy 25-mL pipette mounted on an adjustable pipette rack (figs. 3A1a1–1, 3A1a1–2, and 3A1a1–3). Obtain an aliquot of <20-µm fraction sample from the cylinder. Slowly lower the closed pipette to a depth of 10 cm in the cylinder. Turn on the vacuum and withdraw an aliquot at the calculated time in table 3A1a1b–1. Regulate the vacuum such that the pipette fills in ≈12 s.

8.15 Dispense the aliquot into a tared and numbered, 90-mL weighing bottle. Rinse the pipette twice with RO water, placing the rinse water into the tared weighing bottle.

8.16 Wash and tare <2-µm employed bottles after every use. Wash and tare <20-µm bottles after every fourth use.

8.17 To obtain an aliquot of <2-µm size fraction, pipette after one of the following time intervals: 4.5, 5, 5.5, or 6.5 h.

8.18 Record temperature (T2) of blank. Use the average of T1 and T2 to adjust the pipette depth in the suspension as indicated in table 3A1a1b–2. Perform the aliquot withdrawal for the <2-µm size fraction the same as described for the <20-µm fraction. Regulate the vacuum such that the pipette fills in ≈12 s.

8.19 Dry the aliquots at 110 °C overnight and cool in a desiccator. Record the weight of the residue (RW) to the nearest 0.1 mg. Retain sample cylinder if optical mineralogy, fine-clay, or carbonate-clay determinations are requested.

Table 3A1a1b–1.—Sampling times at 10-cm depth for 0.4408 g L^{-1} sodium hexametaphosphate solution, assuming 2.65 g cc^{-1} particle density.

Temp	20 µm		5 µm		Temp	20 µm		5 µm	
(°C)	(min)	(s)	(min)	(s)	(°C)	(min)	(s)	(min)	(s)
15.00	5	17	84	--	24.25	4	12	67	13
16.00	5	9	82	--	24.50	4	11	66	50
17.00	5	1	80	--	24.75	4	9	66	27
18.00	4	53	78	--	25.00	4	8	66	4
18.50	4	50	77	--	25.25	4	6	65	42
19.00	4	46	76	--	25.50	4	5	65	19
19.50	4	42	75	--	25.75	4	4	64	57
20.00	4	39	74	--	26.00	4	2	64	35
20.25	4	37	73	--	26.25	4	1	64	13
20.50	4	36	73	--	26.50	3	59	63	52
20.75	4	34	73	--	26.75	3	58	63	30
21.00	4	32	72	--	27.00	3	57	63	9
21.25	4	31	72	--	27.25	3	56	62	48
21.50	4	29	71	--	27.50	3	54	62	27
21.75	4	27	71	--	27.75	3	53	62	7
22.00	4	26	70	--	28.00	3	52	61	46
22.25	4	24	70	27	28.25	3	50	61	26
22.50	4	23	70	2	28.50	3	49	61	6
22.75	4	21	69	37	28.75	3	48	60	46
23.00	4	20	69	13	29.00	3	47	60	26
23.25	4	18	68	48	29.25	3	45	60	6
23.50	4	17	68	24	29.50	3	44	59	47
23.75	4	15	68	0	29.75	3	43	59	28
24.00	4	14	67	37	30.00	3	42	59	9

8.19.1 If optical mineralogy is requested, decant remaining sample suspension and transfer the sediment to a 400-mL beaker.

8.20 Fill the beaker to a height of 5.5 cm. Stir the sediment and allow to settle for 5 minutes. Discard the supernatant. Refill the beaker to a height of 5.5 cm. Stir again, allow to settle for 3 min, and then decant. Fill, stir, and decant after 2-minute settling. Repeat filling and decanting until the top half of liquid in the beaker is clear.

8.21 Transfer the sediment to a labeled drying dish. Wash with ethanol, air-dry, and save in the drying dish for optical mineralogy. Sediment is ≈20 to 50 µm.

Table 3A1a1b–2.—Sampling Depths (cm) for 2-micron Pipetting of 0.4408 g L^{-1} Sodium Hexametaphosphate Solution, Assuming 2.65 g cc^{-1} Particle Density.

Temp	Sampling Depth in cm at Specified Times					Temp	Sampling Depth in cm at Specified Times				
(°C)	*4.5 (h)*	*5.0 (h)*	*5.5 (h)*	*6.0 (h)*	*6.5 (h)*	*(°C)*	*4.5 (h)*	*5.0 (h)*	*5.5 (h)*	*6.0 (h)*	*6.5 (h)*
15.00	5.11	5.67	6.24	6.81	7.38	24.25	6.43	7.14	7.85	8.57	9.28
16.00	5.25	5.83	6.41	6.99	7.58	24.50	6.46	7.18	7.90	8.62	9.34
17.00	5.38	5.98	6.58	7.18	7.77	24.75	6.50	7.22	7.95	8.67	9.39
18.00	5.52	6.14	6.75	7.37	7.98	25.00	6.54	7.26	7.99	8.72	9.44
18.50	5.59	6.22	6.84	7.46	8.08	25.25	6.58	7.31	8.04	8.77	9.50
19.00	5.66	6.29	6.92	7.55	8.18	25.50	6.61	7.35	8.08	8.82	9.55
19.50	5.74	6.37	7.01	7.65	8.29	25.75	6.65	7.39	8.13	8.87	9.61
20.00	5.81	6.45	7.10	7.74	8.39	26.00	6.69	7.43	8.18	8.92	9.66
20.25	5.84	6.49	7.14	7.79	8.44	26.25	6.73	7.47	8.22	8.97	9.72
20.50	5.88	6.53	7.19	7.84	8.49	26.50	6.76	7.52	8.27	9.02	9.77
20.75	5.92	6.57	7.23	7.89	8.54	26.75	6.80	7.56	8.31	9.07	9.83
21.00	5.95	6.61	7.27	7.93	8.60	27.00	6.84	7.60	8.36	9.12	9.88
21.25	5.99	6.65	7.32	7.98	8.65	27.25	6.88	7.64	8.41	9.17	9.94
21.50	6.02	6.69	7.36	8.03	8.70	27.50	6.92	7.69	8.45	9.22	9.99
21.75	6.06	6.73	7.41	8.08	8.75	27.75	6.96	7.73	8.50	9.27	10.05
22.00	6.10	6.77	7.45	8.13	8.81	28.00	6.99	7.77	8.55	9.32	10.10
22.25	6.13	6.81	7.49	8.18	8.86	28.25	7.03	7.81	8.59	9.38	10.16
22.50	6.17	6.85	7.54	8.22	8.91	28.50	7.07	7.86	8.64	9.43	10.21
22.75	6.21	6.89	7.58	8.27	8.96	28.75	7.11	7.90	8.69	9.48	10.27
23.00	6.24	6.94	7.63	8.32	9.02	29.00	7.15	7.94	8.74	9.53	10.33
23.25	6.28	6.98	7.67	8.37	9.07	29.25	7.19	7.99	8.78	9.58	10.38
23.50	6.32	7.02	7.72	8.42	9.12	29.50	7.23	8.03	8.83	9.63	10.44
23.75	6.35	7.06	7.76	8.47	9.18	29.75	7.27	8.07	8.88	9.69	10.49
24.00	6.39	7.10	7.81	8.52	9.23	30.00	7.30	8.12	8.93	9.74	10.55

8.22 For fine clay determination (<0.2 µm), the distance from the center of rotation to the surface of the suspension must be constant for each centrifuge bottle. The particle density (ρp) of the fine clay is assumed to be 2.5 g cc^{-1} (Jackson, 1969). The suspension temperature must be known before the correct liquid viscosity can be entered in the equation.

8.23 Stir the silt and clay suspension with mechanical stirrer for 5 minutes. Remove sample from mechanical stirrer and place on lab bench. Agitate

sample with a hand stirrer. Draw the rod up-and-down through the length of the cylinder for 30 seconds. Allow the suspension to settle for 15 minutes.

8.24 Pour the suspension into a centrifuge bottle and fill to the 13 cm line (distance from the center of rotation to the surface of the suspension) marked on the bottle. Stopper and shake well to mix the suspension.

8.25 Record the temperature of the suspensions.

8.26 Centrifuge at 1,500 rpm. Time will vary according to temperature of the suspension. Refer to table 3A1a1b–3 below.

Table 3A1a1b–3.—Centrifuge Times for <0.2-micron Pipetting. (Based on Stokes' Law, s=15 cm, r=18 cm, $N_{m=}$1,500 rpm, and $\rho_{p=}$2.5 g cc^{-1})

Temp	Viscosity	Delta-Density	Time
(°C)	*(η)*	*(Δρ)*	*(Min)*
18	0.01055	1.501	39.0
19	0.01029	1.501	38.0
20	0.01004	1.502	37.1
21	0.00980	1.502	36.2
22	0.00957	1.502	35.3
23	0.00934	1.502	34.5
24	0.00913	1.502	33.7
25	0.00892	1.503	32.9
26	0.00872	1.503	32.2
27	0.00853	1.503	31.4
28	0.00834	1.503	30.8
29	0.00816	1.504	30.1
30	0.00799	1.504	29.4

8.27 Dispense the aliquot into a tared and numbered, 90-mL weighing bottle. Rinse the pipette twice with RO water, placing the rinse water into the tared weighing bottle.

8.28 Wash and tare <2-µm bottles after every use; wash and tare <20-µm bottles after every fourth use.

8.29 Place weighing bottle with aliquot in oven. Dry overnight at 110 °C. Remove sample from oven, place in desiccator, and cool to ambient temperature.

8.30 Weigh residue weight (RW) to nearest 0.1 mg.

8.31 Carbonate Clay (<2 µm): Manometer Calibration

8.31.1 Before analyzing carbonate clay samples, a sodium carbonate solution is used to establish a slope and intercept curve for sample analytes and equipment calibration. Calibrate every six months or when equipment changes.

8.31.2 Place 0.0 to 20.0 mL of Na_2CO_3 solution into numbered, tared, 90-mL weighing bottles. Weigh samples in triplicate. Dry the standard samples in the oven overnight at 110 °C. Remove samples from oven, place in desiccator, and cool to ambient temperature. Record the weight of the standard samples to nearest 0.1 mg.

8.31.3 Lay a thin bead of glycerin along O-ring of the bottle lid.

8.31.4 Fill gelatin capsules with 3 mL of 6 *N* HCl. If HCl leaks from the capsule, discard the capsule. Place the capsule into the glass bottle and immediately cap the bottle. Release pressure in the bottle by piercing the septa with a hypodermic needle that is not connected to the manometer. Allow 3 to 5 s for internal pressure in bottle to equalize.

8.31.5 After the gelatin capsule has dissolved, slowly swirl the bottle to saturate the standard sample adhering to the sides of the bottle. Handle only the cap to avoid changing the temperature of the container. Allow sample to stand for at least 30 minutes.

8.31.6 Adjust the manometer to zero before taking measurements. Insert the manometer's hypodermic needle in the septa. Measure the pressure inside the weighing bottle. Record the manometer readings (mm Hg) to the nearest whole number.

8.32 Carbonate Clay (<2 µm) Analysis

8.32.1 Perform the effervescence test (method 4E3a1a1) on <2-mm soil samples. Samples qualify for carbonate clay analysis if the soil contains an effervescence reading of "slight" or greater. Use the 90-mL, square-bottomed weighing bottles for analysis.

8.32.2 Lay a thin bead of glycerin along O-ring of the bottle lid.

8.32.3 Dispense 3 mL of 6 *N* HCl into a gelatin capsule and place the top on the capsule. If HCl leaks from the capsule, discard the capsule. Place the capsule into the glass bottle and immediately cap the bottle. Release any pressure in the bottle by piercing the septa with hypodermic needle only for 3 to 5 seconds.

8.32.4 Include three blanks for each set of samples (≤24 samples). These blanks are needed for final calculations.

8.32.5 After the gelatin capsule has dissolved, slowly swirl the bottle to saturate the clay adhering to the sides of the bottle. Handle only the cap to avoid changing the temperature of the container. Allow sample to stand for at least 30 minutes.

8.32.6 Adjust the manometer to zero before taking measurements. Attach the hypodermic needle to the transducer. Pierce the needle in the sample bottle septa stopper. Measure the pressure inside the weighing bottle and record the manometer readings (MR) to the nearest whole number (mm Hg). Begin readings with the blank (BR).

8.32.7 Compare the sample readings to those of the standard curve established with the slope and intercept $NaCO_3$ standards.

9. Calculations

9.1 Clay % = 100 x [(RW$_2$ − DW) x (CF / TW)]

RW$_2$ = Residue weight (g), <2-µm fraction

DW = Dispersing agent weight (g) = (0.4408 / CF)

CF = 1,000 mL / DV

DV = Dispensed pipette volume

TW = Total weight (g), H_2O_2-treated, oven-dry sample

9.2 Fine Silt % = 100 x [(RW$_{20}$ − DW) x (CF / TW)] − Clay %

RW20 = Residue weight (g) of <20-µm fraction

9.3 Sand % = $\sum$ (SWi / TW) x 100

SW$_i$ = Weight of sand fractions (1.0, 0.5, 0.25, 0.1, and 0.047 mm)

9.4 Coarse silt % = 100 − (Clay % + Fine silt % + Sand %)

% = weight percent

9.5 Fine Clay (%) = 100 x [(RW − DW) x (CF / TW)]

RW = Residue weight (g) of <0.2-µm fraction

DW = Dispersing agent weight (g) = (0.4364 / CF)

CF = 1,000 mL / DV

DV = Dispensed pipette volume

TW = Total weight of H_2O_2-treated, oven-dry sample

9.6 Calculate carbonate clay percentage

Establish corrected (CR) linear regression equations to estimate the g of $CaCO_3$ in the sample. Correct the manometer reading as follows:

CR = (MR − BR)

CR = Corrected reading

MR = Manometer reading

BR = Average of three blank readings run with each batch (≤24 samples).

9.7 Calculate two regression equations; i.e., one for corrected manometer readings <100 and another for corrected readings ≥100. Use the Na_2CO_3 weights as the dependent variable (regressed or predicted values) and the corresponding manometer readings as the independent variable.

9.8 Carbonate Clay Equivalent (<2 µm) (%) = [(g $CaCO_3$) x 100 x CF] / TW

CF = 1,000 mL / dispensed pipette volume (mL)

TW = Total weight of H_2O_2-treated oven-dry sample

9.9 Noncarbonate Clay (<2 µm) (%) = Total Clay (%) − Carbonate Clay Equivalent (%)

9.10 The time of centrifugation is determined from the following equation modified from Stokes' law (Jackson, 1969).

$tm = [63.0 \times 10^8 \eta \log (r\ s^{-1})]\ (Nm^2\ D\mu^2\ \Delta\rho)^{-1}$

tm = Time in minutes

η = Viscosity in poises

r = Radius in cm from center of rotation to sampling depth (3 cm + s)

s = Radius in cm from center of rotation to surface of suspension

Nm = rpm (1,500)

Dµ = Particle diameter in microns (0.2 µm)

Δρ = Difference in specific gravity between solvated particles and suspension liquid

63.0×10^8 = Combination of conversion factors for convenient units of time in minutes, t_{min}, Nm as rpm, and particle diameter in microns, Dµ.

9.11 The sedimentation equation that is used to measure the settling rates of particles of different sizes is as follows:

$\nu = 2\ r^2\ g\ (\rho_s - \rho_l) / (9\ \eta)$

ν = Velocity of fall

r = Particle radius

g = Acceleration due to gravity

ρ_s = Particle density

ρ_l = Liquid density

η = Fluid viscosity

9.12 Report each particle-size fraction to the nearest 0.1 percent.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

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Particle-Size Distribution Analysis (3A)

Particles <2 mm (3A1)

Pipette Analysis (3A1a)

Carbonate Removal (3A1a2)

<2-mm Field-Moist (3A1a2b)

1. Introduction to Field-Moist Carbonate Removal

This method is performed in conjunction with the standard analysis for PSDA (method 3A1a1a) and is not appropriate for all samples.

2. Scope and Field of Application

Soils that have a high carbonate content do not readily disperse. Treatment of these soils with acid removes the carbonates (Grossman and Millet, 1961; Jackson, 1969; Gee and Bauder, 1986; Gee and Or, 2002). The determination of particle-size distribution after the removal of carbonates is used primarily for studies of soil genesis and parent material.

3. Principle

Samples are prepared in duplicate for analysis. A 1 *N* sodium acetate (NaOAc) solution buffered to pH 5 is used to dissolve carbonates until bubbles no longer evolve. After carbonates are removed, the samples are filtered and then treated with hydrogen peroxide and any additional method needed for the removal of interfering matrices. Samples are filtered to remove treatment solution.

One of the samples is analyzed according to the field-moist PSDA method (3A1a1b). The second sample is treated with sodium hexametaphosphate, mechanically shaken, and dried in an oven to obtain the initial weight. The sand fraction is removed from the suspension by wet sieving and then fractionated by dry sieving. The clay and fine silt fractions are determined by extracting aliquots of sample from sedimentation cylinders at specific time and depth intervals. Coarse silt is the difference between 100 percent and the sum of the sand, clay, and fine silt percentages.

The soil suspension from the sedimentation cylinder is used to determine the fine-clay fraction. This suspension is stirred, poured into a centrifuge bottle, and centrifuged at 1,500 rpm. A 25-mL aliquot is withdrawn with a pipette. The aliquot is dried in an oven and weighed, and the percentage of fine clay is calculated based on the total sample weight. Both the air-dry and moist PSDA data are determined as percent of the <2-mm fraction on an oven-dry basis.

3.1 Interferences

The removal of carbonates with 1 *N* NaOAc (pH 5) results in sample acidification. This treatment can destroy the primary mineral structure of clay (Gee and Bauder, 1986).

4. Apparatus

4.1 KIMAX 250-mL GL-45 bottles, tared to 1 mg. Wash and tare bottles every 6 months.

4.2 Ceramic filters, .3-µm absolute retention. (The KSSL can be contacted for more information.)

4.3 Rack to hold ceramic filters and sample containers

4.4 Hot plate capable of 90 °C

4.5 Vacuum, 0.8 bar (80 kPa)

4.6 Thermometer, 0 to 150 °C

4.7 Glass stirring rod

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Sodium acetate solution, 1 *N,* buffered to pH 5

Components: Sodium acetate ($C_2H_3NaO_2$) (CAS# 127-09-3) anhydrous; acetic acid (CH_3CO_2H) (CAS# 64-19-7); RO water

- To a 5-L glass carboy, add the following in order:
  - 4 L of RO water
  - 680 g of sodium acetate
  - ≈250 mL of acetic acid
  - Fill to volume with RO water.
  - Buffer solution to pH 5
- Swirl to mix.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Dispense concentrated acids and bases in fume hood. Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids.

7. Sample Preparation

Representative, field-state, whole-soil samples are sieved to <2-mm and should be kept in the refrigerator until testing. If the soil is dry at the time of testing, add water and let stand to saturate.

8. Procedure

8.1 Weigh two samples of <2-mm field-moist soil so each sample will weigh ≈10 g after carbonate removal (e.g., if the sample contains 50% carbonates, weigh 20 g of soil). Place samples into numbered, tared vessels.

8.2 Add ≈200 mL of the 1 *N* NaOAc solution to both samples, mix with a stirring rod, and cover with a watch glass. Allow the samples to stand overnight.

8.3 Place the sample on the hot plate and heat to ≈90 °C. Continue heating until bubbles are no longer visible. Do not boil. Decant the solution, taking care not to pour off any sample. Add another 200 mL of sodium acetate solution. If a reaction occurs, repeat the heating and decanting procedure until no effervescence is observed. The speed of dissolution can be increased by lowering the pH of the 1 *N* NaOAc solution (Rabenhorst and Wilding, 1984).

8.4 When effervescence has stopped, place the vessel on the filter rack and place a ceramic filter in the sample vessel. Apply vacuum and filter the sample until <5 mL of solution remains. Rinse once with 200 mL of RO water.

8.5 Add ≈50 mL of RO water and 7.5 mL of H_2O_2 to each soil sample and allow initial oxidation of organic matter.

8.6 Place the sample on a hot plate and heat to 90 °C. Add H_2O_2 in four increments of 7.5 mL at 30-min intervals. If oxidation of organic matter is incomplete, add additional H_2O_2 until oxidation is complete. Record any unusual sample reactions. If the reaction is violent, try:

8.6.1 Adding small increments of ethanol to the sample to lower surface tension of the bubbles and thereby dissipate any foaming; or

8.6.2 Transferring sample to a larger beaker or split the sample into multiple beakers to better contain and control the reaction.

8.7 Place the sample vessels on the filter rack. Add RO water up to the 150-mL mark. Place the filter in the sample, connect to the vacuum trap assembly with tubing, turn on the vacuum. Filter until liquid is removed and approximately 5 mL remain in the bottom of the vessel.

8.8 Wash the sample from the filter and add ≈150 mL of RO water four additional times. Stir the sample with the filter to ensure all soil particles are rinsed.

8.8.1 During aspiration, it may be necessary to occasionally apply back-pressure to the filter to remove soil obstructing the pores in the ceramic.

8.8.2 Samples that contain gypsum require additional treatment and filtering.

- 1–5% gypsum: Stir the sample with a magnetic stirrer for 5 min and rinse five times with ≈250 mL of RO water each time.
- 5–10% gypsum: Place the sample in a 1,000-mL beaker, add ≈800 mL of RO water, stir the sample with a magnetic stirrer for 5 min, and then rinse with ≈800 mL five times.

- 10–20% gypsum: Place the sample in a 1,000-mL beaker, add ≈800 mL of RO water, add 100 g sodium chloride (NaCl), and stir the sample with a magnetic stirrer for 10 minutes. Rinse the sample with ≈800 mL of RO water five times.
- 20–40% gypsum: Place the sample in a 1,000-mL beaker, add ≈800 mL of RO water, add 100 g sodium chloride (NaCl), stir the sample with a magnetic stirrer for 10 minutes, and filter once. Remove sample from the rack, repeat sodium chloride treatment, and return sample to rack. Rinse the sample with ≈800 mL of RO water five times
- 40–60% gypsum: Repeat sodium chloride treatment and single filtering three times. Rinse the sample with ≈800 mL of RO water five times.
- 60–80% gypsum: Repeat sodium chloride treatment four times. Rinse the sample with ≈800 mL of RO water five times.
- >80% gypsum: Repeat sodium chloride treatment five times and rinse five times.

8.9 Place one of the samples in the oven and dry overnight at 110 °C. Remove the sample from the oven, place in a desiccator, and cool to ambient temperature.

8.10 Record the total weight (TW) of the H_2O_2-treated, oven-dry sample to the nearest mg.

8.11 Using the second sample, proceed to step 8.8 of the field-moist PSDA method 3A1a2b and follow through to end of the method.

9. Calculations

Report the calculations for PSDA standard analysis method 3A1a1b.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Refer to PSDA standard analysis method 3A1a1b.

Particle-Size Distribution Analysis (3A)
Particles <2 mm (3A1)
Pipette Analysis (3A1a)
Iron Removal (3A1a3)
<2-mm Field-Moist (3A1a3b)

1. Introduction to PSDA Field-Moist Iron Removal

This method is performed in conjunction with the standard analysis for PSDA (method 3A1a1b) and is not appropriate for all samples.

2. Scope and Field of Application

Iron oxides (Fe_2O_3) are some of the most common oxides that coat and bind particles of sand, silt, and clay to form aggregates. Soils with iron cementation do not readily disperse. The iron oxides are removed using bicarbonate-buffered, sodium dithionite-citrate solution (Mehra and Jackson, 1960; Gee and Bauder, 1986; Gee and Or, 2002).

3. Principle

Samples are prepared in duplicate for analysis. Soil samples are treated with H_2O_2 to remove organic matter. Samples are treated with bicarbonate-buffered, sodium dithionite-citrate solution and heated until the sample changes to a grayish color. The suspension is flocculated with saturated NaCl solution and filtered to remove soluble salts. After removal of iron oxides, follow method 3A1a1b: <2-mm field-moist PSDA.

3.1 Interferences

If the temperature of the water bath exceeds 80 °C during iron removal, elemental sulphur can precipitate (Mehra and Jackson, 1960). This treatment can destroy primary mineral grains in the clay fraction (El-Swaify, 1980).

4. Apparatus

4.1 KIMAX 250-mL GL-45 bottles, tared to 1 mg. Wash and tare bottles every 6 months.

4.2 Ceramic filters, .3-µm absolute retention. (The KSSL can be contacted for more information.)

4.3 Rack to hold ceramic filters and sample containers

4.4 Hot plate capable of 90 °C

4.5 Vacuum, 0.8-bar (80-kPa)

4.6 Thermometer, 0 to 150 °C

4.7 Glass stirring rod

4.8 Water bath

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Hydrogen peroxide, 30 to 35% (H_2O_2) (CAS# 7722-84-1)

5.3 Ethanol (CH_3CH_2OH) (CAS# 64-17-5), 95%, U.S.P.

5.4 Sodium bicarbonate ($NaHCO_3$) (CAS# 144-55-8)

5.5 Sodium chloride (NaCl) (CAS# 7647-14-5)

5.6 Sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) (CAS# 6132-04-3)

5.7 Sodium dithionite ($Na_2S_2O_4$, hydrosulphite) (CAS# 7775-14-6)

5.8 Sodium citrate solution, 0.3 M

Components: Sodium citrate ($Na_3C_6H5O_7 \cdot 2H_2O$), RO water

- Place a magnetic stir bar in a 1-L glass beaker and add the following in order:
  - 800 mL of RO water
  - 88.4 g of sodium citrate
- Stir until dissolved.
- Fill to volume with RO water.

5.9 Sodium bicarbonate buffer solution, 1 M

Components: Sodium bicarbonate ($NaHCO_3$), RO water

- Place a magnetic stir bar in a 1-L glass beaker and add the following in order:
  - 800 mL of RO water
  - 84.0 g of sodium bicarbonate
- Stir until dissolved.
- Fill to volume with RO water.

5.10 Saturated NaCl solution

Components: Sodium chloride (NaCl), RO water

- Place a magnetic stir bar in a 1-L glass beaker and add the following in order:
  - 800 mL of RO water
  - 360.0 g of sodium chloride
- Stir until dissolved.
- Fill to volume with RO water.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Dispense concentrated acids and bases in fume hood. Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids.

7. Sample Preparation

Representative, field-state, whole-soil samples are sieved to <2-mm and should be kept in the refrigerator until testing. If the soil is dry at the time of testing, add water and let stand to saturate.

8. Procedure

8.1 Weigh two 10 g samples of <2-mm, moist soil to nearest mg and place into numbered, tared vessels. Since a maximum of ≈0.5 g of Fe_2O_3 can be dissolved in 40 mL of the citrate solution, adjust the weight of the <2-mm, moist soil sample so that no single vessel contains more than 0.5 g of Fe_2O_3. Split the sample into multiple vessels if necessary. Total sample weight after dissolution should be ≈10 g.

8.2 To both samples, add ≈50 mL of RO water and 7.5 mL of hydrogen peroxide at ambient temperature. Allow initial oxidation of organic matter and then place the sample on the hot plate. If the froth from the reaction exceeds the capacity of the vessel, transfer the sample to a larger beaker.

8.3 Place the sample on a hot plate and heat to 90 °C. Add H_2O_2 in increments of 7.5 mL at 30-min intervals until oxidation has completed. Add a minimum total of 30 mL of H_2O_2. If oxidation of organic matter is incomplete, add additional H_2O_2 until oxidation is complete. Heat the sample for an additional 45 min to decompose excess peroxide. If the reaction is violent, add small increments of ethanol to the sample to lower surface tension of the bubbles to dissipate any foaming or split sample into multiple beakers for digestion. After oxidation of organic matter is complete, filter the sample once to remove any remaining peroxide.

8.4 In a fume hood, add 40 mL of sodium citrate solution and 5 mL of sodium bicarbonate solution to the sample.

8.5 Place sample in a water bath and heat sample to 80 °C. Do not exceed this temperature.

8.6 Add ≈1 g of sodium dithionite powder. Stir constantly with a glass rod for 1 min and then occasionally for 15 minutes. Add 10 mL of saturated NaCl solution and mix.

8.7 If the sample contains <0.5 g of Fe_2O_3, repeat the dissolution treatment—steps 8.4 and 8.5—one additional time. If the sample contains >0.5 g of Fe_2O_3, repeat the dissolution treatment two more times.

8.8 Combine samples that have been split into separate vessels and proceed to PSDA field-moist analysis (method 3A1a1b) step 8.4 for filtering. Continue through the field-moist analysis method (3A1a1b).

8.9 Once sample is filtered, place one of the samples in the oven. Dry the sample overnight at 110 °C. Remove the sample from the oven, place in a desiccator, and cool to ambient temperature.

8.10 Record the total weight (TW) of the sample to the nearest mg.

8.11 Using the second sample, proceed to step 8.8 of the field-moist PSDA method (3A1a2b) and follow through remaining steps.

9. Calculations

Report the calculations for PSDA standard analysis method 3A1a1b.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Refer to PSDA standard analysis method 3A1a1b.

Particle-Size Distribution Analysis (3A)
Particles <2 mm (3A1)
Pipette Analysis (3A1a)
Silica Removal (3A1a4)
<2-mm Field-Moist (3A1a4b)

1. Introduction to PSDA Field M-ist Silica Removal

This method is performed in conjunction with the standard analysis for PSDA (method 3A1a1b) and is not appropriate for all samples.

2. Scope and Field of Application

Soils that are cemented by silica (SiO_2) do not completely disperse with hydrogen peroxide treatment and sodium hexametaphosphate. A treatment with sodium hydroxide dissolves the silica bridges and coats and increases the soil dispersion. This determination is used for studies of parent material and soil genesis.

3. Principle

Soils are treated with H_2O_2 to remove organic matter. Soils with silica cementation or coatings are treated with a weak NaOH solution overnight. After removal of siliceous cementing agents, follow method 3A1a1b: <2-mm field-moist PSDA.

3.1 Interferences

The effects of silica removal with 0.1 *N* NaOH on the clay fraction and particle-size distribution are unknown. If possible, mineralogy investigations should use grains from samples not treated with 0.1 *N* NaOH.

4. Apparatus

4.1 KIMAX 250-mL GL-45 bottles, tared to 1 mg. Wash and tare bottles every 6 months.

4.2 Hot plate capable of 90 °C

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Hydrogen peroxide, 30 to 35% (H_2O_2) (CAS# 7722-84-1)

5.3 Ethanol (CH_3CH_2OH) (CAS# 64-17-5), 95%, U.S.P.

5.4 Sodium hydroxide solution, 0.1 *N*

Components: Sodium hydroxide (NaOH) (CAS# 1310-73-2), RO water

- To a 1-L glass beaker, add the following in order:
  - 1 L of RO water
  - 4 g NaOH pellets
- Stir with glass rod to combine

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Dispense concentrated acids and bases in fume hood. Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids.

7. Sample Preparation

Representative, field-state, whole-soil samples are sieved to <2-mm and should be kept in the refrigerator until testing. If the soil is dry at the time of testing, add water and let stand to saturate.

8. Procedure

8.1 Weigh two 10 g samples of <2-mm, field-moist soil to nearest mg and place in numbered, tared vessels.

8.2 Add ≈50 mL of RO water and 7.5 mL of H_2O_2 to both soil samples at ambient temperature. Allow initial oxidation of organic matter and then place the sample on the hot plate.

8.3 Place the sample on a hot plate and heat to 90 °C. Add three additional 7.5 mL increments of H_2O_2 at 30-min intervals. Record any unusual sample reactions. If oxidation is incomplete, add additional H_2O_2 until organic matter oxidation is complete. If the reaction is violent, try:

8.3.1 Adding small increments of ethanol to the sample to lower surface tension of the bubbles and thereby dissipate any foaming; or

8.3.2 Transferring sample to a 1,000-mL beaker to better contain and control the reaction.

8.4 Remove the sample from the hot plate and place on the filter rack. Add RO water to the 150-mL mark and filter once. Remove sample from filter rack.

8.5 Soak the sample overnight in 100 mL of 0.1 *N* NaOH.

8.6 Wash the sample from the filter and add ≈150 mL of RO water four additional times. Stir the sample with the filter to ensure all soil particles will be rinsed.

8.6.1 During aspiration, it may be necessary to occasionally apply back-pressure to the filter to remove soil obstructing the pores in the ceramic.

8.7 Once filtered, the two samples receive different treatments. Take one of the sample vessels and proceed to step 8.8 of the field-moist PSDA method (3A1a1b) and continue treatment.

8.8 Place the other sample in the oven and dry overnight at 110 °C.

8.9 Remove the sample from the oven, place in a desiccator, and cool to ambient temperature. Record the total weight (TW) of the sample to the nearest mg.

9. Calculations

Report the calculations for PSDA standard analysis method 3A1a1b.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Refer to PSDA standard analysis method 3A1a1b.

Particle-Size Distribution Analysis (3A)
Particles <2 mm (3A1)
Pipette Analysis (3A1a)
Ultrasonic Dispersion (3A1a5)
<2-mm Field-Moist (3A1a5b)

1. Introduction to PSDA Field-Moist Ultrasonic Dispersion

This method is performed in conjunction with the standard analysis for PSDA (method 3A1a1a) and is not appropriate for all samples.

2. Scope and Field of Application

Soils that are not completely dispersed by standard PSDA may be better dispersed using ultrasonic methods (Gee and Bauder, 1986; Gee and Or, 2002). Treatments done with ultrasonic dispersion yield maximum clay concentrations (Mikhail and Briner, 1978).

3. Principle

Samples are analyzed in duplicate. Samples are weighed, diluted with RO water and hydrogen peroxide, and placed on a hot plate to oxidize organic matter. Samples are filtered and each sample undergoes a different treatment. One sample is dried in an oven and weighed to obtain the initial weight. Sodium hexametaphosphate solution is added to the other sample, which is then made to 100 mL total volume with RO water. The sample is subjected to ultrasonic vibration for 5 minutes. After dispersion with the ultrasonic probe, method 3A1a1 is followed.

3.1 Interferences

Ultrasonic dispersion has been reported to destroy primary soil particles. Watson (1971) summarized studies that reported the destruction of biotite and breakdown of microaggregates by ultrasonic dispersion. However, Saly (1967) reported that ultrasonic vibration did not cause the destruction of the clay crystalline lattice or the breakdown of primary grains. The samples ranged from sandy to clayey soils. The cementing agents represented humus, carbonates, and hydroxides of iron and aluminum. No standard procedures have been adopted using ultrasonic dispersion.

4. Apparatus

4.1 KIMAX 250-mL GL-45 bottles, tared to 1 mg. Wash and tare bottles every 6 months.

4.2 Beakers, 500-mL or 1,000-mL

4.3 Electronic balance, ±0.10-mg sensitivity

4.4 Hot plate, capable of 100 °C

4.5 Ceramic filters, .3-µm absolute retention. (The KSSL can be contacted for more information.)

4.6 Rack to hold ceramic filters and sample containers

4.7 Watch glasses, 65-mm diameter

4.8 Ultrasonic probe, 19-mm (¾ in) horn, 20 kHz, 600 watts

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Calcium sulfate ($CaSO_4$) (CAS# 7778-18-9) anhydrous, or equivalent desiccant (Reagent example: Drierite)

5.3 Ethanol (CH_3CH_2OH) (CAS# 64-17-5), 95%, U.S.P.

5.4 Hydrogen peroxide, 30 to 35% (H_2O_2) (CAS# 7722-84-1)

5.5 Sodium hexametaphosphate solution

Components: Sodium hexametaphosphate $(NaPO_3)_6$ (CAS# 68915-31-1), reagent grade; sodium carbonate (Na_2CO_3) (CAS# 497-9-8); RO water

- To a 1-L polyethylene bottle, add the following in order:
  - 1 L of RO water
  - 35.7 g of $(NaPO_3)_6$
  - 7.94 g of Na_2CO_3
- Invert to mix.

5.5.1 Standardize each new batch of hexametaphosphate solution. Use only designated weighing bottles for standardization. Wash and tare these bottles after each standardization.

5.5.2 Standards are run in duplicate. Add sodium hexametaphosphate solution to numbered, tared, 90-mL weighing bottles. Aliquots are: 8.5, 9.0, 9.3, 9.6, 10.0, 10.3, 10.6, and 11.0 mL.

5.5.3 Place the 16 weighing bottles and aliquots in the oven overnight and record dry residue weight of sodium hexametaphosphate.

5.5.4 Determine the exact volume of solution needed to add 0.4408 g of sodium hexametaphosphate into each sample by regressing the volume of sodium hexametaphosphate solution against the dry residue weight of sodium hexametaphosphate.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Dispense concentrated acids and bases in fume hood. Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids.

7. Sample Preparation

Representative, field-state, whole-soil samples are sieved to <2-mm and should be kept in the refrigerator until testing. If the soil is dry at the time of testing, add water and let stand to saturate.

8. Procedure

8.1 Weigh two 10 g samples of <2-mm field-moist soil to nearest mg and place into numbered, tared, vessels. A quality control sample is included in each batch (≤24 samples).

8.2 Add ≈50 mL of RO water and 7.5 mL of H_2O_2 to samples at ambient temperature. Allow initial oxidation of organic matter and then place the sample on the hot plate. If the froth from the reaction exceeds the capacity of the vessel, transfer the sample to a larger beaker.

8.3 Place the sample on a hot plate and heat to 90 °C. Add H_2O_2 in three additional increments of 7.5 mL at 30-min intervals. If oxidation is incomplete, add additional H_2O_2 until organic matter oxidation is complete. Record any unusual sample reactions. If the reaction is violent, try:

8.3.1 Adding small increments of ethanol to the sample to lower surface tension of the bubbles and thereby dissipate any foaming; or

8.3.2 Transferring sample to a 1,000-mL beaker to better contain and control the reaction.

8.4 Place both sample vessels on the filter rack. Add RO water up to the 150-mL mark. Place the ceramic filters in the samples, connect to the vacuum trap assembly with tubing, and turn on the vacuum. Filter until liquid is removed and approximately 5 mL remain in the bottom of the vessel.

8.5 Wash the sample from the filter and add ≈150 mL of RO water four additional times. Stir the sample with the filter to ensure all soil particles are rinsed.

8.5.1 During aspiration, it may be necessary to occasionally apply back-pressure to the filter to remove soil obstructing the pores in the ceramic.

8.5.2 Samples that contain gypsum require additional treatment and filtering.

- 1–5% gypsum: Stir the sample with a magnetic stirrer for 5 min and rinse five times with ≈250 mL of RO water each time.
- 5–10% gypsum: Place the sample in a 1,000-mL beaker, add ≈800 mL of RO water, stir the sample with a magnetic stirrer for 5 min, and then rinse with ≈800 mL five times.

- 10–20% gypsum: Place the sample in a 1,000-mL beaker, add ≈800 mL of RO water, add 100 g sodium chloride (NaCl), and stir the sample with a magnetic stirrer for 10 minutes. Rinse the sample with ≈800 mL of RO water five times.
- 20–40% gypsum: Place the sample in a 1,000-mL beaker, add ≈800 mL of RO water, add 100 g sodium chloride (NaCl), stir the sample with a magnetic stirrer for 10 minutes, and filter once. Remove sample from the rack, repeat sodium chloride treatment, and return sample to rack. Rinse the sample with ≈800 mL of RO water five times.
- 40–60% gypsum: Repeat sodium chloride treatment and single filtering three times. Rinse the sample with ≈800 mL of RO water five times.
- 60–80% gypsum: Repeat sodium chloride treatment four times. Rinse the sample with ≈800 mL of RO water five times.
- >80% gypsum: Repeat sodium chloride treatment five times and rinse five times.

8.6 Once filtered, the two samples receive different treatments. Place the first sample in the oven and dry the sample overnight at 110 °C. Remove the sample from the oven, place in a desiccator, and cool to ambient temperature. Record the total weight (TW) of the sample to the nearest mg.

8.7 To the second sample, add the exact volume of sodium hexametaphosphate solution (≈10 mL) needed to add 0.4408 g of sodium hexametaphosphate to sample. Let stand approximately 1 hour or until sample is completely moistened by sodium hexametaphosphate. If sample imbibes hexametaphosphate, add RO water until sample is slightly damp. After 1 hour, swirl sample to loosen it from vessel and pour into a 50-mm diameter beaker. Use a minimum of water to rinse sample from one vessel to the other. Use a rubber policeman to remove any residue adhering to the vessel. Try to keep the volume of the suspension under 100 mL.

8.8 Disperse the suspension with ultrasonic vibrations. Ensure the power supply is properly tuned. (Consult the instruction manual.) Immerse the probe in the suspension to ≈½ inch above bottom of the beaker. Adjust output control as required. Sonicate for 5 minutes. Between samples, clean the probe by placing it in water or alcohol and energizing it for a few seconds if needed.

8.9 After ultrasonic dispersion, proceed to step 8.10 of the <2-mm field-moist method (3A1a1b) and continue sample treatment.

9. Calculations

Report the calculations for PSDA standard analysis method 3A1a1b.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Refer to PSDA standard analysis method 3A1a1b.

Particle-Size Distribution Analysis (3A)
Particles <2 mm (3A1)
Pipette Analysis (3A1a)
Water Dispersible PSDA (3A1a6)
<2-mm Field-Moist (3A1a6b)

1. Introduction to PSDA Water Dispersion

This method is performed in conjunction with the field-moist PSDA method (3A1a1b) and is not appropriate for all samples.

2. Scope and Field of Application

This method provides a means of evaluating the susceptibility of a soil to water erosion. The degree to which a soil disperses without the oxidation of organic matter, the removal of soluble salts, or the addition of a chemical dispersant may be compared with results from chemical dispersion (Bouyoucos, 1929).

3. Principle

Samples are prepared in duplicate for analysis. Water dispersible particle-size distribution analysis may also be determined from a soil suspension without the removal of organic matter or soluble salts or without the use of a chemical dispersant. Results from this analysis are compared to results from the standard PSDA. In the standard PSDA, salts and cementing agents have been removed and grains are thoroughly dispersed.

3.1 Interferences

Soils that irreversibly harden when dried are difficult to disperse. The PSDA for these soils can be determined on moist samples (method 3A1a1b) upon the request of the project coordinator.

4. Apparatus

4.1 KIMAX 250-mL GL-45 bottles, tared to 1 mg. Wash and tare bottles every 6 months.

4.2 Electronic balance, ±0.10-mg sensitivity

4.3 Desiccator

4.4 Cylinders, 1-L, white line fused onto glass at 1-L mark

4.5 Oven, 110 °C

4.6 Mechanical shaker, horizontal, 120 oscillations min^{-1}, 1½-in strokes

4.7 Motor driven stirrer (The KSSL can be contacted for more information.)

4.8 Cyclonic dampening hand stirrer that has a brass rod threaded at one end and a perforated plexiglass disk fastened to the threaded end to reduce

sample vortex from mechanical stirrer. The rod should be slightly longer than the height of the settling cylinders. The plexiglass disk should be ½" narrower than inside diameter of the cylinders.

4.9 Adjustable pipette rack (fig. 3A1a1–1, 3A1a1–2, and 3A1a1–3; Shaw, 1932)

4.10 Lowy pipettes, 25-mL, with overflow bulb. (The KSSL can be contacted for more information.)

4.11 Polyurethane foam pipe insulation that fits snugly around cylinder

4.12 Sieve shaker with 12.7-mm (½ in) vertical and lateral movement at 500 oscillations min^{-1}, accommodates nesting 2-⅜ inch sieves

4.13 Watch glasses, 65-mm diameter

4.14 Evaporating dishes, porcelain, 80-mm diameter, 32-mm height, with lip

4.15 Set of 60-mm (2-⅜ inch) sieves, square-weave stainless steel wire cloth, except 300 mesh, which is twilled weave. U.S. series and Tyler Screen Scale equivalent designations are as follows:

Sand Size	Opening	U.S. No.	Tyler Mesh Size
	(mm)		
Very coarse sand (VCS)	1.0	18	16
Coarse sand (CS)	0.5	35	32
Medium sand (MS)	0.25	60	60
Fine sand (FS)	0.105	140	150
Very fine sand (VFS)	0.047	300	300

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Calcium sulfate ($CaSO_4$) (CAS# 7778-18-9), anhydrous, or equivalent desiccant (Reagent example: Drierite)

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

7. Sample Preparation

Representative, field-state, whole-soil samples are sieved to <2-mm and should be kept in the refrigerator until testing. If the soil is dry at the time of testing, add water and let stand to saturate.

8. Procedure

8.1 Weigh two 10 g samples of <2-mm field-moist soil to nearest mg and place into numbered, tared vessel. A quality control sample is included in each batch (≤24 samples).

8.2 Dry one of the samples in an oven at 110 °C overnight. Remove the sample from the oven, place in a desiccator, and cool to ambient temperature.

8.3 Record the total weight (TW) of the sample to the nearest mg.

8.4 To the second sample (non-oven-dried), add ≈175 mL of RO water. Place the sample in a horizontal shaker at 120 oscillations min^{-1} for 15h (overnight).

8.5 Complete this analysis by following the <2-mm field-moist method (3A1a1b) beginning at step 8.10. Reference tables 3A1a6b–1 and 3A1a6b–2 below for time and sampling.

9. Calculations

9.1 $\text{Clay \%} = 100 \times [(RW_2 \times CF) / TW]$

RW_2 = Residue weight (g), <2-µm fraction

CF = 1,000 mL / DV

DV = Dispensed pipette volume

TW = Total weight (g), oven-dry sample

9.2 $\text{Fine Silt \%} = [(100 \times RW_{20} \times CF) / TW] - \text{Clay \%}$

RW_{20} = Residue weight (g) of <20-µm fraction

9.3 $\text{Sand \%} = \sum (SWi / TW) \times 100$

SWi = Weight of sand fractions (1.0, 0.5, 0.25, 0.1, and 0.047 mm)

9.4 Coarse silt % = 100 − (Clay % + Fine silt % + Sand %)

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Refer to PSDA standard analysis method 3A1a1b.

Table 3A1a6b–1.—Sampling Times for 20-micron and 5-micron Pipetting at 10-cm Depth for RO Water, Assuming 2.65 g cc^{-1} Particle Density. (Use this table with methods 3A1a6a and 3A1a6b.)

Temp	20 µm		5 µm	
(°C)	*Min.*	*Sec.*	*Min.*	*Sec.*
15.00	5	17	84	26
16.00	5	8	82	12
17.00	5	0	80	7
18.00	4	53	78	3
18.50	4	49	77	4
19.00	4	45	76	8
19.50	4	42	75	9
20.00	4	38	74	14
20.25	4	37	73	47
20.50	4	35	73	20
20.75	4	33	72	53
21.00	4	32	72	27
21.25	4	30	72	0
21.50	4	28	71	35
21.75	4	27	71	9
22.00	4	25	70	43
22.25	4	24	70	18
22.50	4	22	69	53
22.75	4	21	69	29
23.00	4	19	69	4
23.25	4	17	68	40
23.50	4	16	68	16
23.75	4	15	67	52
24.00	4	13	67	28

Temp	20 µm		5 µm	
(°C)	*Min.*	*Sec.*	*Min.*	*Sec.*
24.25	4	12	67	5
24.50	4	10	66	42
24.75	4	9	66	19
25.00	4	7	65	56
25.25	4	6	65	34
25.50	4	4	65	11
25.75	4	3	64	49
26.00	4	2	64	27
26.25	4	0	64	6
26.50	3	59	63	44
26.75	3	58	63	23
27.00	3	56	63	1
27.25	3	55	62	40
27.50	3	54	62	20
27.75	3	52	61	59
28.00	3	51	61	39
28.25	3	50	61	18
28.50	3	39	60	58
28.75	3	47	60	38
29.00	3	46	60	19
29.25	3	45	59	59
29.50	3	44	59	40
29.75	3	43	59	21
30.00	3	41	59	1

Table 3A1a6b–2.—Sampling Depths (cm) for 2-micron Pipetting of RO Water, Assuming 2.65 g cc^{-1} Particle Density. (Use this table with methods 3A1a6a and 3A1a6b.)

Temp	Sampling Depth in cm at Specified Times				
(°C)	*4.5 (h)*	*5.0 (h)*	*5.5 (h)*	*6.0 (h)*	*6.5 (h)*
15.00	5.12	5.69	6.25	6.82	7.39
16.00	5.26	5.84	6.42	7.01	7.59
17.00	5.39	5.99	6.59	7.19	7.79
18.00	5.54	6.15	6.77	7.38	8.00
18.50	5.61	6.23	6.85	7.47	8.10
19.00	5.67	6.31	6.94	7.57	8.20
19.50	5.75	6.39	7.03	7.66	8.30
20.00	5.82	6.47	7.11	7.76	8.41
20.25	5.86	6.51	7.16	7.81	8.46
20.50	5.89	6.55	7.20	7.86	8.51
20.75	5.93	6.59	7.24	7.90	8.56
21.00	5.96	6.63	7.29	7.95	8.61
21.25	6.00	6.67	7.33	8.00	8.67
21.50	6.04	6.71	7.38	8.05	8.72
21.75	6.07	6.75	7.42	8.10	8.77
22.00	6.11	6.79	7.47	8.14	8.82
22.25	6.14	6.83	7.51	8.19	8.88
22.50	6.18	6.87	7.55	8.24	8.93
22.75	6.22	6.91	7.60	8.29	8.98
23.00	6.25	6.95	7.64	8.34	9.03
23.25	6.29	6.99	7.69	8.39	9.09
23.50	6.33	7.03	7.73	8.44	9.14
23.75	6.37	7.07	7.78	8.49	9.19
24.00	6.40	7.11	7.83	8.54	9.25

Temp	Sampling Depth in cm at Specified Times				
(°C)	*4.5 (h)*	*5.0 (h)*	*5.5 (h)*	*6.0 (h)*	*6.5 (h)*
24.25	6.44	7.16	7.87	8.59	9.30
24.50	6.48	7.20	7.92	8.64	9.36
24.75	6.51	7.24	7.96	8.69	9.41
25.00	6.55	7.28	8.01	8.74	9.46
25.25	6.59	7.32	8.05	8.79	9.52
25.50	6.63	7.36	8.10	8.84	9.57
25.75	6.66	7.41	8.15	8.89	9.63
26.00	6.70	7.45	8.19	8.94	9.68
26.25	6.74	7.49	8.24	8.99	9.74
26.50	6.78	7.53	8.28	9.04	9.79
26.75	6.82	7.57	8.33	9.09	9.85
27.00	6.85	7.62	8.38	9.14	9.90
27.25	6.89	7.66	8.42	9.19	9.96
27.50	6.93	7.70	8.47	9.24	10.01
27.75	6.97	7.74	8.52	9.29	10.07
28.00	7.01	7.79	8.57	9.34	10.12
28.25	7.05	7.83	8.61	9.40	10.18
28.50	7.09	7.87	8.66	9.45	10.23
28.75	7.12	7.92	8.71	9.50	10.29
29.00	7.16	7.96	8.75	9.55	10.35
29.25	7.20	8.00	8.80	9.60	10.40
29.50	7.24	8.05	8.85	9.65	10.46
29.75	7.28	8.09	8.90	9.71	10.52
30.00	7.32	8.13	8.95	9.76	10.57

Particle-Size Distribution Analysis (3A)
Particles >2 mm (3A2)

Rock and pararock fragments are defined as particles >2 mm in diameter and include all particles with horizontal dimensions less than the size of a pedon (Soil Survey Division Staff, 1993). Rock fragments are further defined as strongly cemented or more resistant to rupture. These cobble- and gravel-sized fragments are generally sieved and excluded from most chemical, physical, and mineralogical analyses. Pararock fragments are less cemented and are broken into particles <2 mm in diameter during the preparation of samples for particle-size analysis in the laboratory. Exceptions are described in method 1B1b2f. It is necessary to know the amount of rock fragments for several applications, e.g., available water capacity and linear extensibility (Grossman and Reinsch, 2002).

Soil variability and sample size are interferences to weight determinations of the >2-mm particles. Field size fractions include:

- 20- to 75-mm fraction, which is generally sieved, weighed, and discarded in the field. This is the preferred and usually most accurate method. Whenever possible, the field samples or “moist” material should have weights two to four times larger (ASTM, 2012). Therefore, sieving and weighing the 20- to 75-mm fraction should be done in the field.
- 75- to 250-mm fraction
- >250-mm fraction, which includes rock and pararock having horizontal dimensions smaller than the size of the pedon.

Enough soil material needs to be sieved and weighed to obtain statistically accurate rock fragment content. To accurately measure rock fragments with maximum particle diameters of 20 and 75 mm, the minimum dry specimen sizes that need to be sieved and weighed are 1.0 and 60.0 kg (2 and 130 pounds). If needed, the 20- to 75-mm fraction can be estimated in the field as a volume percentage of the whole soil.

Volume estimates determined in the field are converted to dry weight percentages of the >20-mm fractions. The conversion of a volume estimate to a weight estimate assumes a particle density of 2.65 g cc^{-1} and a bulk density for the fine-earth fraction of 1.45 g cc^{-1}. Measured values can be substituted for this volume to weight conversion.

The KSSL determines weight percentages as follows:

- >2-mm fractions (field and laboratory) weight measurements: method 3A2a1.
- Conversion of >2-mm fractions estimated by volume in the field: method 3A2b.
- >2-mm fraction volume estimates of the >20-mm fractions: method 3A2a2.
- >2-mm fraction weight determinations of the <20-mm fractions: method 3A2a2.

In the field or in the laboratory, the sieving and weighing of the >2-mm fraction are limited to the <75-mm fractions. Weight measurements for the 2- to 20-mm fraction are obtained in the laboratory. Unless otherwise specified, the particle-size fractions 2 to 5, 5 to 20, 20 to 75, and 0.1 to 75 mm are reported on a <75-mm oven-dry weight percentage basis. The total >2-mm fraction is reported on a whole-soil, oven-dry weight percentage base.

Particle-Size Distribution Analysis (3A)
Particles >2 mm (3A2)
Weight Estimates (3A2a)
By Field and Laboratory Weighing (3A2a1)

1. Introduction to >2-mm Particle Weight Estimation

This method determines weight percentages of the >2-mm fractions by field and laboratory weight measurements. To accurately measure rock fragments with maximum particle diameters of 20 and 75 mm, sieving and weighing the 20- to 75-mm fraction should be done in the field.

2. Scope and Field of Application

To accurately represent the 20- to 75-mm size fraction, the minimum field samples sizes ("dry" weights) that need to be sieved and weighed are approximately 1.0–60.0 kg. Samples received in the laboratory generally have a maximum weight of 4 kg and may not be a representative sample. For additional information, refer to ASTM method D 2488 (ASTM, 2012).

3. Principle

Field weights are determined for the 20- to 75-mm fraction, which is the preferred method due to potentially larger amounts of sample available in the field. When field determinations are not possible, weight measurements for the 20- to 75-mm fraction can be determined in the laboratory. The <20-mm fractions are sieved and weighed in the laboratory, and oven-dry weight percentages are calculated in size fractions from 2- to 75-mm fractions.

3.1 Interferences

Soil variability and sample size are interferences to weight determinations of the >2-mm particles. Enough soil material needs to be sieved and weighed to obtain statistically accurate rock fragment content.

4. Apparatus

4.1 Electronic balance, ±1-g sensitivity and 15-kg capacity

4.2 Trays, fiberglass or heat-resistant plastic, tared

4.3 Sieves, square-hole

- 9 mesh, 2 mm
- 4 mesh, 4.76 mm
- 20 mm, ¾ in
- 76 mm, 3 in

4.4 Mechanical shaker with 9-mesh and 4-mesh sieves
4.5 Rubber roller
4.6 Metal plate, 76 x 76 x 0.5 cm
4.7 Scale, 100-lb (45-kg) capacity
4.8 Brown kraft paper

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water
5.2 Hydrochloric acid (HCl) (CAS# 7647-01-0), concentrated, 12 *N*
5.3 Sodium hexametaphosphate $(NaPO_3)_6$ (CAS# 68915-31-1), reagent grade
5.4 Sodium carbonate (Na_2CO_3) (CAS# 497-9-8)
5.5 Hydrochloric acid solution,1 *N*

Components: Hydrochloric acid (HCl), RO water

- To a 2-L polyethylene bottle, add the following in order:
  - 1 L of RO water
  - 83.3 mL of concentrated HCl
- Invert to mix.

5.6 Sodium hexametaphosphate solution

Components: Sodium hexametaphosphate $(NaPO_3)_6$, sodium carbonate (Na_2CO_3), RO water

- To a 2-L polyethylene bottle, add the following in order:
  - 1 L of RO water
  - 35.7 g of sodium hexametaphosphate
  - 7.94 g of sodium carbonate
- Invert to mix.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

7. Sample Preparation

A representative sample weighing up to 60kg (estimated dry weight) is taken from the pit face or horizon exposure.

8. Procedure

8.1 In the field

8.1.1 Sieve approximately 40–60 kg of representative horizon sample

with a 76-mm sieve. 30 kg provides the minimum representative sample.

8.1.2 Discard the >75-mm material.

8.1.3 Sieve the <75-mm fraction with a 20-mm sieve.

8.1.4 Record weight (lbs) of 20- to 75-mm fraction and then discard the material.

8.1.5 Record weight (lbs) of <20-mm fraction.

8.1.6 Place a subsample of the <20-mm material in a plastic bag. Label and send to laboratory for analyses.

8.2 In the laboratory

8.2.1 Distribute the field sample on a plastic tray, weigh, and record moist weight. Air-dry sample at 30 ±5 °C (≈3 to 7 days), weigh, and record weight.

8.2.2 Process air-dry material on a flat, metal plate that is covered with brown kraft paper. Place sample on kraft paper and then, using the paper as a funnel, pour sample through sieve stack. Place fragments captured on each sieve into their own pie plate for collecting weights later.

8.2.3 Place material captured on the 2-mm sieve and in the lower pan onto kraft paper. Using a wooden rolling pin or rubber roller, roll over material. Break peds into smaller pieces that can pass through the 2-mm sieve. Tips for processing:

- Peds from air-dry clay-rich soils are difficult to break down to <2 mm. Use a floor model adjustable plate crusher or field hammer to break apart peds.
- Try to not break rock fragments during rolling and grinding of sample material. Once soil has been broken away from lithics, sieve sample.
- Large sample sizes can be rolled and sieved in small batches. This helps ensure sufficient pressure to break apart peds, saving time and effort.

8.2.4 For samples that do not require 80-mesh sample preparation but contain large pieces of organic litter (such as sticks and leaves), capture organic litter on the appropriate sieve size and discard so as not to skew organic measurements of soil or rock fragment weights.

8.2.5 Soils that are considered to have organic material as a part of their composition will have an O horizon designation or 80-mesh sample preparation request.

8.2.6 Smaller, clay-rich peds may need to be slaked:

8.2.6.1 Weigh up to 100 g sample material captured on 2-mm sieve.

8.2.6.2 Soak in sodium hexametaphosphate solution for 12 h.

8.2.6.3 Rinse sample of solution and clay.

8.2.6.4 Dry remaining rock fragment in 110 °C oven.

8.2.6.5 Record final weight.

8.2.7 Once sample is processed to <2 mm, collect weights of:

- >75 mm
- 20 to 75 mm
- 5 to 20 mm

8.2.8 Fragments >2 mm can be discarded.

9. Calculations

9.1 Convert field weights of the <75-mm and the 20- to 75-mm fractions from pounds to grams. Laboratory measurements are determined in grams.

9.2 Determine field-moist weight of the subsample as received in the laboratory. Determine air-dry weight of subsample. Air-dry weight is defined as a constant sample weight obtained after drying at 30 ±5 °C (≈3 to 7 days).

9.3 Determine ratio of slaked, air-dried weight (g) to unslaked, air-dried weight (g) for the 2- to 5-mm fraction. Using this ratio, adjust weight of coarse fragments with <5-mm diameter.

9.4 Base coarse-fragment calculation on oven-dry weight. Use the AD/OD (air-dry/oven-dry ratio) (method 3D1) to calculate the oven-dry weight of <2-mm fraction. Use the following equation to determine the percentage of any 2- to 75-mm fraction on a <75-mm oven-dry weight-basis.

$$\text{Percentage >2-mm fraction (<75-mm basis)} = (A/B) \times 100$$

A = Weight of 2- to 75-mm fraction (g)

B = Weight of <75-mm fraction (g)

9.5 Determine oven-dry weight by weighing the sample after oven drying at 110 °C for 24 h or by calculating as follows:

$$\text{Oven-dry weight (g)} = [\text{Air-dry weight (g)}]/\text{AD/OD}$$

AD/OD = Air-dry/oven-dry weight

9.6 Determine oven-dry weight from the field-moist weight of a sample by calculating as follows:

$$\text{Oven-dry weight (g)} = [\text{Field-moist weight (g)}]/[\text{Field-moist weight (g)}/\text{Oven-dry weight (g)}]$$

9.7 In calculations of the oven-dry weight percentages of the >2-mm fraction, make corrections for the field-water content of the <75-mm sample at sampling and for the water content of the air-dry bulk laboratory sample. Base the corrections for the field-water content on the difference between the field-moist weight and air-dry weight of the bulk sample.

9.8 Report field weights

- **9.8.1** Weight (lbs) of field-moist, <75-mm fraction
- **9.8.2** Weight (lbs) of field-moist, 20- to 75-mm fraction
- **9.8.3** Weight (lbs) of field-moist, <20-mm fraction

9.9 Report lab weights

- **9.9.1** Weight (g) of field-moist soil sample
- **9.9.2** Weight (g) of air-dry soil sample
- **9.9.3** Weight (g) of air-dry processed soil sample
- **9.9.4** Weight (g) of 20-to 75-mm fraction
- **9.9.5** Weight (g) of 5- to 20-mm fraction
- **9.9.6** Weight (g) of 2- to 5-mm fraction
- **9.9.7** Weight (g) of subsample 2- to 5-mm fraction before slaking
- **9.9.8** Weight (g) of subsample 2- to 5-mm fraction after slaking

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

American Society for Testing and Materials (ASTM). 2012. Standard practice for description and identification of soils (visual-manual procedure). D 2488. Annual book of ASTM standards. Construction. Section 4. Soil and rock; dimension stone; geosynthesis. Vol. 04.08. ASTM, Philadelphia, PA.

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Soil Survey Division Staff. 1993. Soil survey manual. USDA Agric. Handbook No. 18. USDA–NRCS. U.S. Govt. Print. Office, Washington, DC.

Particle-Size Distribution Analysis (3A)

Particles >2 mm (3A2)

Weight Estimates (3A2a)

From Volume and Weight Estimates (3A2a2)

Volume Estimates (3A2b)

1. Introduction to >2-mm Volume and Weight Estimates

This method outlines the calculations used to derive weight percentages from volume percentages of all the >2-mm sample material. Visual field-volume estimates are determined for size fractions >20 mm.

- <20-mm fractions are sieved and weighed in the laboratory.
- 20- to 75-mm, field volume or measured weight data may be collected (weights are preferred).
- 75- to 250-mm
- >250-mm fractions include stones and cobbles that have horizontal dimensions that are less than those of the pedon.

2. Scope and Field of Application

The conversion of a volume estimate to a weight estimate assumes a particle density of 2.65 g cc^{-1} and a bulk density for the fine-earth fraction of 1.45 g cc^{-1}. If particle density and bulk density measurements are available, they are used in the calculations. Refer to ASTM standard practice D 2488 (ASTM, 2012).

3. Principle

To accurately measure rock fragments that have maximum particle diameters of 20 and 75 mm, the minimum specimen sizes (“dry” weights) that need to be sieved and weighed are approximately 1.0–60.0 kg. Samples received in the laboratory generally have a maximum weight of 4 kg. Therefore, sieving and weighing the 20- to 75-mm fraction should be done in the field. Volume estimates can be applied for any fractions that are >20 mm. The weight estimates are laboratory measurements for the 2- to 20-mm or 2- to 75-mm fractions. The volume estimates for any fractions that are >20 mm are converted to weight percentages. The total >2-mm fraction is reported on an oven-dry weight basis for whole soil.

3.1 Interferences

Soil variability and sample size are interferences to weight determinations of the >2-mm particles. Enough soil material needs to be sieved and weighed to obtain statistically accurate rock fragment content.

4. Apparatus

4.1 Electronic balance, ±1-g sensitivity and 15-kg capacity

4.2 Trays, plastic, tared

4.3 Sieves, square-hole

- 9 mesh, 2 mm
- 4 mesh, 4.76 mm
- 20 mm, ¾ in
- 76 mm, 3 in

4.4 Mechanical shaker with 9-mesh and 4-mesh sieves

4.5 Rubber roller

4.6 Metal plate, 76 x 76 x 0.5 cm

4.7 Scale, 45-kg (100-lb) capacity

4.8 Brown kraft paper

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Hydrochloric acid (HCl) (CAS# 7647-01-0), concentrated, 12 *N*

5.3 Sodium hexametaphosphate $(NaPO_3)_6$ (CAS# 68915-31-1), reagent grade

5.4 Sodium carbonate (Na_2CO_3) (CAS# 497-9-8)

5.5 Hydrochloric acid solution, 1 *N*

Components: Hydrochloric acid (HCl), RO water

- To a 2-L polyethylene bottle, add the following in order:
  - 1 L of RO water
  - 83.3 mL of concentrated HCl
- Invert to mix.

5.6 Sodium hexametaphosphate solution

Components: Sodium hexametaphosphate $(NaPO_3)_6$, sodium carbonate (Na_2CO_3), RO water

- To a 2-L polyethylene bottle, add the following in order:
  - 1 L of RO water
  - 35.7 g of sodium hexametaphosphate
  - 7.94 g of sodium carbonate
- Invert to mix.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or

apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

7. Sample Preparation

A representative sample weighing up to 60 kg (estimated dry weight) is taken from the pit face or horizon exposure.

8. Procedure

8.1 Determine volume estimates as percentages of soil mass for:

- 75- to 250-mm fraction
- >250-mm fraction, which includes stones and boulders that have horizontal dimensions less than those of the pedon.

8.2 Determine either weight measurements in pounds or visual field-volume estimates in percentages for the 20- to 75-mm fragments. Weight measurements provide the best representative data, but volume estimates can be used.

8.3 Determine field weight measurements for the 20- to 75-mm fraction.

8.3.1 Sieve ≈60 kg of horizon material with a 76-mm sieve. A 60-kg sample may not be possible because of limitations of time or soil material. Actual sample size may be 30 or 40 kg.

8.3.2 Discard the >75-mm material.

8.3.3 Weigh and record weight of <75-mm fraction.

8.3.4 Sieve this material with a 20-mm sieve.

8.3.5 Discard the 20- to 75-mm fraction.

8.3.6 Weigh and record weight of <20-mm fraction.

8.3.7 Place a subsample of the <20-mm material in an 8-mil plastic bag. Label and send to laboratory for analyses.

8.4 In the laboratory, distribute the field sample on a plastic tray, weigh, and record moist weight. Air-dry sample at 30 ±5 °C (≈3 to 7 days), weigh, and record weight.

8.4.1 Process air-dry material on a flat, metal plate that is covered with brown kraft paper. Place sample on kraft paper and then, using the paper as a funnel, pour sample through sieve stack. Place fragments captured on each sieve into their own pie plate for collecting weights later.

8.4.2 Place material captured on the 2-mm sieve and in the lower pan onto kraft paper. Using a wooden rolling pin or rubber roller, roll over material. Break peds into smaller pieces that can pass through the 2-mm sieve. Tips for processing:

- Peds from air-dry, clay-rich soils are difficult to break down to <2 mm. Use a floor model adjustable plate crusher or field hammer to break apart peds.

- Try to not break rock fragments during rolling and grinding of sample material. Once soil has been broken away from lithics, sieve sample.
- Large sample sizes can be rolled and sieved in small batches. This helps ensure sufficient pressure to break apart peds, saving time and effort.
- For samples that do not require 80-mesh sample preparation but contain large pieces of organic litter (such as sticks and leaves), capture organic litter on the appropriate sieve size and discard litter so as not to skew organic measurements of soil or rock fragment weights.

8.4.3 Soils that are considered to have organic material as a part of their composition will have an O horizon designation or 80-mesh sample preparation request.

8.4.4 Smaller clay-rich peds may need to be slaked.

8.4.4.1 Weigh up to 100 g sample material captured on 2-mm sieve.

8.4.4.2 Soak in sodium hexametaphosphate solution for 12 h.

8.4.4.3 Rinse sample of solution and clay.

8.4.4.4 Dry remaining rock fragments in 110 °C oven.

8.4.4.5 Record final weight.

8.4.5 Once sample is processed to <2 mm, collect weights of:

- >75 mm
- 20 to 75 mm
- 5 to 20 mm

8.4.6 Fragments >2 mm can be discarded.

9. Calculations

9.1 Calculate weight percentages from volume percentages using measured bulk density (Db_m) and particle density (D_p). If measurements are unavailable, assume a Db_m of 1.45 g cc^{-1} and a D_p of 2.65 g cc^{-1}.

9.2 Use the following equation to convert all volume estimates to weight percentages for specified fractions.

$$\text{Percentage >2 mm (wt basis)} = [100\ D_p\ (x)] / [D_p\ (x) + Db_m\ (1 - x)]$$

D_p = Particle density (2.65 g cc^{-1}, unless measured)

Db_m = Bulk density (1.45 g cc^{-1} for <2-mm fraction, unless measured)

x = [volume fragments >i mm] / [volume whole soil]

i = size fraction above which volume estimates are made and below which weight percentages are determined, usually 20 or 75 mm in diameter

9.3 Use the preceding equation to calculate any individual fraction >j mm (j = any size fraction) by substituting an appropriate value of Db_m representing the fabric <j mm.

9.4 Use the following equation to determine the volume of the <2-mm fraction per unit volume of whole soil.

$$Cm = [\text{Volume moist <2-mm fabric}] / [\text{Volume moist whole-soil}] = [D_p (1 - y) (1 - x)] / [D_p (1 - y) + Db_m (y)]$$

Cm = Rock fragment conversion factor

Volume moist whole soil = Volume of fine earth + rock fragments on moist whole-soil basis

y = [weight material between 2 mm and i mm] / [weight material <i mm]

9.5 Use the following formula to convert laboratory data on a <2-mm weight basis to moist whole-soil volume basis.

$$Cm \times Db_m \times \text{lab datum}$$

9.6 Use the following formula to determine the volume percentage of <2-mm fabric in whole soil.

$$Cm \times 100$$

9.7 Use the following formula to determine the volume percentage of >2-mm fabric in whole soil.

$$100 (1 - Cm)$$

9.8 Use the following formula to report weight of <2-mm fabric per unit volume of whole soil for some soils.

$$(Cm \times Db_m)$$

9.9 Report weights from the field

- **9.9.1** Volume (%) >250-mm fraction (includes stones and boulders with horizontal dimensions smaller than size of a pedon)
- **9.9.2** Volume (%) 75- to 250-mm fraction
- **9.9.3** Volume (%) 20- to 75-mm fraction (not needed if weighed in field)
- **9.9.4** Weight (lbs) <75-mm fraction
- **9.9.5** Weight (lbs) 20- to 75-mm fraction

9.10 Report weights from the laboratory

- **9.10.1** Weight (g) of field-moist soil sample
- **9.10.2** Weight (g) of air-dry soil sample
- **9.10.3** Weight (g) of air-dry processed soil sample
- **9.10.4** Weight (g) of 20- to 75-mm fraction
- **9.10.5** Weight (g) of 5- to 20-mm fraction
- **9.10.6** Weight (g) of 2- to 5-mm fraction

9.10.7 Weight (g) of subsample 2- to 5-mm fraction before slaking

9.10.8 Weight (g) of subsample 2- to 5-mm fraction after slaking

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

American Society for Testing and Materials (ASTM). 2012. Standard practice for description and identification of soils (visual-manual procedure). D 2488. Annual book of ASTM standards. Construction. Section 4. Soil and rock; dimension stone; geosynthesis. Vol. 04.08. ASTM, Philadelphia, PA.

Bulk Density (3B)

Density is defined as mass per unit volume. The bulk density of a soil sample is the ratio of the mass of solids to the total or bulk volume, which includes both solids and pore space. Bulk density is distinguished from particle density, which is mass per unit volume of only the solid phase; pore spaces between particles are excluded. As bulk density (Db) is usually reported for the <2-mm soil fabric, the mass and volume of rock fragments are subtracted from the total mass and volume. Bulk density as a soil characteristic is a function rather than a single value. It can be highly dependent on soil conditions at the time of sampling. Soil mass remains fixed, but the volume of soil may change as water content changes (Blake and Hartge, 1986). Changes in soil volume due to changes in water content alter bulk density.

Methods

There are two broad groupings of bulk density methods: methods for consolidated soils and methods for unconsolidated soils.

Consolidated soils, due to clay content or cementation, may be sampled using clod methods in which the sample has an undefined volume and can be removed from the pit face with near in-situ conditions within the clod. The clods are collected in triplicate, coated with a plastic polymer, and a volume is determined by submergence. A cylinder can also be used for sample extraction.

Unconsolidated soils are too fragile for the removal of a consolidated clod sample and require a different sample extraction approach. An alternative includes a cylinder of known dimensions used to extract a known volume of sample. Samples are extracted in triplicate. Three additional excavation methods can be used to determine field bulk density (Db_f). The methods are compliant cavity (method 3B3a), ring excavation (method 3B4a), and frame excavation (method 3B5a) (Grossman and Reinsch, 2002). The frame-excavation provides for a larger sample area and is advantageous where there is large, very local variability, as in the O horizons of woodlands (Soil Survey Staff, 2014).

Subscripts to the bulk density notation (Db) designate the water state of the sample when the volume was measured. The KSSL uses the following bulk density notations.

- Field-state (Db_f): Value is the bulk density of a soil sample including the water content of the soil in the field at the time of sampling.
- 33-kPa equilibration (Db_{33}): Value is the bulk density of a soil sample that has been desorbed to 33 kPa (⅓ bar).
- Oven-dry (Db_{OD}): Value is the bulk density of a soil sample that has been dried in an oven at 110 °C.
- Rewet bulk density (Db_r): Value is the bulk density of soil sample that has been equilibrated, air-dried, and re-equilibrated. It is used to determine the irreversible shrinkage of soils and subsidence of organic soils.

Exceptions

The difference between the bulk density of the sample and that of the soil is particularly large for oven-dry clods of soils having high extensibility. A representative sample acquired for bulk density analysis is a snapshot of the soil composing the landscape at a given depth. Depending on soil composition (e.g., those with expanding 2:1 clays, concentrations of gypsum or other salts, organic matter), soils may not be scale-independent. The difference between bulk density of the soil and bulk density of the sample is particularly important. Features that would appear on a landscape scale may not be represented in the soil sample. As an example, desiccation cracks that may be present due to shink-swell properties on a landscape level are closed or not represented in a subsample. Clods undergo determination of volume at different water contents and hence volumes. If the water content is at or near field capacity, and the bulk density (Db_{33} or Db_f) is near field capacity, then the soil and the sample are considered the same. However, if the sample is at a water content below field-capacity due to drying after sampling or because the sample was taken below field-capacity, then desiccation cracks that occur on a large scale are excluded from the soil and the bulk density of the sample exceeds that of the soil conditions in situ.

This difference may be difficult to accurately determine for such soils if they are taken through a rewet cycle. In some excavation methods, the representative sample is large enough to include features such as desiccation cracks and therefore the sample and soil bulk density are the same.

Estimates of field-state, soil bulk-density water-content between field capacity and oven dryness, inclusive of desiccation crack space, are discussed by Grossman et al. (1990). Grossman and Reinsch (2002) discuss the manipulation of clod bulk densities at water contents below field capacity to obtain an estimate of soil bulk density at an intermediate water content.

References

Blake, G.R., and K.H. Hartge. 1986. Bulk density. p. 363–382. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Grossman, R.B., F.B. Pringle, R.J. Bigler, W.D. Broderson, and T.M. Sobecki. 1990. Systematics and field morphology for a use-dependent, temporal soil data base for edaphological and environmental applications. p. 452–460. *In* Int. Symp. on Advanced Technology in Natural Resource Management, 2nd. ed. Georgetown Univ., Washington, DC.

Grossman, R.B., and T.G. Reinsch. 2002. Bulk density and linear extensibility. p. 201–228. *In* J.H. Dane and G.C. Topp (eds.) Methods of soil analysis. Part 4. Physical methods. Soil Sci. Am. Book Series No. 5. ASA and SSSA, Madison, WI.

Soil Survey Staff. 2014. Keys to soil taxonomy. 12th ed. USDA–NRCS.

Bulk Density (3B)
Saran-Coated Clods (3B1)
Field-State (Db_f) (3B1a)

1. Introduction to Field State Clods

This method determines the field-state bulk density (Db_f) of a clod sample (field-occurring soil fabric) at field-soil water content at time of sampling. As bulk density (Db) is usually reported for the <2-mm soil fabric, the mass and volume of rock fragments are subtracted from the total mass and volume.

2. Scope and Field of Application

This bulk density measurement is used to convert data from a weight basis to a volume basis, estimate saturated hydraulic conductivity, and identify compacted horizons. Db_f is particularly useful if the soil layers are at or above field capacity or the soils have low extensibility and do not exhibit desiccation cracks even if below field capacity.

3. Principle

Clods (field-occurring fabric) are collected in triplicate from the face of an excavation. One coat of plastic saran lacquer is applied in the field. Additional coats of saran are applied in the laboratory. In field-water state or after equilibration, the clod is weighed in air to measure its mass. Clod volume is measured by water displacement. After the clod is dried in an oven at 110 °C, the mass and volume are determined again. A correction is made for the mass and volume of rock fragments and plastic coatings (Brasher et al., 1966; Blake and Hartge, 1986; Grossman and Reinsch, 2002).

3.1 Interferences

Errors are caused by non-representative samples. Only field-occurring fabric (clods) should be sampled. The whole-soil bulk density may be overestimated because sampled clods frequently exclude larger scale features that may occur along a landscape transect.

The penetration of plastic lacquer into the voids of sandy or organic soils interferes with the corrections for mass and volume of the plastic coat and with the accuracy of water content determinations. Imbibition can be reduced by spraying the clod with water and immediately dipping the clod in the plastic lacquer.

Loss of soil during the procedure invalidates the analyses because all calculations are based on the oven-dry soil mass. Friable clods break apart during analysis and no data will be reported. Unconsolidated soil samples or loose soil types should not be sampled using the saran coated, natural fabric clod method. The confined core, excavation, or compliant cavity sampling methods are commonly more suitable for loose, gravelly, or highly organic soil types.

Holes in the plastic coating, which are detected by air bubbles escaping from submerged clod, introduce errors in volume measurement. An inadequate evaporation of the plastic solvent results in overestimation of the soil mass. A drying time of 1 hour is usually sufficient for evaporation of solvent. However, clods with high content of organic matter may need longer.

Correction for rock fragments >2 mm requires either knowledge or assumption of the rock fragment density. Errors in the estimation or measurement of rock fragment density affect the accuracy of the value for soil bulk density. After drying, clods should be disaggregated and a pycnometer should be used to establish the correct grain density for the rock fragments.

4. Apparatus

4.1 Electronic balance, ±0.01-g sensitivity

4.2 Clod boxes with inserts for creating partitioned clod compartments

4.3 Plastic bags, 1-mil, 127 x 89 x 330 mm

4.4 Wire. The KSSL uses 28-awg, coated copper wire.

4.5 Hairnets

4.6 Stock tags, 25.4-mm (1-in) diameter paper tag, with metal rim

4.7 Hook assembly for weighing below balance

4.8 Plexiglass water tank

4.9 Lift apparatus, powered by compressed air. A lever or second analyst can be used in lieu of the lift.

4.10 Oven, 110 °C

4.11 Sieve, no. 10 (2-mm openings)

4.12 Rope, 3-m

4.13 Clothespins

4.14 Hot plate

4.15 Spray bottle

5. Chemicals

5.1 Acetone (CH_3COCH_3) (CAS# 67-64-1)

5.2 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.3 Sodium carbonate (Na_2CO_3) (CAS# 497-9-8)

5.4 Sodium hexametaphosphate $(NaPO_3)_6$ (CAS# 68915-31-1)

5.5 Saran, polyvinyl dichloride (PVDC) resin. (The KSSL can be contacted for more information.)

5.6 Saran plastic lacquer

Components: Acetone (CH_3COCH_3), saran resin

Saran is prepared in two resin-to-solvent ratios: 1:4 and 1:7 (on a weight

basis). Use the 1:4 plastic lacquer for the initial field and laboratory coatings. Use the 1:7 plastic lacquer for the last two laboratory coatings.

5.6.1 For a 1:4 ratio saran: To a 3.8-L (1-gal) metal paint can, add the following in order:

- 2,700 ±200 mL of acetone (fill to the bottom of handle rivet)
- 540 g saran resin

- For field preparation, stir solvent with a wooden stick or spoon while adding resin.
- For lab preparation, stir solvent with a non-sparking, high speed stirrer while adding resin.
- Stir plastic lacquer for 15 min at ≈25 °C.
- Store plastic lacquer in covered plastic or steel containers.

5.6.2 For a 1:7 ratio saran: To a 3.8-L (1-gal) metal paint can, add the following in order:

- 2,700 ±200 mL of acetone (fill to the bottom of handle rivet)
- 305 g of saran resin

- For field preparation, stir solvent with a wooden stick or spoon while adding resin.
- For lab preparation, stir solvent with a non-sparking, high speed stirrer while adding resin.
- Stir plastic lacquer for 15 min at ≈25 °C.
- Store plastic lacquer in covered plastic or steel containers.
- Note: The only situation in which the 1:7 saran ratio should be used in the field is for samples with low porosity and permeability.

5.7 Sodium hexametaphosphate solution

Components: Sodium hexametaphosphate $(NaPO_3)_6$, sodium carbonate (Na_2CO_3), RO water

- To a 1-L polyethylene bottle, add the following in order:
  - 1 L of RO water
  - 35.7 g of sodium hexametaphosphate
  - 7.94 g of sodium carbonate
- Invert to mix.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or

apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Acetone is highly flammable. Do not use acetone near open flames or electrical equipment. Avoid inhalation or physical contact. Use with adequate ventilation. In closed buildings, use a fume hood.

Saran F-310 resin decomposes rapidly at temperatures >200 °C, releasing hydrogen chloride gas. Disaggregate clods using a hotplate in a fume hood.

Avoid contact with Fe, Zn, Cu, and Al in solution. Avoid all contact with strong bases.

7. Sample Preparation

Clods should represent a given horizon and be approximately the size of a fist or a potato (≈250 to 550 cm^3). They should be carefully preserved in saran, bagged, and boxed for shipment to the KSSL. Additional resources include Field Sample Collection and Preparation (method 1A1b) and the video tutorial "How to Sample Bulk Density in the Field" (https://youtu.be/E7BSZrJ-TDw).

Note: Friable clods commonly break apart during shipping and analysis. In such cases, this method does not return reportable data. For these sample types, the confined core cylinder method (3C1a-d3) is more appropriate.

8. Procedure

8.1 Remove a consolidated piece of soil roughly the size of a potato from the face of sampling pit. From this piece, prepare a clod by gently cutting or breaking protruded peaks and compacted material from clod. If roots are present, trim roots with shears.

8.1.1 If soil is not consolidated, do not use clod method. Refer to the core cylinder method.

8.2 Three clods per horizon are recommended. It is important that these clods be as representative of the bulk sample as possible.

8.3 Using the rope, make a clothesline to hang saran-dipped clods. Place clod in a hairnet. If clod is dry, moisten surface with a fine mist of water. Holding the ends of the hairnet, quickly dip entire clod into plastic lacquer (fig. 3B1a–1). Suspend clod from clothesline to dry (fig. 3B1a–2). Dry clod for 30 min or until odor of solvent dissipates. If the value of Db_f is required, store clods in waterproof plastic bags as soon as coating dries because coating is permeable to water vapor.

8.4 Pack clods in partitioned clod boxes to protect them during transport.

8.5 In the laboratory

8.5.1 Prepare clod for dip in 1:4 saran. Label a round stock tag with sample identification number. Cut the copper wire and loop around the clod. Record weight of tag and wire (typically ≈1.5 g). Loop fine copper wire around clod, leaving a tail to which round stock tag is attached. Record weight of clod (CC1).

Figure 3B1a–1.—Dipping clods with hairnet in plastic lacquer.

Figure 3B1a–2.—After dipping, clods are tied to clothesline to dry.

8.5.2 Dip clod to preserve moisture content:

8.5.2.1 Dip clod in 1:4 plastic lacquer.

8.5.2.2 Wait 7 min and then dip clod in 1:7 saran.

8.5.2.3 Wait 12 min and then dip clod in 1:7 saran.

8.5.2.4 Wait 55 min and then reweigh clod.

8.5.3 If the clod has adsorbed >3% in plastic by clod weight or smells excessively of solvent, allow longer drying time and then reweigh clod and record weight (CC2). The clod should be waterproof and ready for volume measurement by water displacement.

8.5.4 Suspend the clod below the balance, submerge in water, and record weight (WMCW). Dry clod in an oven at 110 °C until weight is constant. Weigh oven-dry clod in air (WODC) and in water (WODCW) and record weights.

8.5.5 If the clod contains >5%, by weight, rock fragments >2-mm—as determined by sample processing bulk sample fragment weights or particle-size data—remove the rock fragments from the clod. Submerge the oven-dry clod in a beaker of water and place on a hot plate. Use a fume hood. Boil ≈1 h. The plastic coating loosens from soil material upon heating. Remove beaker from the hot plate. Allow to cool. Discard plastic coating.

8.5.6 Allow clod to stay in water until soil is fully saturated. If the soil is hydrophobic or clays are consolidated, break clod apart and soak soil in sodium hexametaphosphate solution overnight. Wet sieve the cool soil through a 2-mm, square-hole sieve. Dry and record weight of rock fragments (RF) that are retained on the sieve.

8.5.7 Determine rock fragment density by pycnometer or weighing fragments in air to obtain their mass and in water to obtain their volume. Record density weight (PD) for rock fragments.

8.5.8 In specific circumstances, if rock fragments are light in density, porous in appearance, abundant, and the analyst suspects the porosity of the fragments may contribute to water retention of the soil, do not correct clod mass and volume measurement for rock fragments.

8.5.9 Correct bulk density for weight and volume of plastic coating. The coating has an air-dry density of ≈1.3 g/cm^3. The coating loses 10 to 20% of its air-dry weight when dried in oven at 110 °C.

9. Calculations

9.1 $FCE = 1.5 \times [(CC2 - CC1)/3]$

FCE = Estimate of field-applied plastic saran coat

CC2 = Weight of clod after three laboratory saran dips

CC1 = Weight of clod before three laboratory saran dips

9.2 $MPC = [(CC2 - CC1) + FCE] \times RV$

MPC = Weight of plastic coat before oven drying

CC1 = Weight of clod before three laboratory saran dips

CC2 = Weight of clod after three laboratory saran dips

FCE = Estimate of field-applied plastic saran coat

RV = Percent estimate of remaining clod volume after cutting to obtain flat surface (≈80%)

9.3 $Db_f = [WODC - RF - ODPC - TAG] / \{[(CC2 - WMCW) / WD] - (RF/PD) - (MPC/1.3)\}$

Db_f = Bulk density in g cc^{-1} of <2-mm fabric at field-sampled water state

WODC = Weight of oven-dry coated clod

RF = Weight of rock fragments

ODPC = MPC x 0.85, weight of oven-dry plastic coat

TAG = Weight of tag and wire (typically ≈1.5 g)

CC2 = Weight of clod after three laboratory saran dips

WMCW = Weight of coated clod in water before oven drying

WD = Water density

PD = Density of rock fragments

9.4 $Db_{od} = [WODC - RF - ODPC - TAG] / \{[(WODC - WODCW) / WD] - (RF / PD) - (MPC / 1.3)\}$

Db_{od} = Bulk density in g/cm^3 <2-mm fabric at oven dryness

WODCW = Weight of oven-dry coated clod in water

9.5 $Wf = \{[(CC2 - MPC) - (WODC - ODPC)] / [WODC - RF - ODPC - TAG]\} x 100$

Wf = Percent water weight in sampled clod

CC2 = Weight of clod after three laboratory saran dips

MPC = Weight of plastic coat before oven drying

WODC = Weight of oven-dry coated clod

ODPC = MPC x 0.85, weight of oven-dry plastic coat

RF = Weight of rock fragments

9.5.1 Gypsum bearing soils are a special case because gypsum ($CaSO_4 \cdot 2H_2O$) loses most of its chemically combined water (crystal water) at 105 °C (Nelson et al., 1978). Gypsum content of the soil is determined in method 4E2a1a1.

9.5.2 For gypsum bearing soils, properties that are reported on an oven-dry weight basis, such as 1,500-kPa water content, are converted to

include the weight of crystal water in gypsum. The 1,500-kPa water content is corrected when the gypsum content of the soil is >1%.

9.6 Bulk density is reported to the nearest 0.01 g/cm^3.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Blake, G.R., and K.H. Hartge. 1986. Bulk density. p. 363–382. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Brasher, B.R., D.P. Franzmeier, V.T. Volassis, and S.E. Davidson. 1966. Use of saran resin to coat natural soil clods for bulk density and water retention measurements. Soil Sci. 101:108.

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Bulk Density (3B)
Saran-Coated Clods (3B1)
33-kPA Desorption (Db_{33}) (3B1b)

1. Introduction to 1/3-Bar Bulk Density

Bulk density, as a soil characteristic, is a function rather than a single value. Therefore, subscripts are added to the bulk density notation, Db, to designate the water state of the sample when the volume was measured. The 33-kPa equilibration (Db_{33}) method is the bulk density of a soil sample that has been desorbed to 33 kPa (1/3 bar). It is the most requested saturation tension because it correlates closely to field capacity.

2. Scope and Field of Application

Bulk density is used to convert data from a weight basis to a volume basis, determine the coefficient of linear extensibility, estimate saturated hydraulic conductivity, and identify compacted horizons.

3. Principle

Field-occurring fabric, that is clods, are collected in triplicate from the face of an excavation. One coat of plastic lacquer is applied in the field. Additional coats of plastic lacquer are applied in the laboratory. The clod is desorbed to 33 kPa. After equilibration, the clod is weighed in air to measure its mass and in water to measure its volume. After the clod is dried in an oven at 110 °C, the mass and volume are determined again. A correction is made for the mass and volume of rock fragments and for plastic coatings (Brasher et al., 1966; Blake and Hartge, 1986).

3.1 Interferences

Errors are caused by non-representative samples. Only field-occurring fabric (clods) should be sampled. The whole-soil bulk density may be overestimated because sampled clods frequently exclude larger scale features that may occur along a landscape transect.

The penetration of plastic lacquer into the voids of sandy and organic soils interferes with the corrections for mass and volume of the plastic coat and with the accuracy of water content determinations. Imbibition of saran can be reduced by spraying the clod with water and immediately dipping the clod in the plastic lacquer.

Loss of soil during the procedure invalidates the analyses because all calculations are based on the oven-dry soil mass. Friable clods break apart during analysis and no data is reported. Unconsolidated soils or loose soil types should not be sampled using the saran coated, natural fabric clod method. The confined

core, excavation, or compliant cavity sampling methods are commonly more suitable for loose, gravelly, or highly organic soil types.

Holes in the plastic coating, which are detected by air bubbles escaping from submerged clod, introduce errors in volume measurement. An inadequate evaporation of the plastic solvent results in overestimation of the soil mass. A drying time of 1 hour is usually sufficient for evaporation of solvent. However, clods with high content of organic matter may need longer.

Clods placed in an unsealed plastic bag can lose moisture during storage prior to analysis. If clods irreversibly dry below 33-kPa-water content, then Db_{33} values will be wrong. Completely seal the plastic storage bag to prevent drying.

Correction for rock fragments >2-mm requires either knowledge or assumption of the rock fragment density. Errors in the estimation or measurement of rock fragment density affect the accuracy of the value for soil bulk density. After drying, clods should be disaggregated and a pycnometer should be used to establish the correct grain density for the rock fragments.

4. Apparatus

4.1 Electronic balance, ±0.01-g sensitivity
4.2 Pressure-plate extractor
4.3 Air pressure source, 33-kPa
4.4 Clod boxes with inserts for creating partitioned clod compartments
4.5 Plastic bags, 1-mil, 127 x 89 x 330 mm
4.6 Wire. The KSSL uses 28-awg, coated copper wire.
4.7 Hairnets
4.8 Stock tags, 25.4-mm (1-in) diameter paper tag, with metal rim
4.9 Hook assembly for weighing below balance
4.10 Plexiglass water tank
4.11 Lift apparatus, powered by compressed air. A lever or second analyst can be used in lieu of the lift.
4.12 Oven, 110 °C
4.13 Sieve, no. 10 (2-mm openings)
4.14 Rope, 3-m
4.15 Clothespins
4.16 Knife
4.17 Tile cut−off saw with diamond-edged blade
4.18 Hot plate
4.19 Desiccator with ceramic plate
4.20 Vacuum, 80-kPa (0.8-bar)
4.21 Metal probe

4.22 Spray bottle

4.23 Reinforced paper towels or cheesecloth

4.24 Tension table. The KSSL constructs a tension table by placing porous firebricks, covered with reinforced paper towels, in a tub of RO water.

4.25 1-bar, high flow, ceramic pressure plates

5. Chemicals

5.1 Acetone (CH_3COCH_3) (CAS# 67-64-1)

5.2 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.3 Ethanol (CH_3CH_2OH) (CAS# 64-17-5), 95%, U.S.P.

5.4 Saran, polyvinyl dichloride (PVDC) resin. (The KSSL can be contacted for more information.)

5.5 Saran plastic lacquer

Components: Acetone (CH_3COCH_3), saran resin

Saran is prepared in two resin-to-solvent ratios: 1:4 and 1:7 (on a weight basis). Use the 1:4 plastic lacquer for the initial field and laboratory coatings. Use the 1:7 plastic lacquer for the last two laboratory coatings.

5.5.1 For a 1:4 ratio saran: To a 3.8-L (1-gal) metal paint can, add the following in order:

- 2,700 ±200 mL of acetone (fill to the bottom of handle rivet)
- 540 g saran resin

- For field preparation, stir solvent with a wooden stick or spoon while adding resin.
- For lab preparation, stir solvent with a non-sparking, high speed stirrer while adding resin.
- Stir plastic lacquer for 15 min at ≈25 °C.
- Store plastic lacquer in covered plastic or steel containers.

5.5.2 For a 1:7 ratio saran: To a 3.8-L (1-gal) metal paint can, add the following in order:

- 2,700 ±200 mL of acetone (fill to the bottom of handle rivet)
- 305 g of saran resin

- For field preparation, stir solvent with a wooden stick or spoon while adding resin.
- For lab preparation, stir solvent with a non-sparking, high speed stirrer while adding resin.
- Stir plastic lacquer for 15 min at ≈25 °C.
- Store plastic lacquer in covered plastic or steel containers.

- Note: The only situation in which the 1:7 saran ratio should be used in the field is for samples with low porosity and permeability.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Acetone is highly flammable. Do not use near open flame or electrical equipment. Avoid inhalation or physical contact. Use with adequate ventilation. In closed buildings, use a fume hood. Keep in tightly closed containers. Review acetone safety data sheets (SDS) for safe handling practices.

Saran F-310 resin decomposes rapidly at temperatures >200 °C, releasing hydrogen chloride gas. Disaggregate clods using a hotplate in a fume hood.

Avoid contact with Fe, Zn, Cu, and Al in solution. Avoid all contact with strong bases.

7. Sample Preparation

Clods should represent a given horizon and be approximately the size of a fist or a potato (≈250 to 550 cm^3). They should be carefully preserved in saran, bagged, and boxed for shipment to the KSSL. Additional resources include method 1A1b (Field Sample Collection and Preparation) and the video tutorial "How to Sample Bulk Density in the Field" (https://youtu.be/E7BSZrJ-TDw).

Note: Friable clods commonly break apart during shipping and analysis. In such cases, this method does not return reportable data. For these sample types, the confined core cylinder method (3C1a-d3) is more appropriate.

8. Procedure

8.1 Remove a consolidated piece of soil roughly the size of a potato from the face of sampling pit. From this piece, prepare a clod by gently cutting or breaking protruded peaks and compacted material from clod. If roots are present, trim roots with shears.

8.1.1 If soil is not consolidated, do not use clod method. Refer to the core cylinder method.

8.2 Three clods per horizon are recommended. It is important that these clods be as representative of the bulk sample as possible.

8.3 Using the rope, make a clothesline to hang saran-dipped clods. Place clod in a hairnet. If clod is dry, moisten surface with a fine mist of water. Holding the ends of the hairnet, quickly dip entire clod into plastic lacquer (fig. 3B1b-1). Suspend clod from clothesline to dry (fig. 3B1b-2). Dry clod for 30 min

or until odor of solvent dissipates. If the value of Db_f is required, store clods in waterproof plastic bags as soon as coating dries because coating is permeable to water vapor.

Figure 3B1b–1.—Dipping clods with hairnet in plastic lacquer.

Figure 3B1b–2.—After dipping, clods are tied to clothesline to dry.

8.4 Pack clods in partitioned clod boxes to protect them during transport.

8.5 In the laboratory

8.5.1 Prepare clod for dip in 1:4 saran. Label a round stock tag with sample identification number. Cut the copper wire and loop around the clod. Record weight of tag and wire (typically ≈1.5 g). Loop fine copper wire around clod, leaving a tail to which round stock tag is attached (fig. 3B1b–3). Record weight of clod (CC1).

8.5.2 Dip clod to preserve moisture content:

8.5.2.1 Dip clod in 1:4 plastic lacquer.

8.5.2.2 Wait 7 min and then dip clod in 1:7 saran.

8.5.2.3 Wait 12 min and then dip clod in 1:7 saran.

8.5.2.4 Wait 55 min and then reweigh clod.

8.5.3 If the clod has adsorbed >3% in plastic by clod weight or smells excessively of solvent, allow longer drying time and then reweigh clod and record weight (CC2). The clod should be waterproof and ready for volume measurement by water displacement.

8.6 Using a lapidary saw or tile saw and a diamond-edged sawblade, cut a flat surface on the clod, removing about 20% of the clod. Select the orientation of the cut based on surface area, barriers to capillary rise, or areas of the clod that absorbed saran.

Figure 3B1b–3.—A round stock tag with sample identification number is prepared. The cut copper wire is looped around the clod.

8.7 Place cut surface of clod on a tension table lined with paper towels maintained at 5-cm tension (fig. 3B1b–4). Periodically check clod to determine if it has reached equilibrium. Determination can be made by inserting metal probe to measure equal resistance and comparing saturated weight to initial weight. When clod has reached equilibrium, remove clod and record weight (WSC).

8.8 If the cut area of the clod is hydrophobic, place clod in a desiccator on a water-covered plate with a 0-cm tension. Submerge only the surface of clod in the water. Add a few mL of ethanol. Use in-house vacuum and apply suction until clod has equilibrated at saturation. Remove clod and record weight (WSC).

8.9 Place the clod in a pressure-plate extractor. To provide good contact between clod and ceramic plate, cover the ceramic plate with a paper towel and saturate with water. Place surface of clod on paper towel. Close the container and secure the lid. Apply gauged air pressure of 33 kPa.

8.10 Extraction usually takes 2 to 4 weeks. Monitor water discharge from extractor drain tubes. When water ceases to discharge from outflow tube, clod is at equilibrium. Remove clod and record weight (WMC). Compare WMC to WSC. If WMC ≥ WSC, equilibrate clod on tension table and repeat desorption process.

Figure 3B1b–4.—After a flat surface on the clod is cut with a diamond-edged saw blade, the clod is placed on a tension table and maintained at 5-cm tension.

8.11 Dip clod to preserve moisture content:

8.11.1 Dip clod in 1:4 plastic lacquer.

8.11.2 Wait 7 min and then dip clod in 1:7 saran.

8.11.3 Wait 12 min and then dip clod in 1:7 saran.

8.11.4 Wait 55 min and then reweigh clod.

8.11.5 If the clod has adsorbed >3% in plastic by clod weight or smells excessively of solvent, allow longer drying time and then reweigh clod and record weight (CC3).

8.12 The clod should be waterproof and ready for volume measurement by water displacement.

8.12.1 Suspend clod below the balance and collect a 33-kPa dipped air weight.

8.12.2 Submerge suspended clod in water and record weight (WMCW).

8.12.3 Clods with compromised saran coatings or areas of porosity begin taking on water immediately.

8.12.4 Use caution that buoyant clods do not become detached from the balance suspension hook.

8.13 Dry clod in an oven at 110 °C until weight is constant. Collect oven-dry weights.

8.14 Suspend clod below the balance and collect an oven-dry air weight (WODC).

8.15 Submerge suspended clod in water (WODCW) and record weight. Collect a weight as soon as whole clod is submerged; clods begin taking on water immediately.

8.16 If the clod contains >5%, by weight, rock fragments >2-mm—as determined by sample processing bulk sample fragment weights or particle-size data—remove the rock fragments from the clod. Submerge the oven-dry clod in a beaker of water and place on a hot plate. Use a fume hood. Boil ≈1 h. The plastic coating loosens from soil material upon heating. Remove beaker from the hot plate. Allow to cool. Discard plastic coating.

8.17 Allow clod to stay in water until soil is fully saturated. If the soil is hydrophobic or clays are consolidated, break clod apart and soak soil in sodium hexametaphosphate solution overnight. Wet sieve the cool soil through a 2-mm, square-hole sieve. Dry and record weight of rock fragments (RF) that are retained on the sieve.

8.18 Determine rock fragment density by pycnometer or weighing fragments in air to obtain their mass and in water to obtain their volume. Record density weight (PD) for rock fragments.

8.19 In specific circumstances, if rock fragments are light in density, abundant, and the analyst suspects the porosity of the fragments may contribute to water retention of the soil, do not correct clod mass and volume measurement for rock fragments.

8.20 Correct bulk density for weight and volume of plastic coating. The coating has an air-dry density of ≈1.3 g/cm^3. The coating loses 10 to 20% of its air-dry weight when dried in oven at 110 °C.

9. Calculations

9.1 FCE = 1.5 x [(CC2 − CC1) / 3]

FCE = Estimate of field-applied plastic coat

CC2 = Weight of clod after three laboratory saran dips

CC1 = Weight of clod before three laboratory saran dips

9.2 MPC1 = {[(CC2 − CC1) + FCE] x RV} + (CC3 − WMC)

MPC1 = Weight of plastic coat before oven drying

CC2 = Weight of clod after three laboratory saran dips

CC1 = Weight of clod before three laboratory saran dips

WMC = Weight of coated clod equilibrated at 33-kPa tension

RV = Percent estimate of remaining clod volume after cutting to obtain flat surface (≈80%)

9.3 Db_{33} = [WODC − RF − ODPC − TAG] / {[(CC3 − WMCW) / WD] − (RF/PD) − (MPC1 / 1.3)}

Db_{33} = Bulk density in g cc^{-1} of <2-mm fabric at 33−kPa tension

WODC = Weight of oven-dry coated clod

RF = Weight of rock fragments (step 8.17)

TAG = Weight of tag and wire (typically ≈1.5 g)

ODPC = MPC1 x 0.85, weight of oven-dry plastic coat

CC3 = Weight of equilibrated clod after four additional plastic coats

WD = Water density

PD = Density of rock fragments

MPC1 = Weight of plastic coat before oven drying

WMCW = Weight in water of coated clod equilibrated at 33-kPa tension

9.4 Db_{od} = [WODC−RF−ODPC − TAG] / {[(WODC − WODCW) / WD] − (RF / PD) − (MPC1 / 1.3)}

Db_{od} = Bulk density in g cc^{-1} <2-mm fabric, oven-dry fabric

WODCW = Weight of oven-dry clod coated in water

9.5 W_{33} = {[(CC3 − MPC1) − (WODC − ODPC)] / [(WODC − RF − ODPC − TAG)]} x 100

W_{33} = Percent water weight retained at 33-kPa tension

9.6 Gypsum bearing soils are a special case because gypsum ($CaSO_4 \cdot 2H_2O$) loses most of its chemically combined water (crystal water) at 105 °C (Nelson et al., 1978). Gypsum content of the soil is determined in method 4E2a1a1.

9.7 For gypsum bearing soils, properties that are reported on an oven-dry weight basis, such as 1,500-kPa water content, are converted to include the weight of crystal water in gypsum. The 1,500-kPa water content is corrected when the gypsum content of the soil is >1%.

9.8 Report bulk density to the nearest 0.01 g/cm^3.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Blake, G.R., and K.H. Hartge. 1986. Bulk density. p. 363–382. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

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Bulk Density (3B)
Saran-Coated Clods (3B1)
Oven-Dry (Db_{od}) (3B1c)

1. Introduction to Oven-Dry Clods

This method determines the bulk density value (Db_{od}) of an oven-dry soil clods. Soil clods represent a close facsimile to in situ conditions of soil fabric. As such, the oven-dry bulk density is a reflection of the soil, clays, rock fragments, and larger organic materials (such as roots or sticks) that may influence porosity and permeability of the soil.

2. Scope and Field of Application

Bulk density is used to convert data from a weight basis to a volume basis, determine the coefficient of linear extensibility, estimate saturated hydraulic conductivity, and identify compacted horizons.

3. Principle

Clods (field-occurring fabric) are collected in triplicate from the face of an excavation. One coat of plastic lacquer is applied in the field. Additional coats of plastic lacquer are applied in the laboratory. The clod is dried in an oven at 110 °C and then weighed in air to measure its mass and in water to measure its volume. A correction is made for the mass and volume of rock fragments and for plastic coatings (Brasher et al., 1966; Blake and Hartge, 1986).

3.1 Interferences

Errors are caused by non-representative samples. Only field-occurring fabric (clods) should be sampled. The whole-soil bulk density may be overestimated because sampled clods frequently exclude larger scale features that may occur along a landscape transect.

The penetration of plastic lacquer into the voids of sandy or organic soils interferes with the corrections for mass and volume of the plastic coat and with the accuracy of water content determinations. Imbibition of saran can be reduced by spraying the clod with water and immediately dipping the clod in the plastic lacquer.

Loss of soil during the method invalidates the analyses because all calculations are based on the oven-dry soil mass. Friable clods break apart during analysis and no data can be reported. Unconsolidated soils should not be sampled using the saran coated, natural fabric clod method. The confined core, excavation, or compliant cavity sampling methods are commonly more suitable for loose, gravelly, or highly organic soil types and should be investigated.

Holes in the plastic coating, which are detected by air bubbles escaping from submerged clod, introduce errors in volume measurement. An inadequate evaporation of the plastic solvent results in overestimation of the soil mass. A drying time of 1 hour is usually sufficient for evaporation of solvent. However, clods with high content of organic matter may need longer.

Bulk density is reported for <2-mm soil fabric. Correction for rock fragments >2-mm requires either knowledge or assumption of the rock fragment density. Errors in the estimation or measurement of rock fragment density affect the accuracy of the value for soil bulk density. After drying, clods should be disaggregated and a pycnometer should be used to establish the correct grain density for the rock fragments.

4. Apparatus

4.1 Electronic balance, ±0.01-g sensitivity

4.2 Clod boxes with inserts for creating partitioned clod compartments

4.3 Plastic bags, 1-mil, 127 x 89 x 330 mm

4.4 Wire. The KSSL uses 28-awg, coated copper wire.

4.5 Hairnets

4.6 Stock tags, 25.4-mm (1-in) diameter paper tag with metal rim

4.7 Hook assembly for weighing below balance

4.8 Plexiglass water tank

4.9 Lift apparatus, powered by compressed air. A lever or second analyst can be used in lieu of the lift.

4.10 Oven, 110 °C

4.11 Sieve, no. 10 (2-mm openings)

4.12 Rope, 3-m

4.13 Clothespins

4.14 Hot plate

4.15 Spray bottle

5. Chemicals

5.1 Acetone (CH_3COCH_3) (CAS# 67-64-1)

5.2 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.3 Saran, polyvinyl dichloride (PVDC) resin. (The KSSL can be contacted for more information.)

5.4 Saran plastic lacquer

Components: Acetone (CH_3COCH_3), saran resin

Saran is prepared in two resin-to-solvent ratios: 1:4 and 1:7 (on a weight basis). Use the 1:4 plastic lacquer for the initial field and laboratory coatings. Use the 1:7 plastic lacquer for the last two laboratory coatings.

5.4.1 For a 1:4 ratio saran**:** To a 3.8-L (1-gal) metal paint can, add the following in order:

- 2,700 ±200 mL of acetone (fill to the bottom of handle rivet)
- 540 g saran resin.

- For field preparation, stir solvent with a wooden stick or spoon while adding resin.
- For lab preparation, stir solvent with a non-sparking, high speed stirrer while adding resin.
- Stir plastic lacquer for 15 min at ≈25 °C.
- Store plastic lacquer in covered plastic or steel containers.

5.4.2 For a 1:7 ratio saran: To a 3.8-L (1-gal) metal paint can, add the following in order:

- 2,700 ±200 mL of acetone (fill to the bottom of handle rivet)
- 305 g of saran resin

- For field preparation, stir solvent with a wooden stick or spoon while adding resin.
- For lab preparation, stir solvent with a non-sparking, high speed stirrer while adding resin.
- Stir plastic lacquer for 15 min at ≈25 °C.
- Store plastic lacquer in covered plastic or steel containers.
- Note: The only situation in which the 1:7 saran ratio should be used in the field is for samples with low porosity and permeability.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Acetone is highly flammable. Do not use acetone near open flames or electrical equipment. Avoid inhalation or physical contact. Use with adequate ventilation. In closed buildings, use a fume hood.

Saran F-310 resin decomposes rapidly at temperatures >200 °C, releasing hydrogen chloride gas. Disaggregate clods using a hotplate in a fume hood.

Avoid contact with Fe, Zn, Cu, and Al in solution. Avoid all contact with strong bases.

7. Sample Preparation

Clods should represent a given horizon and be approximately the size of a fist or a potato (≈250 to 550 cm^3). They should be carefully preserved in saran, bagged, and boxed for shipment to the KSSL. Additional resources include method 1A1b (Field Sample Collection and Preparation) and the video tutorial "How to Sample Bulk Density in the Field" (https://youtu.be/E7BSZrJ-TDw).

Note: Friable clods commonly break apart during shipping and analysis. In such cases, this method does not return reportable data. For these sample types, the confined core cylinder method is more appropriate.

8. Procedure

8.1 Remove a consolidated piece of soil roughly the size of a potato from the face of sampling pit. From this piece, prepare a clod by gently cutting or breaking protruded peaks and compacted material from clod. If roots are present, trim roots with shears.

8.1.1 If soil is not consolidated, do not use clod method. Refer to the core cylinder method.

8.2 Three clods per horizon are recommended. It is important that these clods be as representative of the bulk sample as possible.

8.3 Using the rope, make a clothesline to hang saran-dipped clods. Place clod in a hairnet. If clod is dry, moisten surface with a fine mist of water. Holding the ends of the hairnet, quickly dip entire clod into plastic lacquer (fig. 3B1b-1). Suspend clod from clothesline to dry (fig. 3B1b-2). Dry clod for 30 min or until odor of solvent dissipates. If the value of Db_f is required, store clods in waterproof plastic bags as soon as coating dries because coating is permeable to water vapor.

8.4 Pack clods in partitioned clod boxes to protect them during transport.

8.5 In the laboratory

8.5.1 Prepare clod for dip in 1:4 saran. Label a round stock tag with sample identification number. Cut the copper wire and loop around the clod. Record weight of tag and wire (typically ≈1.5 g). Loop fine copper wire around clod, leaving a tail to which round stock tag is attached. Record weight of clod (CC1).

8.5.2 Dip clod to preserve moisture content:

8.5.2.1 Dip clod in 1:4 plastic lacquer.

8.5.2.2 Wait 7 min and then dip clod in 1:7 saran.

8.5.2.3 Wait 12 min and then dip clod in 1:7 saran.

8.5.2.4 Wait 55 min and then reweigh clod.

8.5.3 If the clod has adsorbed >3% in plastic by clod weight or smells excessively of solvent, allow longer drying time and then reweigh clod and record weight (CC2).

8.6 Dry clod in an oven at 110 °C until weight is constant. Collect oven-dry weights.

8.7 Suspend clod below the balance and collect an oven-dry air weight (WODC).

8.8 Submerge suspended clod in water (WODCW) and record weight. Collect a weight as soon as whole clod is submerged; clods begin taking on water immediately.

8.9 If the clod contains >5%, by weight, rock fragments >2-mm—as determined by sample processing bulk sample fragment weights or particle-size data—remove the rock fragments from the clod. Submerge the oven-dry clod in a beaker of water and place on a hot plate. Use a fume hood. Boil ≈1 h. The plastic coating loosens from soil material upon heating. Remove beaker from the hot plate. Allow to cool. Discard plastic coating.

8.10 Allow clod to stay in water until soil is fully saturated. If the soil is hydrophobic or clays are consolidated, break clod apart and soak soil in sodium hexametaphosphate solution overnight. Wet sieve the cool soil through a 2-mm, square-hole sieve. Dry and record weight of rock fragments (RF) that are retained on the sieve.

8.11 Determine rock fragment density by pycnometer or weighing fragments in air to obtain their mass and in water to obtain their volume. Record density weight (PD) for rock fragments.

8.12 In specific circumstances, if rock fragments are light in density, abundant, and the analyst suspects the porosity of the fragments may contribute to water retention of the soil, do not correct clod mass and volume measurement for rock fragments.

8.13 Correct bulk density for weight and volume of plastic coating. The coating has an air-dry density of ≈1.3 g/cm^3. The coating loses 10 to 20% of its air-dry weight when dried in oven at 110 °C.

9. Calculations

9.1 $FCE = 1.5 \times [(CC2 - CC1)/3]$

FCE = Estimate of field-applied plastic coat

9.2 $MPC = [(CC2 - CC1) + FCE] \times RV$

MPC = Weight of plastic coat before oven drying

CC2 = Weight of clod after three laboratory saran dips

CC1 = Weight of clod before three laboratory saran dips

RV = Percent estimate of remaining clod volume after cutting to obtain flat surface (≈80%)

9.3 $Db_{od} = [WODC - RF - ODPC - TAG]/\{[(WODC - WODCW)/WD] - (RF/PD) - (MPC/1.3)\}$

$Db_{od=}$ Bulk density in g/cm^3 of <2-mm, oven-dry fabric

WODC = Weight of oven-dry coated clod

RF = Weight of rock fragments

TAG = Weight of tag and wire (typically ≈1.5 g)

ODPC = MPC1 x 0.85, weight of oven-dry plastic coat

WD = Water density

PD = Density of rock fragments

WODCW = Weight of oven-dry coated clod in water

9.4 Gypsum bearing soils are a special case because gypsum ($CaSO_4 \cdot 2H_2O$) loses most of its chemically combined water (crystal water) at 105 °C (Nelson et al., 1978). Gypsum content of the soil is determined in method 4E2a1a1.

9.5 For gypsum bearing soils, properties that are reported on an oven-dry weight basis, such as 1,500-kPa water content, are converted to include the weight of crystal water in gypsum. The 1,500-kPa water content is corrected when the gypsum content of the soil is >1%.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

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Bulk Density (3B)
Saran-Coated Clods (3B1)
Rewet (Db_r) (3B1d)

1. Introduction to Rewet Clod Bulk Density

The rewet bulk density (Db_r) is used to determine irreversible shrinkage of soils and subsidence of organic soils. This method determines the bulk density value of a re-saturated soil sample.

2. Scope and Field of Application

Bulk density is used to convert data from a weight basis to a volume basis, determine the coefficient of linear extensibility, estimate saturated hydraulic conductivity, and identify compacted horizons.

3. Principle

Clods (field-occurring fabric) are collected in triplicate from the face of an excavation. One coat of plastic lacquer is applied in the field. Additional coats of plastic lacquer are applied at the laboratory. After equilibration, the clod is weighed in air to measure its mass and in water to measure its volume. The clod is air-dried, re-equilibrated, and its mass and volume re-measured. After the clod is dried in an oven at 110 °C, the mass and volume are determined again. A correction is made for the mass and volume of rock fragments and for plastic coatings (Brasher et al., 1966; Blake and Hartge, 1986; Grossman and Reinsch, 2002).

3.1 Interferences

Errors are caused by non-representative samples. Only field-occurring fabric (clods) should be sampled. The whole-soil bulk density may be overestimated because sampled clods frequently exclude larger scale features that may occur along a landscape transect.

The penetration of plastic lacquer into the voids of sandy or organic soils interferes with the corrections for mass and volume of the plastic coat and with the accuracy of water content determinations. Imbibition of saran can be reduced by spraying the clod with water and immediately dipping the clod in the plastic lacquer.

Loss of soil during the procedure invalidates the analyses because all calculations are based on the oven-dry soil mass. Friable clods break apart during analysis, and no data can be reported. Unconsolidated soil samples or loose soil types should not be sampled using the saran coated, natural fabric clod method. The confined core, excavation, or compliant cavity sampling methods are commonly more suitable for loose, gravelly, or highly organic soil types and should be investigated.

Holes in the plastic coating, which are detected by air bubbles escaping from submerged clod, introduce errors in volume measurement. Inadequate drying results in overestimation of the soil mass. An inadequate evaporation of plastic solvent results in overestimation of the soil mass. A drying time of 1 hour is usually sufficient for evaporation of solvent. However, clods with a high content of organic matter may need longer.

Bulk density is reported for <2-mm soil fabric. Correction for rock fragments >2-mm requires either knowledge or assumption of the rock fragment density. Errors in the estimation or measurement of rock fragment density affect the accuracy of the value for soil bulk density. After drying, clods should be disaggregated and a pycnometer should be used to establish the correct grain density for the rock fragments.

4. Apparatus

4.1 Electronic balance, ±0.01-g sensitivity

4.2 Pressure-plate extractor

4.3 1-bar high-flow porous ceramic plate. (The KSSL can be contacted for more information.)

4.4 Air pressure source, 33-kPa

4.5 Clod boxes with inserts for creating partitioned clod compartments

4.6 Plastic bags, 1-mil, 127 x 89 x 330 mm

4.7 Wire. The KSSL uses 28-awg, coated copper wire.

4.8 Hairnets

4.9 Stock tags, 25.4-mm (1-in) diameter paper tag, with metal rim

4.10 Hook assembly for weighing below balance

4.11 Plexiglass water tank

4.12 Lift apparatus, powered by compressed air. A lever or second analyst can be used in lieu of the lift.

4.13 Oven, 110 °C

4.14 Sieve, no. 10 sieve (2-mm openings)

4.15 Rope, 3-m

4.16 Clothespins

4.17 Knife

4.18 Tile cut−off saw with diamond-edged blade

4.19 Hot plate

4.20 Desiccator with ceramic plate

4.21 Vacuum, 80-kPa (0.8-bar)

4.22 Metal probe

4.23 Spray bottle

4.24 Reinforced paper towels or cheesecloth

4.25 Tension table. The KSSL constructs a tension table by placing porous firebricks, covered with reinforced paper towels, in a tub of water.

5. Chemicals

5.1 Acetone (CH_3COCH_3) (CAS# 67-64-1)

5.2 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.3 Ethanol (CH_3CH_2OH) (CAS# 64-17-5), 95%, U.S.P.

5.4 Saran, polyvinyl dichloride (PVDC) resin. (The KSSL can be contacted for more information.)

5.5 Saran plastic lacquer

Components: Acetone (CH_3COCH_3), saran resin

Saran is prepared in two resin-to-solvent ratios: 1:4 and 1:7 (on a weight basis). Use the 1:4 plastic lacquer for the initial field and laboratory coatings. Use the 1:7 plastic lacquer for the last two laboratory coatings.

5.5.1 For a 1:4 ratio saran: To a 3.8-L (1-gal) metal paint can, add the following in order:

- 2,700 ±200 mL of acetone (fill to the bottom of handle rivet)
- 540 g saran resin

- For field preparation, stir solvent with a wooden stick or spoon while adding resin.
- For lab preparation, stir solvent with a non-sparking, high speed stirrer while adding resin.
- Stir plastic lacquer for 15 min at ≈25 °C.
- Store plastic lacquer in covered plastic or steel containers.

5.5.2 For a 1:7 ratio saran: To a 3.8-L (1-gal) metal paint can, add the following in order:

- 2,700 ±200 mL of acetone (fill to the bottom of handle rivet)
- 305 g of saran resin

- For field preparation, stir solvent with a wooden stick or spoon while adding resin.
- For lab preparation, stir solvent with a non-sparking, high speed stirrer while adding resin.
- Stir plastic lacquer for 15 min at ≈25 °C.
- Store plastic lacquer in covered plastic or steel containers.
- Note: The only situation in which the 1:7 saran ratio should be used in the field is for samples with low porosity and permeability.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Acetone is highly flammable. Do not use acetone near open flames or electrical equipment. Avoid inhalation or physical contact. Use with adequate ventilation. In closed buildings, use a fume hood. Keep in tightly closed containers.

Saran F-310 resin decomposes rapidly at temperatures >200 °C, releasing hydrogen chloride gas. Disaggregate clods using a hotplate in a fume hood.

Avoid contact with Fe, Zn, Cu, and Al in solution. Avoid all contact with strong bases.

7. Sample Preparation

Clods should represent a given horizon and be approximately the size of a fist or a potato (≈250 to 550 cm^3). They should be carefully preserved in saran, bagged, and boxed for shipment to the KSSL. Additional resources include method 1A1b (Field Sample Collection and Preparation) and the video tutorial "How to Sample Bulk Density in the Field" (https://youtu.be/E7BSZrJ-TDw).

Note: Friable clods commonly break apart during shipping and analysis. In such cases, this method does not return reportable data. For these sample types, the confined core cylinder method is more appropriate.

8. Procedure

8.1 Remove a consolidated piece of soil roughly the size of a potato from the face of sampling pit. From this piece, prepare a clod by gently cutting or breaking protruded peaks and compacted material from clod. If roots are present, trim roots with shears.

8.1.1 If soil is not consolidated, do not use clod method. Refer to the core cylinder method.

8.2 Three clods per horizon are recommended. It is important that these clods be as representative of the bulk sample as possible.

8.3 Using the rope, make a clothesline to hang saran-dipped clods. Place clod in a hairnet. If clod is dry, moisten surface with a fine mist of water. Holding the ends of the hairnet, quickly dip entire clod into plastic lacquer (fig. 3B1b–1). Suspend clod from clothesline to dry (fig. 3B1b–2). Dry clod for 30 min or until odor of solvent dissipates. If the value of Db_f is required, store clods in waterproof plastic bags as soon as coating dries because coating is permeable to water vapor.

8.4 Pack clods in partitioned clod boxes to protect them during transport.

8.5 In the laboratory

8.5.1 Prepare clod for dip in 1:4 saran. Label a round stock tag with sample identification number. Cut the copper wire and loop around the clod. Record weight of tag and wire (typically ≈1.5 g). Loop fine copper wire around clod, leaving a tail to which round stock tag is attached. Record weight of clod (CC1).

8.5.2 Dip clod to preserve moisture content:

8.5.2.1 Dip clod in 1:4 plastic lacquer.

8.5.2.2 Wait 7 min and then dip clod in 1:7 saran.

8.5.2.3 Wait 12 min and then dip clod in 1:7 saran.

8.5.2.4 Wait 55 min and then reweigh clod.

8.5.2.5 If the clod has adsorbed >3% in plastic by clod weight or smells excessively of solvent, allow longer drying time and then reweigh clod and record weight (CC2). The clod should be waterproof and ready for volume measurement by water displacement.

8.6 Using lapidary saw or tile saw and a diamond-edged sawblade, cut a flat surface on the clod, removing about 20% of the clod. Select the orientation of the cut based on surface area, barriers to capillary rise, or areas of the clod that absorbed saran.

8.7 Place cut surface of clod on a tension table lined with paper towels maintained at 5-cm tension (fig. 3B1b–4). Periodically check clod to determine if it has reached equilibrium. Determination can be made by inserting metal probe to measure equal resistance and comparing saturated weight to initial weight. When clod has reached equilibrium, remove clod and record weight (WSC).

8.8 If the cut area of the clod is hydrophobic, place clod in a desiccator on a water-covered plate with a 0-cm tension. Submerge only the surface of clod in the water. Add a few mL of ethanol. Use in-house vacuum and apply suction until clod has equilibrated at saturation. Remove clod and record weight (WSC).

8.9 Place the clod in a pressure-plate extractor. To provide good contact between clod and ceramic plate, cover the ceramic plate with a paper towel and saturate with water. Place cut surface of clod on paper towel. Close the container and secure the lid. Apply gauged air pressure of 33 kPa.

8.10 Extraction usually takes 2 to 4 weeks. Monitor water discharge from extractor drain tubes. When water ceases to discharge from outflow tube, clod is at equilibrium. Remove clod and record weight (WMC). Compare WMC to WSC. If WMC ≥ WSC, equilibrate clod on tension table and repeat desorption process.

8.11 Dip clod to preserve moisture content:

8.11.1 Dip clod in 1:4 plastic lacquer.

8.11.2 Wait 7 min and then dip clod in 1:7 saran.

8.11.3 Wait 12 min and then dip clod in 1:7 saran.

8.11.4 Wait 55 min and then reweigh clod.

8.11.5 If the clod has adsorbed >3% in plastic by clod weight or smells excessively of solvent, allow longer drying time and then reweigh clod and record weight (CC3).

8.12 The clod should be waterproof and ready for volume measurement by water displacement.

8.12.1 Suspend clod below the balance and collect a 33-kPa dipped air weight.

8.12.2 Submerge suspended clod in water and record weight (WMCW).

8.12.3 Clods with compromised saran coatings or areas of porosity begin taking on water immediately.

8.12.4 Use caution that buoyant clods do not become detached from the balance suspension hook.

8.13 Remove layer of plastic from cut surface of clod.

8.14 Dry clod at ambient room temperature (≈20 to 25 °C) for 4 to 6 days.

8.15 Air-dry clod at 40 to 50 °C for 2 to 3 days or until weight is constant.

8.16 Place clod on tension table and repeat steps 8.7– 8.10. After equilibrium is obtained in the pressure plate extractor, remove clod and record weight (WAR).

8.17 Dip clod to preserve moisture content:

8.17.1 Dip clod in 1:4 plastic lacquer.

8.17.2 Wait 7 min and then dip clod in 1:7 saran.

8.17.3 Wait 12 min and then dip clod in 1:7 saran.

8.17.4 Wait 55 min and then reweigh clod.

8.17.5 If the clod has adsorbed >3% in plastic by clod weight or smells excessively of solvent, allow longer drying time and then reweigh clod.

8.18 The clod should be waterproof and ready for volume measurement by water displacement.

8.18.1 Suspend clod below the balance.

8.18.2 Collect a 33-kPa rewet air weight (CC4).

8.18.3 Submerge suspended clod in water and record weight (WARW).

8.18.4 Clods with compromised saran coatings or areas of porosity begin taking on water immediately.

8.18.5 Use caution that buoyant clods do not become detached from the balance suspension hook.

8.19 Dry clod in an oven at 110 °C until weight is constant; collect oven-dry weights.

8.19.1 Suspend clod below the balance.

8.19.2 Collect an oven-dry air weight (WODC).

8.19.3 Submerge suspended clod in water (WODCW) and record weight.

8.19.4 Collect a weight as soon as whole clod is submerged; clods begin taking on water immediately.

8.19.5 Use caution that buoyant clods do not become detached from the balance suspension hook.

8.20 If the clod contains >5%, by weight, rock fragments >2-mm—as determined by sample processing bulk sample fragment weights or particle-size data—remove the rock fragments from the clod. Submerge the oven-dry clod in a beaker of water and place on a hot plate. Use a fume hood. Boil ≈1 h. The plastic coating loosens from soil material upon heating. Remove beaker from the hot plate. Allow to cool. Discard plastic coating.

8.21 Allow clod to stay in water until soil is fully saturated. If the soil is hydrophobic or clays are consolidated, break clod apart and soak soil in sodium hexametaphosphate solution overnight. Wet sieve the cool soil through a 2-mm, square-hole sieve. Dry and record weight of rock fragments (RF) that are retained on the sieve.

8.22 Determine rock fragment density by pycnometer or weighing fragments in air to obtain their mass and in water to obtain their volume. Record density weight (PD) for rock fragments.

8.23 In specific circumstances, if rock fragments are light in density, abundant, and the analyst suspects the porosity of the fragments may contribute to water retention of the soil, do not correct clod mass and volume measurement for rock fragments.

8.24 Correct bulk density for weight and volume of plastic coating. The coating has an air-dry density of ≈1.3 g/cm^3. The coating loses 10 to 20% of its air-dry weight when dried in oven at 110 °C.

9. Calculations

9.1 $FCE = 1.5 \times [(CC2 - CC1)/3]$

FCE = Estimate of field-applied plastic coat.

CC2 = Weight of clod after three laboratory plastic coats

CC1 = Weight of clod before three laboratory plastic coats

9.2 $MPC1 = \{[(CC2 - CC1) + FCE] \times RV\} + (CC3 - WMC)$

MPC1 = Weight of plastic coat before air-drying and rewet

CC3 = Weight of equilibrated clod after four additional plastic coats

CC2 = Weight of clod after three laboratory plastic coats

CC1 = Weight of clod before three laboratory plastic coats

WMC = Weight of coated clod equilibrated at 33-kPa tension

FCE = Estimate of field-applied plastic coat

RV = Percent estimate of remaining clod volume after cutting to obtain flat surface (≈80%)

9.3 Db_{33} = [WODC – RF – ODPC – TAG] / {[(CC3 – WMCW) / WD] – (RF / PD) – (MPC1/1.3)}

Db_{33} = Bulk density in g cm^{-3} of <2-mm fabric at 33-kPa tension

WODC = Weight of oven-dry coated clod

RF = Weight of rock fragments

ODPC = MPC1 x 0.85, weight of oven-dry plastic coat

TAG = Weight of tag and wire (typically ≈1.5 g)

CC3 = Weight of equilibrated clod after four additional plastic coats

WD = Water density

PD = Density of rock fragments

WMCW = Weight in water of coated clod equilibrated at 33-kPa tension

MPC1 = Weight of plastic coat before air-drying and rewet

9.4 MPC2 = {[(CC2 – CC1) + FCE] x RV2} + (CC3 – WMC) + (CC4 – WAR)

MPC2 = Weight of plastic coat after rewetting and before oven drying

CC1 = Weight of clod before three laboratory plastic coats

CC2 = Weight of clod after three laboratory plastic coats

CC3 = Weight of equilibrated clod after four additional plastic coats

CC4 = Weight of clod after twelve plastic coats

FCE = Estimate of field-applied plastic coat

WMC = Weight of coated clod equilibrated at 33-kPa tension

WAR = Weight of clod after rewet equilibration

RV2 = Percent estimate of remaining clod volume after remaining layer of plastic (≈0.95)

9.5 Db_r = [WODC – RF – ODPC – TAG] / {[(CC4 – WARW) / WD] – (RF / PD) – (MPC2 / 1.3)}

Db_r = Bulk density in g/cm^3 <2-mm fabric at 33-kPa tension after re-wetting

CC4 = Weight of clod after twelve plastic coats

WARW = Weight in water of coated clod equilibrated at 33-kPa tension after rewetting

9.6 Db_{od} = [WODC – RF– ODPC – TAG] / {[(WODC – WODCW) / WD] – (RF / PD) – (MPC2 / 1.3)}

Db_{od} = Bulk density in g cm^{-3} of <2-mm fabric at oven dryness

WODCW = Weight in water of oven-dry coated clod

9.7 W_{33} = {[(CC3 – MPC1) – (WODC – ODPC)] / (WODC – RF – ODPC – TAG)} x 100

W_{33} = Percent water weight retained at 33-kPa tension

9.8 W_r ={[(CC4 – MPC2) – (WODC – ODPC)] / [WODC – RF – ODPC – TAG]} x 100

W_r = Percent water weight retained at 33-kPa tension after rewet

9.9 Gypsum bearing soils are a special case because gypsum ($CaSO_4 \cdot 2H_2O$) loses most of its chemically combined water (crystal water) at 105 °C (Nelson et al., 1978). Gypsum content of the soil is determined in method 4E2a1a1.

9.10 For gypsum bearing soils, properties that are reported on an oven-dry weight basis, such as 1,500-kPa water content, are converted to include the weight of crystal water in gypsum. The 1,500-kPa water content is corrected when the gypsum content of the soil is >1%.

9.11 Bulk density is reported to the nearest 0.01 g/cm^3.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Blake, G.R., and K.H. Hartge. 1986. Bulk density. p. 383–382. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

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Bulk Density (3B)
Reconstituted (3B2)
33-kPa Desorption (Db33) (3B2a)
Oven-Dry (Db_{od}) (3B2b)

1. Introduction to Reconstituted Clods and 1/3 Bar Desorption

The reconstituted bulk density provides a single, reproducible value for horizons that are subject to tillage or other mechanical disturbances followed by an extreme water-state cycle (Reinsch and Grossman, 1995).

2. Scope and Field of Application

Bulk density is used to convert data from a weight basis to a volume basis, determine the coefficient of linear extensibility, estimate saturated hydraulic conductivity, and identify compacted horizons.

3. Principle

The <2-mm sample is formed into a clod by cycles of wetting and desiccation that simulate reconsolidation by water in a field setting. Plastic lacquer is applied in the laboratory to form an impermeable coat on the clod. The clod is desorbed to 33 kPa. After equilibration, the clod is weighed in air to measure the mass and in water to measure the volume. After the clod is oven dried at 110 °C, its mass and volume are determined again (Brasher et al., 1966; Blake and Hartge, 1986; Grossman and Reinsch, 2002).

3.1 Interferences

Some samples disintegrate when they are removed from the cells.

Material may be lost during the initial dip in 1:4 saran. Spritz the manufactured clod with water to keep sample intact.

4. Apparatus

4.1 Electronic balance, ±0.01-g sensitivity

4.2 Pressure-plate extractor with porous ceramic plate

4.3 Air pressure source, 33-kPa

4.4 Clod forming cylinder. The KSSL constructs the cell by attaching a brass ring or schedule 20 or 40 PVC pipe that is 5.4-cm diameter and 6 to 7 cm high to a 100-kPa ceramic plate. The ring or pipe is attached with waterproof glue and caulk.

4.5 Anti-sorting wires. To reduce natural sorting caused by placing the sample in the cell, the KSSL uses a device created by attaching a perpendicular wire to the center of a 5.2-cm diameter wire screen with 0.5-cm openings.

4.6 Wire. The KSSL uses 28-awg coated copper wire.

4.7 Hairnets

4.8 Stock tags, 1-inch diameter paper tag with metal rim

4.9 Hook assembly for suspending clod below balance

4.10 Plexiglass water tank

4.11 Lift apparatus, powered by compressed air. (The KSSL can be contacted for more information.)

4.12 Oven, 110 °C

4.13 Plastic tub at least 10 cm deep

4.14 Paper discs cut from water-insoluble, permeable paper

4.15 Tile saw with diamond-edged blade

4.16 Desiccator with ceramic plate

4.17 Vacuum, 80-kPa (0.8-bar)

4.18 Metal probe or pottery needle tool

4.19 Spray bottle

4.20 Reinforced paper towels or cheesecloth

4.21 Tension table. The KSSL constructs a tension table by placing porous firebricks, covered with reinforced paper towels, in a tub of water.

5. Chemicals

5.1 Acetone (CH_3COCH_3) (CAS# 67-64-1)

5.2 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.3 Ethanol (CH_3CH_2OH) (CAS# 64-17-5), 95%, U.S.P.

5.4 Saran, polyvinyl dichloride (PVDC) resin. (The KSSL can be contacted for more information.)

5.5 Saran plastic lacquer

Components: Acetone (CH_3COCH_3), saran resin

Saran is prepared in two resin-to-solvent ratios: 1:4 and 1:7 (on a weight basis). Use the 1:4 plastic lacquer for the initial field and laboratory coatings. Use the 1:7 plastic lacquer for the last two laboratory coatings.

5.5.1 For a 1:4 ratio saran: To a 3.8-L (1-gal) metal paint can, add the following in order:

- 2,700 ±200 mL of acetone (fill to the bottom of handle rivet)
- 540 g saran resin

- For field preparation, stir solvent with a wooden stick or spoon while adding resin.
- For lab preparation, stir solvent with a non-sparking, high speed stirrer while adding resin.

- Stir plastic lacquer for 15 min at ≈25 °C.
- Store plastic lacquer in covered plastic or steel containers.

5.5.2 For a 1:7 ratio saran: To a 3.8-L (1-gal) metal paint can, add the following in order:

  - 2,700 ±200 mL of acetone (fill to the bottom of handle rivet)
  - 305 g of saran resin

- For field preparation, stir solvent with a wooden stick or spoon while adding resin.
- For lab preparation, stir solvent with a non-sparking, high speed stirrer while adding resin.
- Stir plastic lacquer for 15 min at ≈25 °C.
- Store plastic lacquer in covered plastic or steel containers.
- Note: The only situation in which the 1:7 saran ratio should be used in the field is for samples with low porosity and permeability.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Acetone is highly flammable. Do not use near open flame or electrical equipment. Avoid inhalation or physical contact. Use with adequate ventilation. In closed buildings, use a fume hood. Keep in tightly closed containers. Review acetone safety data sheets for safe handling practices.

Saran F-310 resin decomposes rapidly at temperatures >200 °C, releasing hydrogen chloride gas.

Avoid contact with Fe, Zn, Cu, and Al in solution. Avoid all contact with strong bases.

7. Sample Preparation

7.1 The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

7.2 Drape a hairnet in the manufactured clod cell. Place a paper disc in the bottom of the cell. Place the anti-sorting screen into the cell. Add <2-mm, prepared sample to within a few mm of the top of the cell. Lift the anti-sorting screen from the cell.

7.3 Place the cell on a tension table with the top of the cell 5-cm below the top

of the table. After equilibration, place the cell into a tub and add water to a level higher than the surface of the soil in the cell but below the top lip of the cell. This allows the soil to become inundated from beneath. Allow the sample to equilibrate.

7.4 Remove the cell from the tub and allow to dry at room temperature. After the clod has dried, remove the clod from the cell by knotting the edges of the hairnet together. Using the knot, gently pull the clod from the cell. If the soil is well consolidated, invert the cell lightly and tamp the base of the cell to dislodge the clod from the cell.

8. Procedure

8.1 Prepare a round stock tag with sample identification number. Cut the copper wire to loop around the clod. Record the weight of the tag and wire (typically ≈1.5 g). Loop fine copper wire around the clod, leaving a tail to which the round stock tag is attached. Record the weight of the clod (CC1).

8.2 Mist the clod with water to create a film of water on the surface of the clod.

8.3 Dip clod to preserve moisture content:

- **8.3.1** Dip clod in 1:4 plastic lacquer.
- **8.3.2** Wait 7 min and then dip clod in 1:7 saran.
- **8.3.3** Wait 12 min and then dip clod in 1:7 saran.
- **8.3.4** Wait 55 min and then reweigh clod.
- **8.3.5** If the clod has adsorbed >3% in plastic by clod weight or smells excessively of solvent, allow longer drying time and then reweigh clod and record weight (CC2).

8.4 Using a lapidary saw or tile saw and a diamond-edged saw blade, cut a flat surface on the clod, removing about 20% of the clod. Place the cut surface of the clod on a tension table maintained at 5-cm tension. Periodically check clod to determine if it has reached equilibrium. Determination can be made by inserting metal probe or pottery needle to measure equal resistance and comparing saturated weight to initial weight. When the clod has reached equilibrium, remove the clod and record the weight (WSC).

8.5 If the clod does not adsorb water, place the clod in a desiccator that has water covering the desiccator plate. Add a few mL of alcohol. Apply suction using in-house vacuum for 24 h. Remove the clod and record the weight (WSC).

8.6 Place the clod in a pressure-plate extractor. To provide good contact between the clod and ceramic plate, cover the ceramic plate with a paper towel and saturate with water. Place the cut surface of the clod on the paper towel. Close the container and secure the lid. Apply gauged air pressure of 33 kPa. When water stops discharging from the outflow tube (usually after 2 or 3 weeks in the extractor), the clod is at equilibrium. Remove the clod and record the weight (WMC). Compare WMC to WSC.

If WMC is greater than or equal to WSC, equilibrate the clod on the tension table and repeat the desorption process.

8.7 Dip clod to preserve moisture content:

8.7.1 Dip clod in 1:4 plastic lacquer.

8.7.2 Wait 7 min and then dip clod in 1:7 saran.

8.7.3 Wait 12 min and then dip clod in 1:7 saran.

8.7.4 Wait 55 min and then reweigh clod.

8.7.5 If the clod has adsorbed >3% in plastic by clod weight or smells excessively of solvent, allow longer drying time and then reweigh clod and record weight (CC3).

8.8 The clod should be waterproof and ready for volume measurement by water displacement.

8.8.1 Suspend clod below the balance and collect a 33-kPa dipped air weight.

8.8.2 Submerge suspended clod in water and record weight (WMCW).

8.8.3 Clods with compromised saran coatings or areas of porosity begin taking on water immediately.

8.8.4 Use caution that buoyant clods do not become detached from the balance suspension hook.

8.9 Dry clod in an oven at 110 °C until weight is constant; collect oven-dry weights.

8.9.1 Suspend clod below the balance.

8.9.2 Collect an oven-dry air weight (WODC).

8.9.3 Submerge suspended clod in water (WODCW) and record weight.

8.9.4 Collect a weight as soon as whole clod is submerged; clods begin taking on water immediately.

8.9.5 Use caution that buoyant clods do not become detached from the balance suspension hook.

8.10 Correct bulk density for weight and volume of the plastic coating. The coating has an air-dry density of about 1.3 g/cm^{-3}. The coating loses 10 to 20 percent of its air-dry weight on oven drying at 110 °C.

9. Calculations

9.1 $MPC1 = \{[(CC2 - CC1)] \times RV\} + (CC3 - WMC)$

MPC1 = Weight of plastic coat before oven drying

CC2 = Weight of clod after four laboratory saran dips

CC1 = Weight of clod before four laboratory saran dips

RV = Percent estimate of remaining clod volume after cutting to obtain flat surface (≈95%)

WMC = Weight of coated clod equilibrated at 33-kPa tension

9.2 Db_{33} = [WODC – RF – ODPC – TAG] / {[(CC2 – WMCW) / WD] – (RF / PD) – (MPC1 / 1.3)}

Db_{33} = Bulk density in grams per cubic centimeter of <2-mm fabric at 33-kPa tension

WODC = Weight of oven-dry coated clod

ODPC = MPC x 0.85, weight of oven-dry plastic coat

TAG = Weight of tag and wire (typically ≈1.5 g)

CC3 = Weight of equilibrated clod after four additional saran dips

WMCW = Weight of coated clod equilibrated at 33-kPa tension in water

MPC1 = Weight of plastic coat before oven drying

WD = Water density

9.3 Db_{od} = [WODC – ODPC – TAG] / {[(WODC – WODCW) / WD] – (MPC1 / 1.3)}

Db_{od} = Bulk density in grams per cubic centimeter of <2-mm fabric at oven-dryness

WODCW = Weight of oven-dry coated clod in water

WODC = Weight of oven-dry coated clod

ODPC = MPC x 0.85, weight of oven-dry plastic coat

TAG = Weight of tag and wire (typically ≈1.5 g)

WD = Water density

9.4 W_{33} = {[(CC3 – MPC1) – (WODC – ODPC)] / [WODC – ODPC – TAG)]} x 100

W_{33} = Weight percentage of water retained at 33-kPa tension

CC3 = Weight of equilibrated clod after four additional saran dips

MPC1 = Weight of plastic coat before oven drying

WODC = Weight of oven-dry coated clod

ODPC = MPC x 0.85, weight of oven-dry plastic coat

TAG = Weight of tag and wire (typically ≈1.5 g)

9.5 Gypsum bearing soils are a special case because gypsum ($CaSO_4 \cdot 2H_2O$) loses most of its chemically combined water (crystal water) at 105 °C (Nelson et al., 1978). Gypsum content of the soil is determined in method 4E2a1a1.

9.6 For gypsum bearing soils, properties that are reported on an oven-dry weight basis, such as 1,500-kPa water content, are converted to include the weight of crystal water in gypsum. The 1,500-kPa water content is corrected when the gypsum content of the soil is >1%.

9.7 Bulk density is reported to the nearest 0.01 g/cm^3.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

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Bulk Density (3B)
Compliant Cavity (3B3)
Field-State (3B3a)

1. Introduction to Compliant Cavity

This method is applicable to layers that can be described as cohesionless, that have a high content of rock fragments >5 mm, or are thin (<5 cm thick) and for which the clod method is unsuitable (Grossman and Reinsch, 2002). The compliant cavity method was designed for fragile, cultivated, near-surface layers and O horizons of forestland soils. This method has the important advantage that it is not necessary to flatten the ground surface on steep slopes or to remove irregularities; i.e., the surficial zone is usually not altered.

2. Scope and Field of Application

Bulk density is used to convert data from a weight basis to a volume basis, determine the coefficient of linear extensibility, identify compacted horizons, and estimate saturated hydraulic conductivity. Compliant cavity is outlined in detail in the video “How to Sample Bulk Density in the Field” (https://youtu.be/E7BSZrJ-TDw).

3. Principle

The cavity volume on the zone surface is lined with thin plastic, water is added to a datum level and a measurement is recorded. Soil within the ring is excavated to a determined depth and bagged. Water is again added to the lined ring and recorded. The difference between the initial volume and that after excavation is the sample volume.

Collect three cavity samples from each site. At the laboratory, the excavated soil is dried in an oven and then weighed. A correction is made for the weight and volume of rock fragments.

3.1 Interferences

Bulk density by the compliant cavity method can be made on soils with rock fragments but is more complex than other methods (Grossman and Reinsch, 2002).

4. Apparatus

4.1 Fabricated plexiglass rings, 9-mm thick, 130-mm inside diameter, and ≥200-mm outside diameter.

4.1.1 Make three 16-mm diameter holes that are 10 mm from the outer edge of ring.

4.1.2 Position holes equidistant apart.

4.1.3 Use three, 25 x 50 mm, plexiglass pieces as guides. Attach two pieces on one side to form an “L.” Allow a 15-mm gap to permit removal of soil material.

4.1.4 On the other side, position the single piece in line with the longer leg of the “L” so that an adjacent, parallel line forms a diameter (fig. 3B3a–1).

4.2 Make 50-mm thick foam rings from flexible polyurethane with an “Initial Load Displacement” of 15 to 18 kg. The foam rings have the same inside diameter as the plexiglass rings.

4.3 Fabricated 240-mm crossbar: 5 x 18 mm metal stock (fig. 3B3a–2)

4.3.1 Weld legs 25 mm high and 180 x 180 mm in cross section to metal stock

Figure 3B3a–1.—Plexiglass ring assembly.

Figure 3B3a–2.—Hook gauge and crossbar assembly with liner.

4.3.2 Drill a hole 100 mm from one end of the crossbar and 7 mm from the edge

4.3.3 Insert no. 6 machine bolt through drilled holes.

4.3.4 Mount hook gauge on crossbar. Make hook gauge from no. 6, round-headed, 100-mm long machine bolts with hexagonal nuts.

4.3.5 Obtain the machine bolts from toggle bolt assemblies.

4.3.6 Sharpen the machine bolt to a sharp point.

4.3.7 Drill a hole in the center of the crossbar. Place machine bolt through hole.

4.3.8 Place nuts above and below the crossbar. The two nuts adjust the hook length below the crossbar and provide rigidity. Hold the machine bolt by the tightened nuts and heat the bolt.

4.3.9 After softening, sharply bend the bolt upward to form a U-shape.

4.3.10 Use wing nuts and three threaded rods (250- to 400-mm long and 10- to 13-mm diameter) to mount and position the compliant cavity ring. Sharpen the rods. Place two regular nuts at the end of threaded rod to increase the area of surface struck.

4.4 Syringe, 60-mL

4.5 Plastic film, ½-mil, 380-mm wide or wider; 460-mm wide for larger ring

4.6 Plastic bags, 110 °C capability, with ties

4.7 Fine-point permanent marker

4.8 Graduate cylinders, plastic, 500-mL and 1,000-mL

4.9 Level, small

4.10 Kitchen knife, small

4.11 Scissors, small, to cut fine roots

4.12 Hack saw blade to cut large roots

4.13 Weights for plastic film

4.14 Clothespins. If conditions are windy, use the clothespins for corners of plastic film.

4.15 Hard rubber or plastic mallet

4.16 Sieve, square-hole, 10-mesh, 2-mm

5. Chemicals

5.1 Tap water

6. Health and Safety

Follow standard field and laboratory safety precautions.

7. Sample Preparation

No preparation is required. Sample is retained during excavation.

8. Procedure

8.1 Place a ring of plastic foam on ground and cover with rigid ring (130-mm inside diameter). Place threaded rods with wing nuts through rigid ring holes and drive rods into the ground. Tighten ring with wing nuts.

8.2 Place hook gauge across the top of the rigid ring. Note the orientation of the hook gauge; the gauge will need to be placed in the same orientation after the sample has been collected.

8.3 Line cavity with ½-mil plastic, make sure plastic isn't pulled or tenting. Fill one cylinder with 500 mL of water. Fill the cavity to tip of hook gauge. Measure the amount of water in the cavity by noting how much water remains in the cylinder.

8.4 Record the volume of water to tip of hook gauge. This volume (Vd) is the measurement of cavity volume prior to excavation (dead space).

8.5 Excavate soil to a determined depth (2"-3") and place in a labeled sample bag.

8.6 Line the excavated cavity with ½-mil plastic; ensure plastic isn't pulled or tenting. Place hook gauge in the same orientation from step 8.2. Fill a cylinder with 1,000 mL of water. Fill the excavation cavity to tip of hook gauge with water from graduated cylinder. Measure the volume of water. This volume (Vf) is the measurement of excavated soil and dead space.

8.7 The difference between the two water volumes (Vf – Vd) is the volume of excavated soil (Ve).

8.8 Collect three samples from each site.

8.9 The excavated soil is dried in an oven and weighed. If necessary, make a correction for weight and volume of >2-mm material (Vg).

8.10 For field-determination of rock fragments:

- **8.10.1** Record weight of rock fragments.
- **8.10.2** Place rock fragment in a graduated cylinder and measure displacement.

8.11 For laboratory-determination of rock fragments:

- **8.11.1** Using a roller, disaggregate the soil from the rock fragments.
- **8.11.2** Pass sample through a 2-mm sieve.

8.12 Record weight and density of rock fragments >2 mm.

8.13 Record the weight of leaf litter, duff, or other macroscopic vegetal material (g cm^{-3}) for reference purposes. This weight is not used in calculations.

9. Calculations

9.1 $Ve = Vf - Vd - Vg$

Ve = Excavation volume of <2-mm fraction (cc)

Vf = Water volume measurement of excavated soil and dead space (cc)

Vd = Water volume measurement of dead space (cc)

Vg = Gravel volume (>2-mm fraction) (cc). Calculate Vg by dividing the weight of >2-mm fraction by particle density of the >2-mm fraction. Default value is 2.65 g cc^{-1}.

9.2 Wf = Wo – Wc

Wf = Oven-dry weight of <2-mm soil (g)

Wo = Oven-dry weight of excavated soil (g)

Wc = Oven-dry weight of rock fragments (g)

9.3 Db = Wf / Ve

Db = Bulk density (g cc^{-1})

Wf = Oven-dry weight of <2-mm soil (g)

Ve = Excavation volume of <2-mm material (cc)

9.4 Bulk density is reported to the nearest 0.01 g/cm^3.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Grossman, R.B., and T.G. Reinsch. 2002. Bulk density and linear extensibility. p. 201–228. *In* J.H. Dane and G.C. Topp (eds.) Methods of soil analysis, Part 4. Physical methods. Soil Sci. Am. Book Series No. 5. ASA and SSSA, Madison, WI.

Bulk Density (3B)
Ring Excavation (3B4)
Field-State (3B4a)

1. Introduction to Ring Excavation

The ring excavation method is robust, simple, rapid, and applicable to layers that can be described as cohesionless, that have a high content of rock fragments >5 mm, or are thin (<5 cm thick) and for which the clod method is unsuitable (Grossman and Reinsch, 2002). This method is good for O horizons in the woods where local variability is large. The diameter can range from 15 cm to 30 cm or more.

2. Scope and Field of Application

Bulk density is used to convert data from a weight basis to a volume basis, determine the coefficient of linear extensibility, estimate saturated hydraulic conductivity, and identify compacted horizons.

3. Principle

A 20-cm ring is inserted into the ground. A piece of shelf standard is placed across the ring near to a diameter. The distance to the ground surface is measured at eight points equally spaced along the diameter using the depth-measurement tool. The piece of shelf is rotated 90°, and eight more measurements are made. The 16 measurements are then averaged.

The soil is excavated to the desired depth. It is not necessary to excavate from the whole area within the ring. A limit of 2 cm on the minimum thickness of the sample should be considered. The distance measurements are repeated and the change in distance is calculated on the removal of the soil. This change in distance is then multiplied by the inside cross-sectional area of the ring to obtain the volume of soil.

The excavated soil is oven-dried and weighed. If rock fragments are present, the weight and volume of >2-mm material in the sample are corrected and bulk density is computed. Bulk density of soil is reported in g/cm^3.

3.1 Interferences

Rock fragments may make insertion of ring into the ground impossible.

4. Apparatus

4.1 Metallic cylinder, 20-cm diameter, 10- to 20-cm high, and about 1-mm deep

4.2 Shelf standard (slotted rod), 1.5-cm wide, 1-cm high, and 25-cm long

4.3 Piece of retractable ruler, 30-cm long with 0.1-mm divisions

4.4 Piece of wood, 10 x 10 x 30 cm

4.5 Hand digging equipment

4.6 Depth-measurement tool (Grossman and Reinsch, 2002; the KSSL can be contacted for more information.)

5. Chemicals

No chemicals are needed.

6. Health and Safety

Follow standard field and laboratory safety precautions.

7. Sample Preparation

No preparation is required. Sample is retained during excavation.

8. Procedure

8.1 Insert a 20-cm diameter ring below the depth of excavation.

8.2 Place a piece of shelf standard across the ring near to or along a diameter. Measure the distance to the ground surface at eight points equally spaced along the diameter using the depth-measurement tool.

8.3 Rotate the piece of shelf standard 90° and make eight more measurements. Average the 16 measurements.

8.4 Excavate soil to a determined depth and place in a labeled sample bag. Repeat the distance measurements.

8.5 Calculate the change in distance on removal of the soil. Multiply the change in distance by the inside cross-sectional area of the ring to obtain the volume of the soil (Ve).

8.6 The excavated soil is dried in an oven and weighed. If necessary, make a correction for weight and volume of >2-mm material (Vg).

8.7 For field-determination of rock fragments:

- **8.7.1** Record weight of rock fragments.
- **8.7.2** Place rock fragments in a graduated cylinder and measure displacement.

8.8 For laboratory-determination of rock fragments:

- **8.8.1** Using a roller, disaggregate the soil from the rock fragments.
- **8.8.2** Pass sample through a 2-mm sieve.
- **8.8.3** Record weight and density of rock fragments >2 mm.
- **8.8.4** Record the weight of leaf litter, duff, or other macroscopic vegetal material (g cm^{-3}) for reference purposes. This weight is not used in calculations.

9. Calculations

9.1 Wf = Wo – We

Wf = Oven-dry weight of <2-mm soil (g)

Wo = Oven-dry weight of excavated soil (g)

Wc = Oven-dry weight of rock fragments (g)

9.2 Db = Wf / Ve

Db = Bulk density (g cm^{-3})

Wf = Oven-dry weight of <2-mm soil (g)

Ve = Excavation volume of <2-mm material (cm^{-3})

9.3 Bulk density is reported to the nearest 0.01 g cm^{-3}.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Grossman, R.B., and T.G. Reinsch. 2002. Bulk density and linear extensibility. p. 201–228. *In* J.H. Dane and G.C. Topp (eds.) Methods of soil analysis, Part 4. Physical methods. Soil Sci. Am. Book Series No. 5. ASA and SSSA, Madison, WI.

Bulk Density (3B)
Frame Excavation (3B5)
Field-State (3B5a)

1. Introduction to Frame Excavation

Frame excavation is applicable to layers that can be described as cohesionless, that have a high content of rock fragments >5 mm, or are thin (<5 cm thick) and for which the clod method is unsuitable (Grossman and Reinsch, 2002).

2. Scope and Field of Application

Frame excavation is good for O horizons in the woods where local variability is large and rock fragments are commonly present. The size of 0.1 m^2 is sufficient to account for considerable local variability.

3. Principle

The frame is assembled and secured onto the soil surface; plastic is placed over the frame and secured. The depth-measurement tool is placed on top of a slot to measure the distance to the soil surface. The slots are traversed, and measurements of the distance to the ground surface are made at about 40 regularly spaced intervals. The plate is then removed, and soil is excavated and retained. Measurements of the distance to the ground surface are repeated. The volume of soil is determined by taking the difference in height and multiplying by 1,000 cm^2. Rock fragments up to 20 mm are included in the sample. Excavated soil is oven-dried and weighed. Bulk density of soil is reported in g cm^{-3}.

3.1 Interferences

None.

4. Apparatus

4.1 Trowel, shovel or scoop for sample collection

4.2 Wood frame with 0.1 m^2 inside area. Frame is made from 8 pieces of lumber.

- 4 blocks, 4 x 5 x 9 cm
- Parts A: Two sections, 2 x 4 x 53 cm with wooden blocks attached
- Parts B: Two sections 2 x 4 x 46 cm that fasten to Parts A by half lap joints set 5 cm from the end
- Parts C: Threaded rods, 50 cm x 0.6 cm diameter that run through holes in 53-cm lengths
- Parts D: Depth measurement tool (Grossman and Reinsch, 2002; the KSSL can be contacted for more information.)

4.2.1 Attach the 9 cm side of a 4 x 5 x 9 cm block to each end of both 53-cm long pieces.

4.2.2 Make two 1-cm wide cuts half-way across each of the 46- and 53-cm long pieces to provide half-lap joints. The cuts are 5 cm in for the 46-cm long pieces.

4.2.3 Drill 1.0–1.5 cm diameter holes in the center of the attached blocks.

4.2.4 Join the four pieces by the vertical half-lap joints to form a square frame. (Grossman and Reinsch, 2002; the KSSL can be contacted for more information.)

4.3 Square plexiglass, 35 cm on edge x 0.6 cm thick, with 5 parallel equally spaced slots, 1.5 cm across x 28 cm long

4.4 Four threaded rods, 50 cm long x 0.6 cm diameter, with wing nuts

4.5 Depth-measurement tool

5. Chemicals

None.

6. Health and Safety

Follow standard field and laboratory safety precautions.

7. Sample Preparation

No preparation is required. Sample is retained during excavation.

8. Procedure

8.1 Assemble the square wooden frame.

8.2 Place the frame on the ground surface. Push the four threaded rods through the holes in the corners of the frame deep. Push far enough to hold the frame in place without shifting. Secure onto the soil surface by screwing down wing nuts.

8.3 Place the plastic plate over the frame and secure.

8.4 Place the depth-measurement tool on top of a slot and measure the distance to the soil surface.

8.5 Traverse the slots, making measurements of the distance to the ground surface at about 40 regularly spaced intervals. Remove the plate.

8.6 Excavate soil to a determined depth and place in a labeled sample bag. The walls of the cavity should be vertical and coincident with the edge of the frame.

8.7 Repeat the measurements of the distance to the ground surface. Determine the difference in height and multiply by 1,000 cm^2 to obtain the volume of soil excavated. Usually, rock fragments up to 20 mm are included in the sample.

8.8 Dry the excavated soil in an oven and weigh. If necessary, make a correction for weight and volume of >2-mm material in sample and computed bulk density.

8.9 For field-determination of rock fragments:

8.9.1 Record weight of rock fragments.

8.9.2 Place rock fragment in a graduated cylinder and measure displacement.

8.10 For laboratory-determination of rock fragments:

8.10.1 Using a roller, disaggregate the soil from the rock fragments.

8.10.2 Pass sample through a 2-mm sieve.

8.10.3 Record weight and density of rock fragments >2 mm.

8.10.4 Record the weight of leaf litter, duff, or other macroscopic vegetal material (g cm^{-3}) for reference purposes. This weight is not used in calculations.

9. Calculations

9.1 Wf = Wo – We

Wf = Oven-dry weight of <2-mm soil (g)

Wo = Oven-dry weight of excavated soil (g)

We = Oven-dry weight of rock fragments (g)

9.2 Db = Wf / Ve

Db = Bulk density (g cm^{-3})

Wf = Oven-dry weight of <2-mm soil (g)

Ve = Excavation volume of <2-mm material (cm^{-3})

9.3 Bulk density is reported to the nearest 0.01 g cm^{-3}.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Grossman, R.B., and T.G. Reinsch. 2002. Bulk density and linear extensibility. p. 201–228. *In* J.H. Dane and G.C. Topp (eds.) Methods of soil analysis, Part 4. Physical methods. Soil Sci. Am. Book Series No. 5. ASA and SSSA, Madison, WI.

Bulk Density (3B)
Soil Cores (3B6)
Field-State (3B6a)

1. Introduction to Field-State Soil Cores

This method determines the bulk density value of a moist soil core of known volume. Bulk density is used to: convert data from a weight basis to a volume basis, determine the coefficient of linear extensibility, estimate saturated hydraulic conductivity, and identify compacted horizons

2. Scope and Field of Application

Field bulk density (Db_f) offers the opportunity to obtain relatively cheaply bulk density information without the expense incurred to obtain water retention. Db_f is particularly useful if the soil layers are at or above field capacity and/or the soils have low extensibility and do not exhibit desiccation cracks even if below field capacity.

3. Principle

A metal cylinder is pressed or driven into the soil. The cylinder is removed, extracting a sample of known volume. Samples are collected in triplicate. The moist sample weight is recorded. The sample is then dried in an oven and weighed. Reference the following tutorial for comprehensive instructions: “How to Sample Bulk Density in the Field” (https://youtu.be/E7BSZrJ-TDw).

3.1 Interferences

During coring process, compaction of the sample is a common problem. Compression can be observed by comparing the soil elevation inside the cylinder with the original soil surface outside the cylinder. If compression is excessive, soil core may not be a valid sample for analysis.

Rock fragments in the soil interfere with core collection.

Dry or hard soils often shatter when hammering the cylinder into the soil. Pressing the cylinder into the soil reduces the risk of shattering the sample.

If soil cracks are present, select the sampling area so that crack space is representative of sample, if possible. If this is not possible, make measurements between the cracks and determine the aerial percentage of total cracks or of cracks in specimen.

4. Apparatus

4.1 Containers, air-tight, tared, with lids

4.2 Electronic balance, ±0.01-g sensitivity

4.3 Oven 110 °C

4.4 Sieve, no. 10 (2-mm openings)

4.5 Coring equipment. Sources described in Grossman and Reinsch (2002).

5. Chemicals

None.

6. Health and Safety

Follow standard field and laboratory safety precautions.

7. Sample Preparation

No preparation is required. Sample is retained during excavation.

8. Procedure

8.1 Record the empty core weights (CW).

8.2 Prepare a flat surface, either horizontal or vertical, at the required depth in sampling pit.

8.3 Press or drive core sampler into soil. Use caution to prevent compaction. Remove core from the inner liner, trim protruding soil flush with ends of cylinder, and place in air-tight container for transport to laboratory. Collect three soil cores per layer. If soil is too loose to remain in the liner, use core sampler without the inner liner and deposit only the soil sample in air-tight container. Moisture cans may also be pushed directly into a prepared face. For fibrous organic materials, trim sample to fit snugly into a moisture can.

8.4 Dry core in an oven at 110 °C until weight is constant. Record oven-dry weight (ODW).

8.5 Measure and record cylinder volume (CV).

8.6 If sample contains rock fragments, wet-sieve sample through a 2-mm sieve. Dry and weigh the rock fragments that are retained on sieve. Record weight of rock fragments (RF). Determine density of rock fragments (PD).

9. Calculations

9.1 $Db = (ODW - RF - CW) / [CV - (RF / PD)]$

Db = Bulk density of <2-mm fabric at sampled, field-water state (g cm^{-3})

ODW = Oven-dry weight

RF = Weight of rock fragments

CW = Empty core weight

CV = Core volume

PD = Density of rock fragments

9.2 Gypsum bearing soils are a special case because gypsum ($CaSO_4 \cdot 2H_2O$) loses most of its chemically combined water (crystal water) at 105 °C (Nelson et al., 1978). Gypsum content of the soil is determined in method 4E2a1a1.

9.3 For gypsum bearing soils, properties that are reported on an oven-dry weight basis, such as 1,500-kPa water content, are converted to include the weight of crystal water in gypsum. The 1,500-kPa water content is corrected when the gypsum content of the soil is >1%.

9.4 Bulk density is reported to the nearest 0.01 g cm^{-3}.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Grossman, R.B., and T.G. Reinsch. 2002. Bulk density and linear extensibility. p. 201–228. *In* J.H. Dane and G.C. Topp (eds.) Methods of soil analysis, Part 4. Physical methods. Soil Sci. Am. Book Series No. 5. ASA and SSSA, Madison, WI.

Bulk Density (3B)
Field Cores (3B7)
Field-State (3B7a)

1. Introduction to Field-State Soil Cores

This method determines the bulk density value of a moist soil core of known volume. Field-state bulk density is effectively determined using the soil moisture content at the time of sampling. Field cores are samples that are taken using a known volume cylinder, removed from the cylinder, and transported as loose, bagged soil material. Bulk density is used to convert data from a weight basis to a volume basis, determine the coefficient of linear extensibility, estimate saturated hydraulic conductivity, identify compacted horizons, calculate other interpretations, and make other predictions.

2. Scope and Field of Application

Field bulk density (Db_f) offers the opportunity to obtain bulk density information relatively easily without the expense incurred to obtain water retention. Db_f is particularly useful if the soil layers are at or above field capacity and/or the soils have low extensibility and do not exhibit desiccation cracks even if below field capacity. Db_f does not account for variation in bulk density due to volume change caused by wetting and drying of expansive soils.

3. Principle

A metal cylinder is pressed or driven into the soil. The cylinder is removed, extracting a sample of known volume. The sample is removed from the cylinder and bagged. Samples are collected in triplicate. Samples are then dried in an oven and weighed. Reference the following tutorial for comprehensive instructions: “How to Sample Bulk Density in the Field” (https://youtu.be/E7BSZrJ-TDw).

3.1 Interferences

During coring process, compaction of the sample is a common problem. Compression can be observed by comparing the soil elevation inside the cylinder with the original soil surface outside the cylinder. If compression is excessive, the soil core may not be a valid sample for analysis.

Rock fragments in the soil interfere with core collection.

Dry or hard soils often shatter when hammering the cylinder into the soil. Pressing the cylinder into the soil reduces the risk of shattering the sample.

If soil cracks are present, select the sampling area so that crack space is representative of sample, if possible. If this is not possible, make measurements between the cracks and determine the aerial percentage of total cracks or of cracks in specimen.

4. Apparatus

4.1 Electronic balance, ±0.01-g sensitivity

4.2 Oven 110 °C

4.3 Sieve, no. 10 (2-mm openings)

4.4 Coring equipment. Sources described in Grossman and Reinsch (2002).

5. Chemicals

None.

6. Health and Safety

Follow standard field and laboratory safety precautions.

7. Sample Preparation

No preparation is required. Sample is retained during excavation.

8. Procedure

8.1 Prepare a flat surface, either horizontal or vertical, at the required depth in sampling pit.

8.2 Press or drive core sampler into soil. Use caution to prevent compaction. Trim protruding soil flush with ends of cylinder, remove soil from the cylinder and place in bags for transport to laboratory. Collect three soil cores per layer. Moisture cans can also be pushed directly into a prepared face. For fibrous organic materials, trim sample to fit snugly into a moisture can. Record the volume (CV) of the cores on the bags and on the Pedon Sample Submission Sheet.

8.3 In the lab, record weight of empty drying tray (TW).

8.4 Remove lose core sample from bag, place on empty drying tray. Dry the sample in an oven at 110 °C until weight is constant. Record oven-dry weight (ODW) of tray and sample.

8.5 If sample contains rock fragments, wet-sieve sample through a 2-mm sieve. Dry and weigh the rock fragments that are retained on sieve. Record weight of rock fragments (RF). Determine density of rock fragments (PD). If PD cannot be determined precisely, assume the density of rock fragments is 2.65 g/cm^3.

9. Calculations

9.1 $Db = (ODW - RF - TW) / [CV - (RF / PD)]$

Db = Bulk density of <2-mm fabric at sampled, field water state (g/cm^3)

ODW = Oven-dry weight

RF = Weight of rock fragments

TW = Weight of empty drying tray

CV = Core volume

PD = Density of rock fragments

9.2 Gypsum bearing soils are a special case because gypsum ($CaSO_4 \cdot 2H_2O$) loses most of its chemically combined water (crystal water) at 105 °C (Nelson et al., 1978). Gypsum content of the soil is determined in method 4E2a1a1.

9.3 For gypsum bearing soils, properties that are reported on an oven-dry weight basis, such as 1,500-kPa water content, are converted to include the weight of crystal water in gypsum. The 1,500-kPa water content is corrected when the gypsum content of the soil is >1%.

9.4 Report field-core field-moist bulk density as the average of the three replicate core samples after eliminating any values outside of acceptable range of variability. Bulk density is reported to the nearest 0.01 g cm^{-3}.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Grossman, R.B., and T.G. Reinsch. 2002. Bulk density and linear extensibility. p. 201–228. *In* J.H. Dane and G.C. Topp (eds.) Methods of soil analysis, Part 4. Physical methods. Soil Sci. Am. Book Series No. 5. ASA and SSSA, Madison, WI.

Water Retention (3C)

Water retention is defined as the soil water content at a given soil water suction. By varying the soil suction and recording the changes in soil water content, a water-retention function or curve is determined. This relationship is dependent on particle-size distribution, clay mineralogy, organic matter, and structure or physical arrangement of the particles and on hysteresis; i.e., whether the water is absorbing into or desorbing from the soil. The data collected in these procedures are from water desorption. Water retention or desorption curves are useful directly and indirectly as indicators of other soil behavior traits, such as drainage, aeration, infiltration, plant-available water, and rooting patterns (Topp et al., 1993).

Two desorption procedures are commonly used to measure water retention: suction or pressure. The KSSL uses the pressure method (U.S. Salinity Laboratory Staff, 1954) with either a pressure-plate or pressure-membrane extractor.

Pressure-Plate Extraction Methods

- **Methods 3C1a-e1** determine water retention at 6, 10, 33, 100, or 200 kPa, (0.06, 0.1, ⅓, 1, or 2 bar) for sieved, <2-mm, air-dry soil samples of non-swelling soils, loamy sand, certain sandy loams, or coarser soil textures.
- **Methods 3C1a-d2 and 3C1a-d3** are used to measure water retention of natural clods or cores that have been equilibrated at 6, 10, or 33 kPa.
- **Methods 3C1a-d2 and 3C1a-d3** are used in conjunction with the bulk density method 3B1b, 33-kPa desorption of saran coated clods.
- **Method 3C1c4** determines the water retention of a clod equilibrated at 33-kPa, air-dried, and re-equilibrated. The resulting data are called rewet water-retention data and are usually used in conjunction with the rewet bulk density data in method 3B1d to estimate changes in physical properties of a soil as it undergoes wetting and drying cycles.

Pressure-Membrane Extraction Methods

- **Method 3C2a1a** determines water retention at 1,500 kPa (15 bar) for <2-mm (sieved), air-dry soil samples.
- **Method 3C2a1b** is used to measure water retention at 1,500 kPa for <2-mm (sieved), field-moist soil samples.
- **Method 3C3** determines field water content at the time of sampling for cores, clods, or bulk samples.

References

Topp, G.C., Y.T. Galganov, B.C. Ball, and M.R. Carter. 1993. Soil water desorption curves. p. 569–579. *In* M.R. Carter (ed.) Soil sampling and methods of analysis. Can. Soc. Soil Sci., CRC Press, Boca Raton, FL.

U.S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. L.A. Richards (ed.). USDA Agric. Handbook 60. U.S. Govt. Print. Office, Washington, DC.

Water Retention (3C)

Pressure-Plate Extraction (3C1)

6, 10, 33, 100, or 200 kPa (3C1a-e)

<2-mm (Sieved), Air-Dry (3C1a-e1a)

1. Introduction to Pressure Plate Extraction

Factors that influence soil moisture retention include texture and composition (percent of organic matter, silt, clay, etc.). Saturating soil samples and placing them under different tensions desorbs soils to a specific point. The compilation of desorbed tensions are used to create moisture curves.

2. Scope and Field of Application

The KSSL uses the pressure desorption method (U.S. Salinity Laboratory Staff, 1954). Ceramic, high-flow pressure-plate extraction is used to determine water retention at 6, 10, 33, 100, or 200 kPa for <2-mm (sieved), air-dry soil samples of non-swelling soils, loamy sand or coarser soil, and for some sandy loams. The data collected are used for water-retention function, water-holding capacity, porosity, and pore-size distribution; to calculate unsaturated hydraulic conductivity; and to determine saturated conductivity of a soil sample at specific water contents.

3. Principle

A sample of <2-mm (sieved), air-dry soil is placed in a retainer ring on a porous ceramic plate in a pressure-plate extractor. The plate is covered with water to wet the samples by capillarity. The sample is equilibrated at the specified pressures. The pressure is kept constant until equilibrium is obtained (Klute, 1986). The gravimetric water content is determined.

3.1 Interferences

A leak in the pressure extractor prevents equilibration of samples.

Monitor the pressure for stability.

Equilibration must be done at constant temperature and humidity.

Ceramic plates can become clogged, restricting water outflow. Clean the porous ceramic plates by flushing sequentially with 500 mL of 10% H_2O_2, 1,000 mL of 1 *N* HCl, and 500 mL of reverse osmosis (RO) water. The solutions are pulled through the plate with a vacuum, and the waste is captured in a trap.

Check the rubber membrane on the bottom of the plate for leaks. Inflate the membrane and then submerge it in water. If air bubbles escape from the membrane, remove the plate from service.

Laboratory-determined water retention data are usually higher than field-determined water retention data because the confining soil pressure is not present

in the laboratory (Bruce and Luxmoore, 1986). Water retention data for soils with expansive clay are overestimated when sieved samples are used in place of natural soil fabric for tensions of 6, 10, and 33 kPa, respectively (Young and Dixon, 1966).

Distilled or deionized water can possibly promote dispersion of clays in samples, and freshly drawn tap water is often supersaturated with air, affecting the water content at a given pressure head (Dane and Hopmans, 2002).

4. Apparatus

4.1 Pressure-plate extractor

4.2 Ceramic pressure plates, high flow. Use appropriate pressure rating.

4.3 Electronic balance, ±0.01-g sensitivity

4.4 Oven, 110 °C

4.5 Pressure source, regulator, and gauge

4.6 Retainer rings, 10-mm high and 50-mm diameter

4.7 Metal weighing cans with lids

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Ethanol (CH_3CH_2OH) (CAS# 64-17-5), 95%, U.S.P.

5.3 Hydrogen peroxide (H_2O_2) (CAS# 7722-84-1), 30% technical grade

5.4 Hydrochloric acid (HCl) (CAS# 7647-01-0), concentrated 12 *N*

5.5 Hydrogen peroxide solution, 10%

Components: Hydrogen peroxide (H_2O_2), RO water

- To a 2-L polyethylene bottle, add the following in order:
  - 1 L of RO water
  - 333 mL of 30% H_2O_2
- Invert to mix.

5.6 Hydrochloric acid solution, 1 *N*

Components: Hydrochloric acid (HCl), RO water

- To a 2-L polyethylene bottle, add the following in order:
  - 1 L of RO water
  - 83.3 mL of concentrated HCl
- Invert to mix.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

High-pressure air lines and moisture traps must be maintained in good working order.

Ensure that the bolts are tightened before applying pressure.

Ensure that the pressure is zero before removing bolts from the pressure extractor lid.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Saturate the ceramic plate by applying RO water to the surface of the plate until water is no longer absorbed into the plate.

8.2 Place the saturated ceramic plate in a pressure-plate extractor and attach discharge tubing to the extractor outlet. Place retainer rings on the ceramic plate.

8.3 Fill retaining ring with 10 to 15 g of <2-mm or fine-grind, air-dry soil. Include a quality control (QC) sample in each pressure-plate extractor.

8.4 Add enough water to cover the ceramic plate but the rings. Continue to add water until all samples have moistened by capillarity. If samples do not moisten, apply ethanol to the surface of the samples. Close the apparatus and let stand overnight.

8.5 Apply o-ring seal and fasten sides of pressure plate extractor. Apply the specified pressure. Monitor the outflow tube for water discharge; samples are equilibrated when water ceases to emit from the outflow tube. Submerge the outflow tube in a burette to determine if water is no longer being discharged. Periodically submerge the outflow tube in water to monitor for air bubbles that indicate ceramic plate failure.

8.6 When samples have equilibrated, quickly transfer the samples to tared water cans (Mc), cover with lids, and record the weights (Ms+w).

8.7 Remove lids, place samples in oven, and dry at 110 °C until weight is constant. Replace lids and record weights (Ms).

9. Calculations

9.1 $H_2O\% = 100 \times [(Ms+w-Ms)/(Ms-Mc)]$

$H_2O\%$ = Percent gravimetric water content

Ms+w = Weight of solids + H_2O + container

Ms = Weight of solids + container

Mc = Weight of container

9.2 Gypsum bearing soils are a special case because gypsum ($CaSO_4 \cdot 2H_2O$) loses most of its chemically combined water (crystal water) at 105 °C (Nelson et al., 1978). Gypsum content of the soil is determined in method 4E2a1a1.

9.3 For gypsum bearing soils, properties that are reported on an oven-dry weight basis, such as 1,500-kPa water content, are converted to include the weight of crystal water in gypsum. The 1,500-kPa water content is corrected when the gypsum content of the soil is >1%.

9.4 Report water content to the nearest 0.1 percent.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Bruce, R.R., and R.J. Luxmoore. 1986. Water retention: Field methods. p. 663–686. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Dane, J.H., and J. W. Hopmans. 2002. Water retention and storage: Laboratory. p. 675–720. *In* J.H. Dane and G.C. Topp (eds.) Methods of soil analysis. Part 4. Physical methods. Soil Sci. Am. Book Series No. 5. ASA and SSSA, Madison, WI.

Klute, A. 1986. Water retention: Laboratory methods. p. 635–662. *In* Klute, A. (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

U.S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. L.A. Richards (ed.). USDA Agric. Handbook 60. U.S. Govt. Print. Office, Washington, DC.

Young, K.K., and J.D. Dixon. 1966. Overestimation of water content at field capacity from sieved-sample data. Soil Sci. 101:104–107.

Water Retention (3C)
Pressure-Plate Extraction (3C1)
6, 10, 33, or 100 kPa (3C1a-d)
Natural Clods (3C1a-d2)

1. Introduction to Clod Pressure Plate Extraction

Clods represent an analog of in situ horizon conditions. They preserve features such as rocks, roots, and aggregates in the soil matrix. Saturating clods and placing them under different tensions will desorb soils to a specific moisture content based on the water holding capacity of the clod. The compilation of desorbed tensions can be used to create moisture curves.

2. Scope and Field of Application

The KSSL uses the pressure desorption method (U.S. Salinity Laboratory Staff, 1954). Ceramic, high-flow pressure-plate extraction is used to determine water retention at 6, 10, 33, 100, or 200 kPa. The data collected are used for water-retention function, water-holding capacity, porosity, and pore-size distribution; to calculate unsaturated hydraulic conductivity; and to determine saturated conductivity of a soil sample at specific water contents.

3. Principle

Natural clods are placed on a tension table and equilibrated at a 5-cm tension at the base of the sample. The clods are then transferred to a porous ceramic plate, which is placed in a pressure-plate extractor. The sample is equilibrated at the specified pressures. The pressure is kept constant until equilibrium is obtained (Klute, 1986). The gravimetric water content is determined.

3.1 Interferences

A leak in the pressure extractor prevents equilibration of samples. Check outflow air to verify that each pressure-plate extractor is functioning properly and does not leak.

Monitor the pressure for stability.

Equilibration must be done at constant temperature and humidity.

After extended use, the porous ceramic plate becomes clogged and water outflow is restricted. Clean the plate by flushing it sequentially with 500 mL of 10% H_2O_2, 1,000 mL of 1 *N* HCl, and 500 mL of RO water. The solutions are pulled through the plate with a vacuum, and the waste is captured in a trap.

Check the rubber membrane on the bottom of the plate for leaks. Inflate the membrane and then submerge it in water. If air bubbles escape from the membrane, remove the plate from service.

Laboratory-determined water retention data are usually higher than field-determined water retention data because the confining soil pressure is not present in the laboratory (Bruce and Luxmoore, 1986).

Distilled or deionized water can possibly promote dispersion of clays in samples, and freshly drawn tap water is often supersaturated with air, affecting the water content at a given pressure head (Dane and Hopmans, 2002).

4. Apparatus

4.1 Electronic balance, ±0.01-g sensitivity
4.2 Pressure-plate extractor with porous ceramic plate
4.3 Pressure source, regulator, and gauge
4.4 Oven, 110 °C
4.5 Clothespins
4.6 Knife
4.7 Tile saw with diamond-edged blade
4.8 Desiccator with ceramic plate
4.9 Vacuum, 80-kPa (0.8-bar)
4.10 Metal probe or pottery needle tool
4.11 Sieve, no. 10 (2-mm openings)
4.12 Hot plate
4.13 Fume hood
4.14 Reinforced paper towels with nylon fibers
4.15 Tension table. The KSSL constructs a tension table by placing porous firebricks, covered with reinforced paper towels, in a tub of water.
4.16 Stock tags, 25.4-mm (1 in) diameter paper tag, with metal rim
4.17 Wire. The KSSL uses 28-awg, coated copper wire.

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water
5.2 Ethanol (CH_3CH_2OH) (CAS# 64-17-5), 95%, U.S.P.
5.3 Acetone (CH_3COCH_3) (CAS# 67-64-1)
5.4 Hydrogen peroxide (H_2O_2) (CAS# 7722-84-1), 30% technical grade
5.5 Hydrochloric acid (HCl) (CAS# 7647-01-0), concentrated 12 *N*
5.6 Saran, polyvinyl dichloride (PVDC) resin. (The KSSL can be contacted for more information.)
5.7 Microbicide for tension table, commercially prepared and available
5.8 Hydrogen peroxide solution, 10%

Components: Hydrogen peroxide (H_2O_2), RO water

- To a 2-L polyethylene bottle, add the following in order:

- 1 L of RO water
- 333 mL of 30% H_2O_2

- Invert to mix.

5.9 Hydrochloric acid solution, 1 *N*

Components: Hydrochloric acid (HCl), RO water

- To a 2-L polyethylene bottle, add the following in order:
  - 1 L of RO water
  - 83.3 mL of concentrated HCl
- Invert to mix.

5.10 Saran plastic lacquer

Components: Acetone (CH_3COCH_3), saran resin

Saran is prepared in two resin-to-solvent ratios: 1:4 and 1:7 (on a weight basis). Use the 1:4 plastic lacquer for the initial field and laboratory coatings. Use the 1:7 plastic lacquer for the last two laboratory coatings.

5.10.1 For a 1:4 ratio saran: To a 3.8-L (1-gal) metal paint can, add the following in order:

- 2,700 ±200 mL of acetone (fill to the bottom of handle rivet)
- 540 g saran resin.

- For field preparation, stir solvent with a wooden stick or spoon while adding resin.
- For lab preparation, stir solvent with a non-sparking, high speed stirrer while adding resin.
- Stir plastic lacquer for 15 min at ≈25 °C.
- Store plastic lacquer in covered plastic or steel containers.

5.10.2 For a 1:7 ratio saran: To a 3.8-L (1-gal) metal paint can, add the following in order:

- 2,700 ±200 mL of acetone (fill to the bottom of handle rivet)
- 305 g of saran resin

- For field preparation, stir solvent with a wooden stick or spoon while adding resin.
- For lab preparation, stir solvent with a non-sparking, high speed stirrer while adding resin.
- Stir plastic lacquer for 15 min at ≈25 °C.
- Store plastic lacquer in covered plastic or steel containers.
- Note: The only situation in which the 1:7 saran ratio should be used in the field is for samples with low porosity and permeability.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Acetone is highly flammable. Do not use near open flame or electrical equipment. Avoid inhalation or physical contact. Use with adequate ventilation. In closed buildings, use a fume hood. Keep in tightly closed containers. Review acetone safety data sheets (SDS) for safe handling practices.

Saran F-310 resin decomposes rapidly at temperatures >200 °C, releasing hydrogen chloride gas.

Avoid contact with Fe, Zn, Cu, and Al in solution. Avoid all contact with strong bases.

High-pressure air lines and moisture traps must be maintained in good working order. Ensure that the pressure is zero before removing bolts from the pressure-apparatus lid. Ensure that the bolts are tightened before applying pressure.

7. Sample Preparation

Clods should represent a given horizon and be approximately the size of a fist or a potato (≈250 to 550 cm^3). They should be carefully preserved in saran, bagged, and boxed for shipment to the KSSL. Additional resources include method 1A1b (Field Sample Collection and Preparation) and the video tutorial "How to Sample Bulk Density in the Field" (https://youtu.be/E7BSZrJ-TDw).

Note: Friable clods commonly break apart during shipping and analysis. In such cases, this method does not return reportable data. For these sample types, the confined core cylinder method is more appropriate.

8. Procedure

8.1 This procedure is usually combined with method 3B1b (Bulk Density, 33-kPA Desorption (Db_{33})).

8.2 Prepare clod for dip in 1:4 saran. Label a round stock tag with sample identification number. Cut the copper wire and loop around the clod. Record weight of tag and wire (typically ≈1.5 g). Loop fine copper wire around clod, leaving a tail to which round stock tag is attached. Record weight of clod (CC1).

8.3 Dip clod to preserve moisture content:

- **8.3.1** Dip clod in 1:4 plastic lacquer.
- **8.3.2** Wait 7 min and then dip clod in 1:7 saran.
- **8.3.3** Wait 12 min and then dip clod in 1:7 saran.
- **8.3.4** Wait 55 min and then reweigh clod.

8.3.5 If the clod has adsorbed >3% in plastic by clod weight or smells excessively of solvent, allow longer drying time and then reweigh clod and record weight (CC2). The clod should be waterproof and ready for volume measurement by water displacement.

8.4 Using a lapidary saw or tile saw and a diamond-edged sawblade, cut a flat surface on the clod, removing about 20% of the clod. Select the orientation of the cut based on surface area, barriers to capillary rise, or areas of the clod that absorbed saran.

8.5 Place cut surface of clod on a tension table lined with paper towels maintained at 5-cm tension (fig. 3C1–1). Periodically check clod to determine if it has reached equilibrium. Determination can be made by inserting metal probe to measure equal resistance and comparing saturated weight to initial weight. When clod has reached equilibrium, remove clod and record weight (WSC).

Figure 3C1–1.—After a flat surface on the clod is cut with a diamond-edged saw blade, the clod is placed on a tension table, maintained at 5-cm tension.

8.6 If the cut area of the clod is hydrophobic, place clod in a desiccator on a water-covered plate with a 0-cm tension. Submerge only the surface of clod in the water. Add a few mL of ethanol. Use in-house vacuum and apply suction until clod has equilibrated at saturation.

8.7 Place the clod in a pressure-plate extractor (fig. 3C1–2). To provide good contact between clod and ceramic plate, cover the ceramic plate with a

Figure 3C1–2.—Clods in pressure-plate extractor following saturation.

paper towel and saturate with water. Place cut surface of clod on paper towel.

8.8 Prepare quality control (QC) sample by placing <2-mm sieved soil standard in water retention ring. Allow sufficient time for the sample to become saturated. Close the extractor and secure the lid.

8.9 Apply gauged air pressure of 6, 10, 33, or 100 kPa (fig. 3C1–3). If more than one water-retention point is requested, begin with the lowest pressure. Extraction usually takes 2 to 4 weeks. Samples are equilibrated when water ceases to emit from the outflow tube. Submerge the outflow tube in a burette to determine if water is no longer being discharged. Periodically submerge the outflow tube in water to monitor for air bubbles that indicate ceramic plate failure.

8.10 Determine the gravimetric water content of the QC sample.

8.10.1 If the water content of the QC is more than twice the standard deviation, apply pressure for additional time. Recheck the QC.

8.10.2 If the water content of the QC is less than twice the standard deviation, rewet the clods and desorb again.

8.10.3 If the water content of the QC is within acceptable limits, the apparatus has functioned properly and equilibrated clod weights should be collected.

8.11 Remove the clod and record the weight (WMC). Compare WMC to WSC. If WMC ≥ WSC, re-equilibrate the clod on the tension table and repeat the desorption process. If additional water-retention points are requested, then

Figure 3C1-3.—Pressure-plate extraction at 33 kPa for clods.

repeat the desorption process at the next higher pressure. When the clod is equilibrated at 33 kPa and bulk density is to be measured, continue with method 3B1b.

8.12 Dry the clod in an oven at 110 °C until weight is constant and record oven-dry weight (WODC).

8.13 If the clod contains >5%, by weight, rock fragments >2-mm—as determined by sample processing bulk sample fragment weights or particle-size data—remove the rock fragments from the clod. Submerge the remaining soil material in a beaker of water and place on a hot plate. Use a fume hood. Boil ≈1 h. The plastic coating loosens from soil material upon heating. Remove beaker from the hot plate. Allow to cool. Discard plastic coating.

8.14 Allow clod to stay in water until soil is fully saturated. Wet sieve the cool soil through a 2-mm sieve. Dry and record the weight (RF) of the rock fragments that are retained on the sieve.

8.15 Correct for rock fragments retained on sieve in clod data. Determine rock fragment density by pycnometer or weighing fragments in air to obtain their mass and in water to obtain their volume.

8.16 In specific circumstances, if rock fragments are light in density, abundant, and the analyst suspects the porosity of the fragments may contribute to water retention of the soil, do not correct clod mass and volume measurement for rock fragments.

8.17 Correct bulk density for weight and volume of plastic coating. The coating has an air-dry density of ≈1.3 g cm^{-3}. The coating loses 10 to 20% of its air-dry weight when dried in oven at 110 °C.

9. Calculations

9.1 $H_2O\% = [(WMC - MPC) - (WODC - ODPC) \times 100] / (WODC - RF - ODPC - TAG)$

$H_2O\%$ = Percent gravimetric water content

WMC = Weight of equilibrated, coated clod

WODC = Weight of oven-dry coated clod

RF = Weight of rock fragments

ODPC = MPC x 0.85, weight of oven-dry plastic coat

TAG = Weight of tag and wire (typically ≈1.5 g)

9.2 $MPC = \{[(CC2 - CC1) + FCE] \times RV\}$

MPC = Weight of plastic coat before oven drying

CC1 = Weight of clod before three laboratory plastic coats

CC2 = Weight of clod after three laboratory plastic coats

RV = Percent estimate of remaining clod volume after cutting to obtain flat surface (≈80%)

9.3 $FCE = 1.5 \times [(CC2 - CC1) / 3]$

FCE = Estimate of field-applied plastic coat, if applied

CC1 = Weight of clod before three laboratory plastic coats

CC2 = Weight of clod after three laboratory plastic coats

9.4 Gypsum bearing soils are a special case because gypsum ($CaSO_4 \cdot 2H_2O$) loses most of its chemically combined water (crystal water) at 105 °C (Nelson et al., 1978). Gypsum content of the soil is determined in method 4E2a1a1.

9.5 For gypsum bearing soils, properties that are reported on an oven-dry weight basis, such as 1,500-kPa water content, are converted to include the weight of crystal water in gypsum. The 1,500-kPa water content is corrected when the gypsum content of the soil is >1%.

9.6 Report water content to the nearest 0.1 percent.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Bruce, R.R., and R.J. Luxmoore. 1986. Water retention: Field methods. p. 663–686. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

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Water Retention (3C)
Pressure-Plate Extraction (3C1)
6, 10, 33, or 100 kPa (3C1a-d)
Soil Cores (3C1a-d3)

1. Introduction to Soil Core Pressure Plate Extraction

Soil cores are obtained in horizons that are not well indurated. Performing pressure-plate extraction on intact soil cores that have weak soil fabric leaves pedogenic features in situ. This provides a greater understanding of soil porosity, permeability, and water holding capacity.

2. Scope and Field of Application

The KSSL uses the pressure desorption method (U.S. Salinity Laboratory Staff, 1954). Ceramic, high-flow pressure-plate extraction is used to determine water retention at 6, 10, 33, 100, or 200 kPa. The data collected are used for water-retention function, water-holding capacity, porosity, and pore-size distribution; to calculate unsaturated hydraulic conductivity; and to determine saturated conductivity of a soil sample at specific water contents.

Laboratory-determined water retention data are usually higher than field-determined water retention data because the confining soil pressure is not present in the laboratory (Bruce and Luxmoore, 1986).

3. Principle

A core cylinder extracts a soil sample of known volume. The sample weight is recorded, and the soil core is placed on a tension table and equilibrated at a 5-cm tension at the base of the sample. The core is then transferred to a porous ceramic plate, which is placed in a pressure-plate extractor. The sample is equilibrated at the specified tension(s). The pressure is kept constant until equilibrium is obtained (Klute, 1986). The sample is dried in an oven and then weighed. The gravimetric water content is determined.

3.1 Interferences

Monitor the pressure for stability. A leak in the pressure extractor prevents equilibration of samples. Check for outflow air to verify that the extractor is functioning properly.

Equilibration must be done at constant temperature and humidity.

After extended use, the porous ceramic plate becomes clogged and water outflow is restricted. Clean the plate by flushing it sequentially with 500 mL of 10% H_2O_2, 1,000 mL of 1 *N* HCl, and 500 mL of RO water. The solutions are pulled through the plate with a vacuum, and the waste is captured in a trap.

Check the rubber membrane on the bottom of the plate for leaks. Inflate the membrane and then submerge it in water. If air bubbles escape from the membrane, remove the plate from service.

Compaction of the sample during the sampling process is a common problem. Compression can be observed by comparing the soil elevation inside the cylinder with the original soil surface outside the cylinder. If compression is excessive, the soil core may not be a valid sample for analysis.

Rock fragments in the soil interfere with core collection. Dry or hard soils often shatter when hammering the cylinder into the soil. Pressing the cylinder into the soil reduces the risk of shattering the sample.

Distilled or deionized water can possibly promote dispersion of clays in samples, and freshly drawn tapwater is often supersaturated with air, affecting the water content at a given pressure head (Dane and Hopmans, 2002).

4. Apparatus

4.1 Electronic balance, ±0.01-g sensitivity

4.2 Pressure-plate extractor with porous ceramic plate

4.3 Pressure source, regulator, and gauge

4.4 Oven, 110 °C

4.5 Desiccator with ceramic plate

4.6 Vacuum, 80-kPa (0.8-bar)

4.7 Metal probe or pottery needle tool

4.8 Sieve, no. 10 (2-mm openings)

4.9 Fume hood

4.10 Coring equipment. Sources described in Blake and Hartge (1986).

4.11 Tension table. The KSSL constructs a tension table by placing porous firebricks, covered with reinforced paper towels, in a tub of water.

4.12 Reinforced paper towels with nylon fibers

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Ethanol (CH_3CH_2OH) (CAS# 64-17-5), 95%, U.S.P.

5.3 Hydrogen peroxide (H_2O_2) (CAS# 7722-84-1), 30% technical grade

5.4 Hydrochloric acid (HCl) (CAS# 7647-01-0), concentrated 12 *N*

5.5 Microbicide for tension table, commercially prepared and available

5.6 Hydrogen peroxide solution, 10%

Components: Hydrogen peroxide (H_2O_2), RO water

- To a 2-L polyethylene bottle, add the following in order:
  - 1 L of RO water

- 333 mL of 30% H_2O_2
- Invert to mix.

5.7 Hydrochloric acid solution, 1 *N*

Components: Hydrochloric acid (HCl), RO water

- To a 2-L polyethylene bottle, add the following in order:
  - 1 L of RO water
  - 83.3 mL of concentrated HCl
- Invert to mix.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

High-pressure air lines and moisture traps must be maintained in good working order.

Ensure that the pressure is zero before removing bolts from the pressure-apparatus lid. Ensure that the bolts are tightened before applying pressure.

7. Sample Preparation

Record the initial weight (CW) of the empty sampling cylinders and submit weights to the KSSL with the samples. The core cylinder is pressed or driven into the soil to capture friable soil textures. Use care not to compact to soil. Shave protruding soil from cylinder ends and cap the cylinder. Label cylinder with horizon and depth. Additional resources include method 1A1b (Field Sample Collection and Preparation).

8. Procedure

This procedure is usually combined with method 3B1b (Bulk Density, 33-kPA Desorption (Db_{33})).

8.1 Record the weight (CW) of the sampling cylinders in the field and submit weights to the KSSL with the core samples.

8.2 In the laboratory, secure cheesecloth on the bottom of the core. Place the flat core surface on a tension table maintained at 5-cm tension. Determination can be made by inserting metal probe to measure equal resistance and comparing saturated weight to initial weight. When clod has reached equilibrium, remove clod and record weight (WSC).

8.2.1 If core is hydrophobic, place it in a desiccator on a water-covered plate with a 0-cm tension. Submerge only the surface of core in the water. Add a few mL of ethanol. Use in-house vacuum and apply

suction until core has equilibrated at saturation. Remove core and record weight (WSC).

8.3 Saturate the ceramic plate by applying RO water to the surface of the plate until water is no longer absorbed into the plate. To provide good contact between core and ceramic plate, cover the ceramic plate with a paper towel and saturate with water. Place a water retention sample ring in the center of the plate.

8.4 Place the saturated ceramic plate in a pressure-plate extractor and attach discharge tubing to the extractor outlet. Place the core on saturated pressure plate with paper towel.

8.5 Prepare quality control (QC) sample by placing <2-mm sieved soil standard in water retention ring. Allow sufficient time for the sample to become saturated. Close the extractor and secure the lid.

8.6 Apply gauged air pressure of 6, 10, 33, or 100 kPa. If more than one water-retention point is requested, begin with the lowest pressure. Samples are equilibrated when water ceases to emit from the outflow tube. Submerge the outflow tube in a burette to determine if water is no longer being discharged. Periodically submerge the outflow tube in water to monitor for air bubbles that indicate ceramic plate failure.

8.7 Determine the gravimetric water content of the QC sample.

8.7.1 If the water content of the QC is more than twice the standard deviation, apply pressure for additional time. Recheck the QC.

8.7.2 If the water content of the QC is less than twice the standard deviation, rewet the clods and desorb again.

8.7.3 If the water content of the QC is within acceptable limits, the apparatus has functioned properly and equilibrated clod weights should be collected.

8.8 Remove core and record the weight (WMC). Compare WMC to WSC. If WMC ≥ WSC, re-equilibrate core on the tension table and repeat the desorption process. If additional water-retention points are requested, then repeat the desorption process at the next higher pressure. When the core is equilibrated at 33 kPa and bulk density is to be measured, continue with method 3B1b.

8.9 Dry core in an oven at 110 °C until weight is constant and record oven-dry weight (WODC).

8.10 Remove soil from core cylinder. If a cylinder weight was not submitted from the field, record the weight of the empty core cylinder (CW).

8.11 If the core contains >5%, by weight, rock fragments >2-mm—as determined by sample processing bulk sample fragment weights or particle-size data—remove the rock fragments from the core. Wet sieve the soil through a 2-mm sieve. Dry and record the weight (RF) of the rock fragments that are retained on the sieve.

8.12 Correct for rock fragments retained on sieve. Determine rock fragment density by pycnometer or weighing fragments in air to obtain their mass and in water to obtain their volume. Record density weight (PD) for rock fragments.

8.12.1 In specific circumstances, if rock fragments are light in density, abundant, and the analyst suspects the porosity of the fragments may contribute to water retention of the soil, do not correct core mass and volume measurement for rock fragments.

9. Calculations

9.1 $H_2O\% = 100 \times [(WMC - WODC) / (WODC - CW - RF)]$

$H_2O\%$ = Percent gravimetric water content

WMC = Weight of solids + H_2O + container

CW = Weight of solids + container

WODC = Weight of container

RF = Weight of rock fragments

9.2 Gypsum bearing soils are a special case because gypsum ($CaSO_4 \cdot 2H_2O$) loses most of its chemically combined water (crystal water) at 105 °C (Nelson et al., 1978). Gypsum content of the soil is determined in method 4E2a1a1.

9.3 For gypsum bearing soils, properties that are reported on an oven-dry weight basis, such as 1,500-kPa water content, are converted to include the weight of crystal water in gypsum. The 1,500-kPa water content is corrected when the gypsum content of the soil is >1%.

9.4 Report water content to the nearest 0.1 percent.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

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Water Retention (3C)
Pressure-Plate Extraction (3C1)
33 kPa (3C1c)
Rewet (3C1c4)

1. Introduction to 1/3 Bar Clod Rewet

Rewet pressure-plate extraction determines the water retention of a clod that is equilibrated at 33-kPa, air-dried, and re-equilibrated. The resulting data are called rewet water-retention data and are usually used in conjunction with the rewet bulk density data in method 3B1d to estimate changes in physical properties of a soil as it undergoes wetting and drying cycles

2. Scope and Field of Application

The rewet water retention aids in determining irreversible shrinkage of soils and subsidence of organic soils. The data collected are used for water-retention function, water-holding capacity, porosity, and pore-size distribution; to calculate unsaturated hydraulic conductivity; and to determine saturated conductivity of a soil sample at specific water contents.

3. Principle

The KSSL uses the pressure desorption method (U.S. Salinity Laboratory Staff, 1954). Natural clods are placed on a tension table and equilibrated at a 5-cm tension at the base of the sample. The clods are then transferred to a porous ceramic plate, which is placed in a pressure-plate extractor. The sample is equilibrated at 33 kPa. The pressure is kept constant until equilibrium is obtained (Klute, 1986). The equilibrated clod weight is recorded. The clod is air dried and then placed on a tension table and desorbed again. After the second equilibration, the gravimetric water content is determined.

3.1 Interferences

A leak in the pressure extractor prevents equilibration of samples. Check outflow air to verify each pressure-plate extractor is functioning properly and does not leak.

Monitor the pressure for stability.

Equilibration must be done at constant temperature and humidity.

After extended use, the porous ceramic plate becomes clogged and water outflow is restricted. Clean the plate by flushing it sequentially with 500 mL of 10% H_2O_2, 1,000 mL of 1 *N* HCl, and 500 mL of RO water. The solutions are pulled through the plate with a vacuum, and the waste is captured in a trap.

Check the rubber membrane on the bottom of the plate for leaks. Inflate the membrane and then submerge it in water. If air bubbles escape from the membrane, remove the plate from service.

Laboratory-determined water retention data are usually higher than field-determined water retention data because the confining soil pressure is not present in the laboratory (Bruce and Luxmoore, 1986).

Distilled or deionized water can possibly promote dispersion of clays in samples, and freshly drawn tap water is often supersaturated with air, affecting the water content at a given pressure head (Dane and Hopmans, 2002).

4. Apparatus

4.1 Electronic balance, ±0.01-g sensitivity
4.2 Pressure-plate extractor with porous ceramic plate
4.3 Pressure source, regulator, and gauge
4.4 Oven, 110 °C capability
4.5 Clothespins
4.6 Knife
4.7 Tile cut−off saw with diamond-edged blade
4.8 Desiccator with ceramic plate
4.9 Vacuum, 80-kPa (0.8-bar)
4.10 Metal probe or pottery needle tool
4.11 Sieve, no. 10 (2-mm openings)
4.12 Hot plate
4.13 Fume hood
4.14 Reinforced paper towels with nylon fibers
4.15 Tension table. The KSSL constructs a tension table by placing porous firebricks, covered with reinforced paper towels, in a tub of water.
4.16 Stock tags, 25.4-mm (1-in) diameter paper tag, with metal rim
4.17 Wire. The KSSL uses 28-awg, coated copper wire.
4.18 Retainer rings, 10-mm high and 50-mm diameter

5. Chemicals

5.1 Reverse osmosis (RO) Water
5.2 Acetone (CH_3COCH_3) (CAS# 67-64-1)
5.3 Ethanol (CH_3CH_2OH) (CAS# 64-17-5), 95%, U.S.P.
5.4 Hydrogen peroxide (H_2O_2) (CAS# 7722-84-1), 30% technical grade
5.5 Hydrochloric acid (HCl) (CAS# 7647-01-0), concentrated 12 *N*
5.6 Microbicide for tension table, commercially prepared and available
5.7 Saran, polyvinyl dichloride (PVDC) resin. (The KSSL can be contacted for more information.)
5.8 **Hydrogen peroxide solution, 10%**
Components: Hydrogen peroxide (H_2O_2), RO water

- To a 2-L polyethylene bottle, add the following in order:
  - 1 L of RO water
  - 333 mL of 30% H_2O_2
- Invert to mix.

5.9 Hydrochloric acid solution, 1 *N*

Components: Hydrochloric acid (HCl), RO water

- To a 2-L polyethylene bottle, add the following in order:
  - 1 L of RO water
  - 83.3 mL of concentrated HCl
- Invert to mix.

5.10 Saran plastic lacquer

Components: Acetone (CH_3COCH_3), saran resin

Saran is prepared in two resin-to-solvent ratios: 1:4 and 1:7 (on a weight basis). Use the 1:4 plastic lacquer for the initial field and laboratory coatings. Use the 1:7 plastic lacquer for the last two laboratory coatings.

5.10.1 For a 1:4 ratio saran: To a 3.8-L (1-gal) metal paint can, add the following in order:

- 2,700 ±200 mL of acetone (fill to the bottom of handle rivet)
- 540 g saran resin
- For field preparation, stir solvent with a wooden stick or spoon while adding resin.
- For lab preparation, stir solvent with a non-sparking, high speed stirrer while adding resin.
- Stir plastic lacquer for 15 min at ≈25 °C.
- Store plastic lacquer in covered plastic or steel containers.

5.10.2 For a 1:7 ratio saran: To a 3.8-L (1-gal) metal paint can, add the following in order:

- 2,700 ±200 mL of acetone (fill to the bottom of handle rivet)
- 305 g of saran resin
- For field preparation, stir solvent with a wooden stick or spoon while adding resin.
- For lab preparation, stir solvent with a non-sparking, high speed stirrer while adding resin.
- Stir plastic lacquer for 15 min at ≈25 °C.
- Store plastic lacquer in covered plastic or steel containers.
- Note: The only situation in which the 1:7 saran ratio should be used in the field is for samples with low porosity and permeability.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Acetone is highly flammable. Do not use near open flame or electrical equipment. Avoid inhalation or physical contact. Use with adequate ventilation. In closed buildings, use a fume hood. Keep in tightly closed containers. Use safety glasses, proper gloves, and a lab coat. Wash hands immediately after handling acetone. Review acetone safety data sheets (SDS) for safe handling practices.

Saran F-310 resin decomposes rapidly at temperatures >200 °C, releasing hydrogen chloride gas.

Avoid contact with Fe, Zn, Cu, and Al in solution. Avoid all contact with strong bases.

High-pressure air lines and moisture traps must be maintained in good working order. Ensure that the pressure is zero before removing bolts from the pressure-plate lid. Ensure that the bolts are tightened before applying pressure.

7. Sample Preparation

Clods should represent a given horizon and be approximately the size of a fist or a potato (≈250 to 550 cm^3). They should be carefully preserved in saran, bagged, and boxed for shipment to the KSSL. Additional resources include method 1A1b (Field Sample Collection and Preparation) and the video tutorial "How to Sample Bulk Density in the Field" (https://youtu.be/E7BSZrJ-TDw).

Note: Friable clods commonly break apart during shipping and analysis. In such cases, this method does not return reportable data. For these sample types, the confined core cylinder method (3C1a-d3) is more appropriate.

8. Procedure

8.1 Remove a consolidated piece of soil roughly the size of a potato from the face of sampling pit. Prepare a clod by gently cutting or breaking protruded peaks and compacted material from clod. If roots are present, trim roots with shears. Three clods per horizon are recommended. It is important that these clods be as representative of the bulk sample as possible.

8.2 Using the rope, make a clothesline to hang saran-dipped clods. Place clod in a hairnet. If clod is dry, moisten surface with a fine mist of water. Suspend clod from clothesline to dry. Dry clod for 30 min or until odor of solvent dissipates. If the value of Db_f is required, store clods in waterproof plastic bags as soon as coating dries; coating is permeable to water vapor.

8.3 Pack clods in partitioned clod boxes to protect them during transport.

8.4 In the laboratory

8.4.1 Prepare clod for dip in 1:4 saran. Label a round stock tag with sample identification number. Cut the copper wire and loop around the clod. Record weight of tag and wire (typically ≈1.5 g). Loop fine copper wire around clod, leaving a tail to which round stock tag is attached. Record weight of clod (CC1).

8.4.2 Dip clod to preserve moisture content:

8.4.2.1 Dip clod in 1:4 plastic lacquer.

8.4.2.2 Wait 7 min and then dip clod in 1:7 saran.

8.4.2.3 Wait 12 min and then dip clod in 1:7 saran.

8.4.2.4 Wait 55 min and then reweigh clod.

8.4.2.5 If the clod has adsorbed >3% in plastic by clod weight or smells excessively of solvent, allow longer drying time and then reweigh clod and record weight (CC2). The clod should be waterproof and ready for volume measurement by water displacement.

8.5 Using a lapidary saw or tile saw and a diamond-edged sawblade, cut a flat surface on the clod, removing about 20% of the clod. Select the orientation of the cut based on surface area, barriers to capillary rise, or areas of the clod that absorbed saran.

8.6 Place cut surface of clod on a tension table lined with paper towels maintained at 5-cm tension. Periodically check clod to determine if it has reached equilibrium. Determination can be made by inserting metal probe to measure equal resistance and comparing saturated weight to initial weight. When clod has reached equilibrium, remove clod and record weight (WSC).

8.6.1 If the cut area of the clod is hydrophobic, place clod in a desiccator on a water-covered plate with a 0-cm tension. Submerge only the surface of clod in the water. Add a few mL of ethanol. Use in-house vacuum and apply suction until clod has equilibrated at saturation. Remove clod and record weight (WSC).

8.7 Saturate the ceramic plate by applying RO water to the surface of the plate until water is no longer absorbed into the plate. To provide good contact between clod and ceramic plate, cover the ceramic plate with a paper towel and saturate with water. Place a water retention sample ring in the center of the plate.

8.8 Place the saturated ceramic plate in a pressure-plate extractor and attach discharge tubing to the extractor outlet. Place the cut surface of the clod on the paper towel on the saturated pressure plate.

8.9 Prepare quality control (QC) sample by placing <2-mm sieved soil standard in water retention ring. Allow sufficient time for the sample to become saturated. Close the extractor and secure the lid.

8.10 Apply gauged air pressure of 33 kPa. If more than one water-retention point is requested, begin with the lowest pressure. When water stops discharging from the outflow tube, the clod is at equilibrium.

8.11 Determine the gravimetric water content of the QC sample.

8.11.1 If the water content of the QC is more than twice the standard deviation, apply pressure for additional time. Recheck the QC.

8.11.2 If the water content of the QC is less than twice the standard deviation, rewet the clods and desorb again.

8.11.3 If the water content of the QC is within acceptable limits, the apparatus has functioned properly and equilibrated clod weights should be collected.

8.12 Remove the clod and record the weight (WMC). Compare WMC to WSC. If WMC ≥ WSC, re-equilibrate the clod on the tension table and repeat the desorption process. If additional water-retention points are requested, then repeat the desorption process at the next higher pressure. When the clod is equilibrated at 33 kPa and bulk density is to be measured, continue with method 3B1d.

8.13 Air-dry the clod at room temperature (≈20 to 25 °C) for 4 to 6 days. Dry the clods at 40 to 50 °C for 2 to 3 days or until weights are constant.

8.14 Repeat steps 8.6 through 8.12. Record clod weight after equilibration (WMC2). Determine bulk density as described in method 3B1d.

8.15 Dry the clod in oven at 110 °C until clod reaches a constant weight (WODC).

8.16 If the clod contains >5%, by weight, rock fragments >2-mm—as determined by sample processing bulk sample fragment weights or particle-size data—remove the rock fragments from the clod. Submerge the remaining soil material in a beaker of water and place on a hot plate. Use a fume hood. Boil ≈1 h. The plastic coating loosens from soil material upon heating. Remove beaker from the hot plate. Allow to cool. Discard plastic coating.

8.17 Allow clod to stay in water until soil is fully saturated. Wet sieve the cool soil through a 2-mm sieve. Dry and record the weight (RF) of the rock fragments that are retained on the sieve.

8.18 Correct for rock fragments retained on sieve in clod data. Determine rock fragment density by pycnometer or weighing fragments in air to obtain their mass and in water to obtain their volume.

8.18.1 In specific circumstances, if rock fragments are light in density, abundant, and the analyst suspects the porosity of the fragments may contribute to water retention of the soil, do not correct clod mass and volume measurement for rock fragments.

9. Calculations

9.1 $H_2O\% = [(WMC - MPC) - (WODC - ODPC) \times 100] / (WODC - RF - ODPC - TAG)$

$H_2O\%$ = Percent gravimetric water content

WMC = Weight of equilibrated, coated clod

WODC = Weight of oven−dry coated clod

RF = Weight of rock fragments

ODPC = MPC x 0.85, weight of oven-dry plastic coat

TAG = Weight of tag and wire (typically ≈1.5 g)

9.2 MPC = {[(CC2 − CC1) + FCE] x RV}

MPC = Weight of plastic coat before oven drying

CC1 = Weight of clod before three laboratory plastic coats

CC2 = Weight of clod after three laboratory plastic coats

RV = Percent estimate of remaining clod volume after cutting to obtain flat surface (≈80%)

9.3 FCE = 1.5 x [(CC2 − CC1) / 3]

FCE = Estimate of field applied plastic coat, if applied

CC1 = Weight of clod before three laboratory plastic coats

CC2 = Weight of clod after three laboratory plastic coats

9.4 H_2O_r % = {[(WMC2 − MPC2) − (WODC − ODPC2)] x 100} / (WODC − RF − ODPC − TAG)

H_2O_r % = Percent water weight retained at 33-kPa tension after rewetting

WMC2 = Weight of equilibrated, coated clod after rewetting

MPC2 = Weight of moist plastic coat after rewetting. Same as MPC unless additional plastic coats were added.

ODPC2 = MPC2 x 0.85, weight of oven-dry plastic coat

WODC = Weight of oven−dry coated clod

ODPC = MPC x 0.85, weight of oven-dry plastic coat

TAG = Weight of tag and wire (typically ≈1.5 g)

9.5 Gypsum bearing soils are a special case because gypsum ($CaSO_4 \cdot 2H_2O$) loses most of its chemically combined water (crystal water) at 105 °C (Nelson et al., 1978). Gypsum content of the soil is determined in method 4E2a1a1.

9.6 For gypsum bearing soils, properties that are reported on an oven-dry weight basis, such as 1,500-kPa water content, are converted to include the weight of crystal water in gypsum. The 1,500-kPa water content is corrected when the gypsum content of the soil is >1%.

9.7 Report water content to the nearest 0.1 percent.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

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Water Retention (3C)
Pressure-Plate Extraction (3C1)
33 kPa (3C1c)
Reconstituted (3C1c5)

1. Introduction to 1/3-Bar Reconstituted Pressure-Plate Extraction

Reconstituted pressure-plate water-retention measurements provide a single, reproducible value for horizons that are subject to tillage or other mechanical disturbances followed by an extreme water-state cycle (Reinsch and Grossman, 1995).

2. Scope and Field of Application

This procedure is usually combined with bulk density method 3B2b and is used to determine the water retention of a reconstituted clod at 33 kPa. The data collected are used for water-retention function, water-holding capacity, porosity, and pore-size distribution; to calculate unsaturated hydraulic conductivity; and to determine saturated conductivity of a soil sample at specific water contents.

3. Principle

The KSSL uses the pressure desorption method (U.S. Salinity Laboratory Staff, 1954). The <2-mm sample is formed into a clod by wetting and desiccation cycles that simulate reconsolidation by water in a field setting. Plastic lacquer is applied in the laboratory to form an impermeable coat on the clod. The reconstituted clods are placed on a tension table and equilibrated at a 5-cm tension at the base of the sample. The samples are then transferred to a porous ceramic plate, which is placed in a pressure-plate extractor. The sample is equilibrated at the specified pressures. The pressure is kept constant until equilibrium is obtained (Klute, 1986). The gravimetric water content is determined.

3.1 Interferences

A leak in the pressure extractor prevents equilibration of samples. Check outflow air to verify that each pressure-plate extractor is functioning properly and does not leak.

Monitor the pressure for stability.

Equilibration must be done at constant temperature and humidity.

After extended use, the porous ceramic plate becomes clogged and water outflow is restricted. Clean the plate by flushing it sequentially with 500 mL of 10% H_2O_2, 1,000 mL of 1 *N* HCl, and 500 mL of RO water. The solutions are pulled through the plate with a vacuum, and the waste is captured in a trap.

Check the rubber membrane on the bottom of the plate for leaks. Inflate the membrane and then submerge it in water. If air bubbles escape from the membrane, remove the plate from service.

Laboratory-determined water retention data are usually higher than field-determined water retention data because the confining soil pressure is not present in the laboratory (Bruce and Luxmoore, 1986).

Distilled or deionized water can possibly promote dispersion of clays in samples, and freshly drawn tap water is often supersaturated with air, affecting the water content at a given pressure head (Dane and Hopmans, 2002).

4. Apparatus

4.1 Electronic balance, ±0.01-g sensitivity

4.2 Pressure-plate extractor with porous ceramic plate

4.3 Pressure source, regulator, and gauge

4.4 Oven, 110 °C

4.5 Clothespins

4.6 Knife

4.7 Tile cut-off saw with diamond-edged blade

4.8 Desiccator with ceramic plate

4.9 Vacuum, 80-kPa (0.8-bar)

4.10 Metal probe or pottery needle tool

4.11 Sieve, no. 10 (2-mm openings)

4.12 Hot plate

4.13 Fume hood

4.14 Reinforced paper towels with nylon fibers

4.15 Tension table. The KSSL constructs a tension table by placing porous firebricks, covered with reinforced paper towels, in a tub of water.

4.16 Stock tags, 25.4-mm (1-in) diameter paper tag, with metal rim

4.17 Wire. The KSSL uses 28-awg, coated copper wire.

4.18 Retainer rings, 10-mm high. Use 50-mm diameter rings for organic soils and 40-mm diameter rings for all other soils.

5. Chemicals

5.1 Acetone (CH_3COCH_3) (CAS# 67-64-1)

5.2 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.3 Ethanol (CH_3CH_2OH) (CAS# 64-17-5), 95%, U.S.P.

5.4 Microbicide for tension table, commercially prepared and available

5.5 Saran, polyvinyl dichloride (PVDC) resin. (The KSSL can be contacted for more information.)

5.6 Saran plastic lacquer

Components: Acetone (CH_3COCH_3), saran resin

Saran is prepared in two resin-to-solvent ratios: 1:4 and 1:7 (on a weight basis). Use the 1:4 plastic lacquer for the initial field and laboratory coatings. Use the 1:7 plastic lacquer for the last two laboratory coatings.

5.6.1 For a 1:4 ratio saran: To a 3.8-L (1-gal) metal paint can, add the following in order:

- 2,700 ±200 mL of acetone (fill to the bottom of handle rivet)
- 540 g saran resin.

- For field preparation, stir solvent with a wooden stick or spoon while adding resin.
- For lab preparation, stir solvent with a non-sparking, high speed stirrer while adding resin.
- Stir plastic lacquer for 15 min at ≈25 °C.
- Store plastic lacquer in covered plastic or steel containers.

5.6.2 For a 1:7 ratio saran: To a 3.8-L (1-gal) metal paint can, add the following in order:

- 2,700 ±200 mL of acetone (fill to the bottom of handle rivet)
- 305 g of saran resin

- For field preparation, stir solvent with a wooden stick or spoon while adding resin.
- For lab preparation, stir solvent with a non-sparking, high speed stirrer while adding resin.
- Stir plastic lacquer for 15 min at ≈25 °C.
- Store plastic lacquer in covered plastic or steel containers.
- Note: The only situation in which the 1:7 saran ratio should be used in the field is for samples with low porosity and permeability.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Acetone is highly flammable. Do not use near open flame or electrical equipment. Avoid inhalation or physical contact. Use with adequate ventilation. In closed buildings, use a fume hood. Keep in tightly closed containers. Use safety glasses, proper gloves, and a lab coat. Wash hands immediately after

handling acetone. Review acetone safety data sheets (SDS) for safe handling practices.

Saran F-310 resin decomposes rapidly at temperatures >200 °C, releasing hydrogen chloride gas.

Avoid contact with Fe, Zn, Cu, and Al in solution. Avoid all contact with strong bases.

High-pressure air lines and moisture traps must be maintained in good working order. Ensure that the pressure is zero before removing bolts from the pressure-apparatus lid. Ensure that the bolts are tightened before applying pressure.

7. Sample Preparation

7.1 The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

7.2 Drape a hairnet in the manufactured clod cell. Place a paper disc in the bottom of the cell. Place the anti-sorting screen into the cell. Add <2-mm, prepared sample to within a few mm of the top of the cell. Lift the anti-sorting screen from the cell.

7.3 Place the cell on a tension table with the top of the cell 5-cm below the top of the table. After equilibration, place the cell into a tub and add water to a level higher than the surface of the soil in the cell but below the top lip of the cell. This allows the soil to become inundated from beneath. Allow the sample to equilibrate.

7.4 Remove the cell from the tub and allow to dry at room temperature. After the clod has dried, remove the clod from the cell by knotting the edges of the hairnet together. Using the knot, gently pull the clod from the cell. If the soil is well consolidated, invert the cell and lightly tamp the base of the cell to dislodge the clod from the cell.

8. Procedure

8.1 Prepare a round stock tag with sample identification number. Cut the copper wire to loop around the clod. Record the weight of the tag and wire (typically ≈1.5 g). Loop fine copper wire around the clod, leaving a tail to which the round stock tag is attached. Record the weight of the clod (CC1).

8.2 Mist the reconstituted clod with water to create a film of water on the surface of the clod.

8.3 Dip clod to preserve moisture content:

- **8.3.1** Dip clod in 1:4 plastic lacquer.
- **8.3.2** Wait 7 min and then dip clod in 1:7 saran.
- **8.3.3** Wait 12 min and then dip clod in 1:7 saran.
- **8.3.4** Wait 55 min and then reweigh clod.

8.3.5 If the clod has adsorbed >3% in plastic by clod weight or smells excessively of solvent, allow longer drying time and then reweigh clod and record weight (CC2).

8.4 Using a diamond-edged saw blade, cut a flat surface on the clod, removing about 20% of the clod. Place the cut surface of the clod on a tension table maintained at 5-cm tension. Periodically check clod to determine if it has reached equilibrium. Determination can be made by inserting metal probe or pottery needle to measure equal resistance and comparing saturated weight to initial weight. When the clod has reached equilibrium, remove the clod and record the weight (WSC).

8.5 If the clod does not adsorb water, place the clod in a desiccator that has water covering the desiccator plate. Add a few mL of alcohol. Apply suction using in-house vacuum for 24 h. Remove the clod and record the weight (WSC).

8.6 Saturate the ceramic plate by applying RO water to the surface of the plate until water is no longer absorbed into the plate. To provide good contact between clod and ceramic plate, cover the ceramic plate with a paper towel and saturate with water. Place a water retention sample ring in the center of the plate.

8.7 Place the saturated ceramic plate in a pressure-plate extractor and attach discharge tubing to the extractor outlet. Place the cut surface of the clod on the paper towel on the saturated pressure plate.

8.8 Prepare quality control (QC) sample by placing <2-mm sieved soil standard in water retention ring. Allow sufficient time for the sample to become saturated. Close the extractor and secure the lid.

8.9 Place the clod in a pressure-plate extractor. To provide good contact between the clod and ceramic plate, cover the ceramic plate with a paper towel and saturate with water. Place the cut surface of the clod on the paper towel. Close the container and secure the lid. Apply gauged air pressure of 33 kPa. When water stops discharging from the outflow tube (usually after 2 or 3 weeks in the extractor), the clod is at equilibrium. Remove the clod and record the weight (WMC). Compare WMC to WSC. If WMC is greater than or equal to WSC, equilibrate the clod on the tension table and repeat the desorption process.

8.10 Determine the gravimetric water content of the QC sample.

8.10.1 If the water content of the QC is more than twice the standard deviation, apply pressure for additional time. Recheck the QC.

8.10.2 If the water content of the QC is less than twice the standard deviation, rewet the clods and desorb again.

8.10.3 If the water content of the QC is within acceptable limits, the apparatus has functioned properly and equilibrated clod weights should be collected.

8.11 Remove the clod and record the weight (WMC). Compare WMC to WSC. If WMC ≥ WSC, re-equilibrate the clod on the tension table and repeat the desorption process. If additional water-retention points are requested, then repeat the desorption process at the next higher pressure. When the clod is equilibrated at 33 kPa and bulk density is to be measured, continue with method 3B1b.

8.12 Dry the clod in an oven at 110 °C until weight is constant and record oven-dry weight (WODC).

9. Calculations

9.1 $H_2O\% = [(WMC - MPC) - (WODC - ODPC) \times 100] / (WODC - RF - ODPC - TAG)$

$H_2O\%$ = Percent gravimetric water content

WMC = Weight of equilibrated, coated clod

WODC = Weight of oven-dry coated clod

RF = Weight of rock fragments

ODPC = MPC x 0.85, weight of oven-dry plastic coat

TAG = Weight of tag and wire (typically ≈1.5 g)

9.2 $MPC = \{[(CC2 - CC1) + FCE] \times RV\}$

MPC = Weight of plastic coat before oven drying

CC1 = Weight of clod before three laboratory plastic coats

CC2 = Weight of clod after three laboratory plastic coats

RV = Percent estimate of remaining clod volume after cutting to obtain flat surface (≈80%)

9.3 $FCE = 1.5 \times [(CC2 - CC1) / 3]$

FCE = Estimate of field-applied plastic coat, if applied

9.4 Gypsum bearing soils are a special case because gypsum ($CaSO_4 \cdot 2H_2O$) loses most of its chemically combined water (crystal water) at 105 °C (Nelson et al., 1978). Gypsum content of the soil is determined in method 4E2a1a1.

9.5 For gypsum bearing soils, properties that are reported on an oven-dry weight basis, such as 1,500-kPa water content, are converted to include the weight of crystal water in gypsum. The 1,500-kPa water content is corrected when the gypsum content of the soil is >1%.

9.6 Report water content to the nearest 0.1 percent.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Bruce, R.R., and R.J. Luxmoore. 1986. Water retention: Field methods. p. 663–686. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

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Water Retention (3C)
Pressure-Membrane Extraction (3C2)
1500-kPa (3C2a)
<2-mm (Sieved), Air-Dry or Field-Moist (3C2a1a-b)

1. Introduction to 15-Bar Pressure-Membrane Extraction

Desorption at 15 bar represents the permanent wilting point of a soil. This tension provides information about the ability of the soil composition, particularly clays, to retain moisture. Tension of 15 bar is not included in moisture curves but represents extreme circumstances.

2. Scope and Field of Application

This method determines water retention for <2-mm (sieved) air-dry and field-moist samples at 1,500 kPa. The data collected are used for water-retention function and water-holding capacity, to calculate unsaturated hydraulic conductivity, and to determine saturated conductivity of a soil sample at specific water contents.

3. Principle

The KSSL uses the pressure desorption procedure (U.S. Salinity Laboratory Staff, 1954). A sample of <2-mm (sieved) air-dry or field-moist soil is placed in a retainer ring sitting on a cellulose membrane in a pressure-membrane extractor. The membrane is covered with water to wet the samples by capillarity. The sample is equilibrated at 1,500 kPa. The pressure is kept constant until equilibrium is obtained (Klute, 1986). The gravimetric water content is determined.

3.1 Interferences

A leak in the pressure extractor prevents equilibration of samples. Check outflow air to verify that the pressure membrane extractor is functioning properly and does not leak.

Monitor the pressure for stability.

Equilibration must be done at constant temperature and humidity. Samples that do not wet by capillarity are moistened with ethanol.

Laboratory-determined water retention data are usually higher than field-determined water retention data because the confining soil pressure is not present in the laboratory (Bruce and Luxmoore, 1986).

Distilled or deionized water can possibly promote dispersion of clays in samples, and freshly drawn tap water is often supersaturated with air, affecting the water content at a given pressure head (Dane and Hopmans, 2002).

4. Apparatus

4.1 Pressure membrane extractor (figs. 3C2a–1 and 3C2a–2)

Figure 3C2a–1.—Pressure-membrane extraction at 1,500 kPa for <2-mm samples.

Figure 3C2a–2.—Sieved (<2-mm) soil placed in pressure-membrane extractor.

4.2 Cellulose membrane
4.3 Retainer rings, 10-mm height and 40-mm diameter
4.4 Electronic balance, ±0.01-g sensitivity
4.5 Oven, 110 °C
4.6 Pressure source, regulator, and gauge
4.7 Metal weighing cans, tared, with lids
4.8 Vacuum trap assembly
4.9 Vacuum, 80-kPa (0.8-bar)

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water
5.2 Ethanol (CH_3CH_2OH) (CAS# 64-17-5), 95%, U.S.P.

6. Health and Safety

Personal Protective Equipment (PPE).—Use disposable gloves with appropriate polymer rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents or samples.

High-pressure air lines and moisture traps must be maintained in good working order. Ensure that the pressure is zero before removing bolts from the pressure-apparatus lid. Ensure that the bolts are tightened before applying pressure.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Submerge a cellulose membrane in RO water for 12 h or more before use. Install the wet cellulose membrane in the pressure extractor.
8.2 Add water and retaining rings. Add enough water to keep membrane moist. Water level should be less than the height of the retaining rings.
8.3 Fill retaining rings with 10 to 15 g of <2-mm or fine-grind, air-dry or field-moist soil sample. Include a quality control (QC) sample with each plate. Continue to add water until all samples have moistened by capillarity. If samples do not moisten, apply ethanol to the surface of the sample. Allow ethanol to evaporate. Cover samples with rubber diaphragm to reduce evaporation, close the extractor, and let stand overnight.
8.4 Remove excess water from the plate with disposable pipette.

8.5 Assemble the extractor and uniformly tighten the bolts. Using a torque wrench, torque the bolts on both sides of the hinge to 138.0 kPa (200 psi). Torque the remaining bolts to 103.5 kPa (150 psi).

8.6 Increase air pressure by ≈150 kPa every 15 min until 1,500 kPa is reached (220 psi). The next day, apply the pressure differential (±5 psi). This forces the rubber diaphragm against the top of the samples. The samples are equilibrated when water ceases to emit from the outflow tube.

8.7 At equilibrium, open the extractor and quickly transfer the samples to water cans, cover with lids, and record the weights (Ms+w).

8.8 Remove the lids, place samples in the oven, and dry at 110 °C until weight is constant. Remove samples from the oven, replace the lids, allow cans to cool to ambient temperature, and record the weights (Ms).

8.9 Record the weights of the empty cans (Mc).

9. Calculations

9.1 $H_2O\% = 100 \times [(Ms+w - Ms)/(Ms - Mc)]$

$H_2O\%$ = Percent gravimetric water content

Ms+w = Weight of solids + H_2O + container

Ms = Weight of solids + can

Mc = Weight of container

9.2 Gypsiferous/gypseous soils are a special case because gypsum ($CaSO_4 \cdot 2H_2O$) loses most of its chemically combined water (crystal water) at 105 °C (Nelson et al., 1978). Gypsum content of the soil is determined in method 4E2a1a1.

9.3 Properties of gypsiferous/gypseous soils, such as 1,500-kPa water content, that are reported on an oven-dry weight basis are converted to include the weight of crystal water in gypsum. The 1,500-kPa water content is corrected when the gypsum content of the soil is >1%. The corrections and calculations are found in methods 3D3 and 4E2a1a1.

9.4 Report water content to the nearest 0.1 percent.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Bruce, R.R., and R.J. Luxmoore. 1986. Water retention: Field methods. p. 663–686. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Dane, J.H., and J. W. Hopmans. 2002. Water retention and storage: Laboratory. p. 675–720. *In* J.H. Dane and G.C. Topp (eds.) Methods of soil analysis. Part 4. Physical methods. Soil Sci. Am. Book Series No. 5. ASA and SSSA, Madison, WI.

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Nelson, R.E., L.C. Klameth, and W.D. Nettleton. 1978. Determining soil content and expressing properties of gypsiferous soils. Soil Sci. Soc. Am. J. 42:659–661.

U.S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. L.A. Richards (ed.). USDA Agric. Handbook 60. U.S. Govt. Print. Office, Washington, DC.

Water Retention (3C)
Pressure-Membrane Extraction (3C2)
500-kPa (3C2b)
<2-mm (Sieved), Air-Dry or Field-Moist (3C2b1a-b)

1. Introduction to 5 Bar Pressure-Membrane Extraction

The KSSL conducts water extractions from air-dried processed soils at 6, 10, 33, 100, and 500 kPa to create moisture curves. Measurement at 5-bar tension is requested less often than other tensions, but it is appropriate for soils that have a large content of smectitic clays. Smectitic clay has a high shrink-swell potential.

2. Scope and Field of Application

This method determines water retention for <2-mm (sieved) air-dry and field-moist samples at 500 kPa. The data collected are used for water-retention function and water-holding capacity, to calculate unsaturated hydraulic conductivity, and to determine saturated conductivity of a soil sample at specific water contents.

3. Principle

The KSSL uses the pressure desorption procedure (U.S. Salinity Laboratory Staff, 1954). A sample of <2-mm (sieved) air-dry or field-moist soil is placed in a retainer ring sitting on a cellulose membrane in a pressure-membrane extractor. The membrane is covered with water to wet the samples by capillarity. The sample is equilibrated at 500 kPa. The pressure is kept constant until equilibrium is obtained (Klute, 1986). The gravimetric water content is determined.

3.1 Interferences

A leak in the pressure extractor prevents equilibration of samples. Check outflow air to verify that the pressure membrane extractor is functioning properly and does not leak.

Monitor the pressure for stability.

Equilibration must be done at constant temperature and humidity. Samples that do not wet by capillarity are moistened with ethanol.

Laboratory-determined water retention data are usually higher than field-determined water retention data because the confining soil pressure is not present in the laboratory (Bruce and Luxmoore, 1986).

Distilled or deionized water can possibly promote dispersion of clays in samples, and freshly drawn tap water is often supersaturated with air, affecting the water content at a given pressure head (Dane and Hopmans, 2002).

4. Apparatus

4.1 Pressure membrane extractor (figs. 3C2b–1 and 3C2b–2)

Figure 3C2b–1.—Pressure-membrane extraction at 1,500 kPa for <2-mm samples.

Figure 3C2b–2.—Sieved (<2-mm) soil placed in pressure-membrane extractor.

4.2 Cellulose membrane
4.3 Retainer rings, 10-mm height and 40-mm diameter
4.4 Electronic balance, ±0.01-g sensitivity
4.5 Oven, 110 °C
4.6 Pressure source, regulator, and gauge
4.7 Metal weighing cans, tared, with lids
4.8 Vacuum trap assembly
4.9 Vacuum, 80-kPa (0.8-bar)

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water
5.2 Ethanol (CH_3CH_2OH) (CAS# 64-17-5), 95%, U.S.P.

6. Health and Safety

Personal Protective Equipment (PPE).—Use disposable gloves with appropriate polymer rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents or samples.

High-pressure air lines and moisture traps must be maintained in good working order. Ensure that the pressure is zero before removing bolts from the pressure-apparatus lid. Ensure that the bolts are tightened before applying pressure.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Submerge a cellulose membrane in RO water for 12 h or more before use. Install the wet cellulose membrane in the pressure extractor.
8.2 Add water and retaining rings. Add enough water to keep membrane moist. Water level should be less than the height of the retaining rings.
8.3 Fill retaining rings with 10 to 15 g of <2-mm or fine-grind, air-dry or field-moist soil sample. Include a quality control (QC) sample with each plate. Continue to add water until all samples have moistened by capillarity. If samples do not moisten, apply ethanol to the surface of the sample. Allow ethanol to evaporate. Cover samples with rubber diaphragm to reduce evaporation, close the extractor, and let stand overnight.
8.4 Remove excess water from the plate with disposable pipette.

8.5 Assemble the extractor and uniformly tighten the bolts. Using a torque wrench, torque the bolts on both sides of the hinge to 138.0 kPa (200 psi). Torque the remaining bolts to 103.5 kPa (150 psi).

8.6 Increase air pressure by ≈150 kPa every 15 min until 500 kPa is reached. The next day, apply the pressure differential (±5 psi). This forces the rubber diaphragm against the top of the samples. The samples are equilibrated when water ceases to emit from the outflow tube.

8.7 At equilibrium, open the extractor and quickly transfer the samples to water cans, cover with lids, and record the weights (Ms+w).

8.8 Remove the lids, place samples in the oven, and dry at 110 °C until weight is constant. Remove samples from the oven, replace the lids, allow cans to cool to ambient temperature, and record the weights (Ms).

8.9 Record the weights of the empty cans (Mc).

9. Calculations

9.1 $H_2O\% = 100 \times [(Ms+w - Ms)/(Ms - Mc)]$

$H_2O\%$ = Percent gravimetric water content

Ms+w = Weight of solids + H_2O + container

Ms = Weight of solids + can

Mc = Weight of container

9.2 Gypsiferous/gypseous soils are a special case because gypsum ($CaSO_4 \cdot 2H_2O$) loses most of its chemically combined water (crystal water) at 105 °C (Nelson et al., 1978). Gypsum content of the soil is determined in method 4E2a1a1.

9.3 Properties of gypsiferous/gypseous soils, such as 500-kPa water content, that are reported on an oven-dry weight basis are converted to include the weight of crystal water in gypsum. The 500-kPa water content is corrected when the gypsum content of the soil is >1%. The corrections and calculations are found in methods 3D3 and 4E2a1a1.

9.4 Report water content to the nearest 0.1 percent.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Bruce, R.R., and R.J. Luxmoore. 1986. Water retention: Field methods. p. 663–686. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

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Nelson, R.E., L.C. Klameth, and W.D. Nettleton. 1978. Determining soil content and expressing properties of gypsiferous soils. Soil Sci. Soc. Am. J. 42:659–661.

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Water Retention (3C)
Field-State (3C3)

1. Introduction to Field-State Water Retention

Soil saturation during or after a rain event, flooding, hydraulic flow, geomorphology, organic matter content, and clay types and abundance are all factors that influence water retention in soils. Field-state water retention analysis offers a snapshot to the amount of water retained within a soil at a specific moment. Such information is helpful in determining suitability for agriculture or irrigation.

2. Scope and Field of Application

Field-water content can be determined by weighing, drying, and reweighing a soil sample. The resulting data are used to estimate the water content at the time of sampling.

3. Principle

Soil samples are collected in the field. The samples are stored in plastic or metal containers to prevent drying and then transported to the laboratory. Gravimetric water content is determined (Gardner, 1986).

3.1 Interferences

Leaks in the plastic or metal storage containers cause the samples to dry, resulting in an underestimation of the field water content.

4. Apparatus

4.1 Electronic balance, ±0.01-g sensitivity

4.2 Oven, 110 °C

4.3 Moisture cans, tared

5. Chemicals

None.

6. Health and Safety

Personal Protective Equipment (PPE).—Use insulated gloves to remove samples from the oven.

7. Sample Preparation

Sample collection is the only preparation. The analyses is conducted on the field-moist soil as submitted.

8. Procedure

8.1 Collect soil samples in the field. Place samples in airtight, metal or plastic containers.

8.2 Record sample weight (Ms+w).

8.3 Dry sample in an oven at 110 °C until weight is constant. Record oven-dry weight (Ms).

8.4 Record weight of container (Mc).

9. Calculations

9.1 $H_2O\% = 100 \times [(Ms+w - Ms) / (Ms - Mc)]$

$H_2O\%$ = Percent gravimetric water content

Ms+w = Weight of solids + H_2O + container

Ms = Weight of solids + container

Mc = Weight of container

9.2 Report water content to the nearest 0.1 percent.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Gardner, W.H. 1986. Water content. p. 493–544. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Ratios and Estimates Related to Particle-Size Analysis, Bulk Density, and Water Retention (3D)
Air-Dry/Oven-Dry Ratio (AD/OD) (3D1)
Field-Moist/Oven-Dry Ratio (FM/OD) (3D2)
Correction for Crystal Water (3D3)

1. Introduction to Crystal Water Gypsum Correction

In the following method, the AD/OD ratio is converted to a crystal water basis (Nelson et al., 1978). Gypsiferous/gypseous soils are a special case because gypsum ($CaSO_4 \cdot 2H_2O$) loses most of its chemically combined water (crystal water) at 105 °C. For gypsiferous/gypseous soils, properties that are reported on an oven-dry weight basis should be converted to include the weight of crystal water in gypsum. The inclusion of gypsum crystal water weight allows the properties of gypsiferous/gypseous soils to be compared with nongypsiferous/nongypseous soils. This conversion also avoids the possible calculation error of obtaining >100% gypsum when the data are expressed on an oven-dry basis (Nelson, 1982). The equation for calculating percent gypsum, corrected, assumes the crystal-water content of gypsum is 19.42% (Nelson et al., 1978) as opposed to the theoretical water content (20.21%).

2. Scope and Field of Application

Air-dry (AD) and oven-dry (OD) weights are defined as constant sample weights obtained after drying at 30 ±5 °C (≈3 to 7 days) and at 110 ±5 °C (≈12 to 16 h). As a general rule, air-dry soils contain about 1 to 2 percent water and are drier than soils at 1,500-kPa water content. Field-moist weight (FM) is defined as the sample weight obtained without drying and prior to laboratory analysis. In general, these weights are indicative of the water content at the time of sample collection.

Unless otherwise specified, soil properties reported by the KSSL are expressed on an oven-dry weight basis. The AD/OD ratio (method 3D1) is determined on a <2-mm sieved sample and is used in calculations to adjust all results to an oven-dry basis. It is also used to calculate the sample weight equivalent to the required oven-dry soil weight. Field-moist/oven-dry (FM/OD) ratio (method 3D2) is used in special circumstances.

3. Principle

A sample is weighed, dried to a constant weight in an oven, and reweighed. The moisture content is expressed as a ratio of the air-dry weight to the oven-dry weight (AD/OD) or as a ratio of field-moist weight to the oven-dry weight (FM/OD). For gypsiferous/gypseous soils, properties that are reported on an oven-dry weight basis are converted to include the weight of the crystal water. When reporting the

water content of gypsiferous/gypseous soils, the crystal water content must be subtracted from the total oven-dry water content. The AD/OD ratio is corrected to a crystal water basis when the gypsum content of the soil is ≥1%. Gypsum content of the soil is determined in method 4E2a1a1.

3.1 Interferences

Samples may not reach a constant weight when dried overnight. The most frequently used definition for a dry soil is the soil mass after it has come to a constant weight at a temperature of 100 to 110 °C (ASTM, 2012).

Temperatures that are >50 °C may promote oxidation or decomposition of some forms of organic matter.

Do not add moist samples to an oven that already contains samples unless the initial samples have been in the oven for at least 12 to 16 hours.

Weigh samples within 30 minutes of the samples cooling. Samples may adsorb significant amounts of atmospheric moisture.

The removal of structural water, most commonly in gypsum, can produce a positive error. When reporting the water content of gypsiferous/gypseous soils, the crystal water content must be subtracted from the total oven-dry water content.

Gypsum, hydrous oxides, and amorphous material may be affected by heating.

4. Apparatus

4.1 Electronic balance, ±1-mg sensitivity

4.2 Oven, thermostatically controlled, 110 ±5 °C

4.3 Thermometer, 0 to 200 °C

4.4 Tin dishes, 4.5-cm diameter x 3-cm height, with covers

5. Chemicals

None.

6. Health and Safety

Personal Protective Equipment (PPE).—Use safety glasses, lab coat or apron, and heat resistant gloves to remove weighing containers from a hot oven. Follow standard laboratory procedures.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Tare the moisture dishes. Record each sample number and associated dish number.

8.2 Add 10 to 20 g <2-mm, air-dry soil to each moisture dish for AD/OD determination. For FM/OD determination, add enough <2-mm or fine-grind, moist soil to achieve ≈10 to 20 g sample of air-dry soil. Weigh the dish plus the sample and record the weight to the nearest 1 mg. Place the sample dish in a drying oven at 110 ±5 °C. Allow the sample to remain in the oven overnight (12 to 16 h).

8.3 Remove the sample dish and allow it to cool before reweighing. Do not allow the sample dish to remain at room temperature for more than 30 min.

8.4 Record the oven-dry weight to the nearest 1 mg.

8.5 Discard the sample.

8.6 Refer to the calculations for the correction for crystal water of gypsum in gypsiferous/gypseous soils.

9. Calculations

9.1 Calculations for AD/OD ratio (method 3D1)

9.1.1 AD/OD ratio = AD / OD

AD = (Air-dry weight) − (Tin tare weight)

OD = (Oven-dry weight) − (Tin tare weight)

9.1.2 $H_2O = [(AD - OD) \times 100] / OD$

H_2O = % Water content

AD = (Air-dry weight) − (Tin tare weight)

OD = (Oven-dry weight) − (Tin tare weight)

9.2 Calculations for FM/OD ratio (method 3D2)

9.2.1 FM/OD ratio = FM / OD

FM = (Field-moist weight) − (Tin tare weight)

OD = (Oven-dry weight) − (Tin tare weight)

9.2.2 $H_2O = [(FM - OD) \times 100] / OD$

FM = (Field-moist weight) − (Tin tare weight)

OD = (Oven-dry weight) − (Tin tare weight)

9.3 Calculations for gypsum H_2O correction (method 3D3)

9.3.1 $(AD/OD)c = (AD/OD)uc / [1 + (Gypsum \times 0.001942)]$

AD/ODc = Air-dry/oven-dry ratio, corrected basis, gypsiferous/gypseous soils

AD/ODuc = Air-dry/oven-dry ratio, uncorrected basis

Gypsum = % Gypsum uncorrected (uc)

Table 3D–1.—Convert EC Reading (mmhos cm^{-1}) to Gypsum Content (meq L^{-1}).

EC	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.0						0.40				
0.1	0.80	0.89	0.98	1.10	1.22	1.31	1.40	1.50	1.60	1.70
0.2	1.80	1.90	2.00	2.10	2.20	2.30	2.40	2.50	2.60	2.70
0.3	2.80	2.90	3.00	3.10	3.20	3.30	3.40	3.50	3.60	3.72
0.4	3.85	3.98	4.10	4.22	4.35	4.48	4.60	4.70	4.80	4.90
0.5	5.00	5.12	5.25	5.38	5.50	5.62	5.75	5.88	6.00	6.12
0.6	6.25	6.35	6.45	6.58	6.70	6.82	6.95	7.05	7.15	7.28
0.7	7.40	7.52	7.65	7.78	7.90	8.04	8.18	8.32	8.45	8.58
0.8	8.70	8.82	8.95	9.05	9.15	9.28	9.40	9.55	9.70	9.85
0.9	10.00	10.12	10.25	10.38	10.50	10.62	10.75	10.88	11.00	11.15
1.0	11.30									

9.3.2 $\%\ Gypsum_{uc} = [Gypsum \times Water \times 0.08609 \times AD/OD] / [Sample\ Weight(g) \times 5]$

Gypsum = meq/100 g as determined in table 3D–1

Water = 100 mL of RO water

0.08609 = Conversion factor (gypsum % = meq 100 g^{-1} x 0.08609)

AD/OD = Air-dry/oven-dry ratio (method 3D1)

5 = Filtrate (5 mL)

9.3.3 $H_2Oc = [H_2O_{uc} - (Gypsum \times 0.1942)] / [1 + (Gypsum \times 0.001942)]$

H_2O_c = % Water content, corrected basis, gypsiferous/gypseous soils

H_2O_{uc} = % Water content, uncorrected basis

Gypsum = % Gypsum uncorrected

9.4 $AD = (OD_r) / [1 - (H_2O / 100)]$

AD = Required weight of air-dry soil

OD_r = Desired weight of oven-dry soil

H_2O = Percent water determined from AD/OD

9.4.1 The equation $AD = (OD_r) / [1 - (H_2O / 100)]$ calculates the weight of air-dry soil needed to provide a given weight of oven-dry soil for other analytical procedures.

9.5 AD/OD ratio and FM/OD ratio are reported as dimensionless values to the nearest 0.01 unit.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

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Ratios and Estimates Related to Particle-Size Analysis, Bulk Density, and Water Retention (3D)
Coefficient of Linear Extensibility (COLE) (3D4)

Introduction

Coefficient of linear extensibility (COLE) is a derived value that denotes the fractional change in the clod dimension from a moist to a dry state (Franzmeier and Ross, 1968; Grossman et al., 1968; Holmgren, 1968). COLE may be used to make inferences about shrink-swell capacity and clay mineralogy, but it does not include irreversible shrinkage, such as that occurring in organic soils and some andic soils. Certain soils with relatively high contents of smectite clay have the capacity to swell significantly when moist and to shrink and crack when dry. This shrink-swell potential is important for soil physical qualities (e.g., large, deep cracks in dry seasons) as well as for genetic processes and soil classification (Buol et al., 1980).

Calculations

COLE can be expressed as percent:

$$LEP = COLE \times 100$$

LEP = linear extensibility percent

Note: LEP is not the same as LE. In soil taxonomy, linear extensibility (LE) of a soil layer is the product of the thickness (cm) multiplied by the COLE of the layer in question. The LE of a soil is defined as the sum of these products for all soil horizons (Soil Survey Staff, 2014).

Ratios and Estimates Related to Particle-Size Analysis, Bulk Density, and Water Retention (3D)
Coefficient of Linear Extensibility (COLE) (3D4)
Air-Dry or Oven-Dry to 33-kPa Tension (3D4a)

Introduction

The following equations outline how the KSSL calculates COLE for the whole soil (air-dry or oven-dry to 33-kPa suction). COLE is reported in units of cm cm^{-1}.

Calculations

Calculate COLE as follows if coarse fragments are present:

$$COLE_{ws} = \{1 / [Cm \times (Db_{33<2mm} / Db_{d<2mm}) + (1 - Cm)]\}^{1/3} - 1$$

$COLE_{ws}$ = Coefficient of linear extensibility on a whole-soil base

$Db_{33<2mm}$ = Bulk density at 33-kPa water content on a <2-mm base (g cm^{-3})

$Db_{d<2mm}$ = Bulk Density, oven-dry or air-dry, on a <2-mm base (g cm^{-3})

Cm = Coarse fragment (moist) conversion factor

- If no coarse fragments are present, Cm = 1.
- If coarse fragments are present, calculate Cm as follows:

$Cm = Vol_{<2mm} / Vol_{whole}$

- $Vol_{<2mm}$ = Volume moist <2-mm fabric (cm^3)
- Vol_{whole} = Volume moist whole soil (cm^3)

Alternatively: $Cm = (100 - Vol_{>2mm}) / 100$

- $Vol_{>2mm}$ = Volume percentage of the >2-mm fraction

If no coarse fragments are present, the previous equation reduces to the following:

$COLE_{ws} = (Dbd_{<2mm}/Db33_e)^{⅓} - 1$

$COLE_{ws}$ = Coefficient of linear extensibility on a whole-soil base

$Dbd_{<2mm}$ = Bulk Density, oven-dry or air-dry, on a <2-mm base (g cm^{-3})

$Db_{33<2mm}$ = Bulk Density at 33-kPa water content on a <2-mm base (g cm^{-3})

Note: If no coarse fragments are present, Cm = 1.

References

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Ratios and Estimates Related to Particle-Size Analysis, Bulk Density, and Water Retention (3D)
Water Retention Difference (WRD) (3D5)

Introduction

Water retention difference (WRD) is a calculated value that denotes the volume fraction for water in the whole soil that is retained between 1,500-kPa suction and an upper limit of usually 33- or 10-kPa suction. The volume of rock fragments is considered a filler that has no appreciable porosity or permeability and is unable to contain water. WRD does not allow for restriction of roots from the soil layer or osmotic pressure.

Scope and Application

Calculating WRD is considered the initial step in approximating available water capacity (AWC).

- The upper limit (lower suction) is selected so that the volume of water retained approximates the volume of water held at field capacity.
- The 10-, 33- and 1,500-kPa gravimetric water contents are then converted to a whole-soil volume basis by multiplying by the bulk density (Db_{33}) and adjusting downward for the volume fraction of any rock fragments in the soil.
- The lower suctions, e.g., 10- or 5-kPa, are used for coarse materials.

Refer to Soil Survey Staff Division Staff (1993) and Grossman et al. (1994) for additional discussion on coarse materials and the significance of soil water content at lower suctions and for suggestions related to the selection of these lower suctions for the determination of water retention difference (WRD).

Ratios and Estimates Related to Particle-Size Analysis, Bulk Density, and Water Retention (3D)
Water Retention Difference (WRD) (3D5)
Between 33-kPa and 1500-kPa Tension (3D5a)

Scope and Application

The KSSL calculates the water retention difference (WRD) between 33- and 1,500-kPa suctions in the whole soil by the equations below. WRD is reported as centimeters of water per centimeter of depth of soil (cm cm^{-1}). The numbers do not change when other units, e.g., in in^{-1} or ft ft^{-1}, are needed.

Calculations

Water Retention Difference, whole soil

WRD is reported as cm cm^{-1} and has W_{33} as the upper limit of suction. WRD on a whole-soil basis is calculated as follows:

$$WRD_{ws} = [(W_{33<2mm} - W_{1500<2mm}) \times (Db_{33<2mm}) \times Cm] / (Pw \times 100)$$

WRD_{ws} = Volume fraction (cm^3 cm^{-3}) of water retained in the whole soil between 33-kPa and 1,500-kPa suction, reported in cm cm^{-1}

$W_{33<2mm}$ = Weight percentage of water retained at 33-kPa suction on a <2-mm soil basis

$W_{1500<2mm}$ = Weight percentage of water retained at 1,500-kPa suction on a <2-mm soil basis

- Note: If available, moist 1,500-kPa (method 3C2a1b) is the first option in the WRD calculation; otherwise, dry 1,500-kPa (method 3c2a1a) is used.

$Db_{33<2mm=}$ Bulk density at 33-kPa water content on a <2-mm base (g cm^{-3})

Pw = Density of water (1 g cm^{-3})

Cm = Coarse fragment material conversion factor

- Note: If no coarse fragments are present, Cm = 1. If coarse fragments are present, calculate Cm as follows:
- $Cm = Vol_{<2mm} / Vol_{whole}$
  - $Vol_{<2mm=}$ Volume moist <2-mm fabric (cm^3)
  - Vol_{whole} = Volume moist whole soil (cm^3)
- Alternatively: $Cm = (100 - Vol_{>2mm}) / 100$
  - $Vol_{>2mm}$ = Volume percentage of the >2-mm fraction.

Ratios and Estimates Related to Particle-Size Analysis, Bulk Density, and Water Retention (3D)

Water Retention Difference (WRD) (3D5)

Between 10-kPa and 1500-kPa Tension (3D5b)

Scope and Application

This method is used to calculate the Water Retention Difference (WRD) using suctions between 10 kPa (W_{10}) and 1,500 kPa (W_{1500}). This WRD value can be calculated by substituting W_{10} in place of W_{33} in the equation for method 3D5a. W_{10} may be used as the upper limit of plant-available water for coarse soil materials.

Calculation

$WRD_{ws} = [(W_{10<2mm} - W_{1500<2mm}) \times (Db_{33<2mm}) \times Cm] / (Pw \times 100)$

See method 3D5a above for additional information.

Ratios and Estimates Related to Particle-Size Analysis, Bulk Density, and Water Retention (3D)
Water Retention Difference (WRD) (3D5)
Between 33-kPa Rewet and 1500-kPa (Air-Dry) Tension (3D5c)

Scope and Application

This method is designed for use in organic materials and calculates the Water Retention Difference (WRD) between 33-kPa rewet (W_r) and W_{1500}. This WRD value can be calculated by substituting W_r in place of W_{33} in the equation for method 3D5a.

Calculation

$WRD_{ws} = [(W_{r<2mm} - W_{1500<2mm}) \times (Db_{33<2mm}) \times Cm] / (Pw \times 100)$

See method 3D5a above for additional information

References

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Ratios and Estimates Related to Particle-Size Analysis, Bulk Density, and Water Retention (3D)
1500-kPa Water Content/Total Clay (3D6)

Introduction

In the past, the ratios of 1,500-kPa water to clay were reported as g g^{-1}. This approach—reporting a ratio—provides information on the influence of quantity and type of clay on water retention.

Calculation

Divide the 1,500-kPa water retention (method 3C2a) by the total clay percentage (method 3A1a). This ratio is reported as a dimensionless value. For more detailed information on the application of this ratio, refer to Soil Survey Staff (2011 and 2014).

Ratios and Estimates Related to Particle-Size Analysis, Bulk Density, and Water Retention (3D)
Total Silt Fraction (3D7)

Scope and Application

Total silt is a soil separate that has particle diameter of 0.002 to 0.05 mm. The KSSL determines the fine silt separate by pipette analysis and the coarse silt separate by difference (3A1a). Total silt is reported as a weight percentage on a <2-mm basis (3D7). For more information on these data, refer to Soil Survey Staff (2011).

Ratios and Estimates Related to Particle-Size Analysis, Bulk Density, and Water Retention (3D)
Total Sand Fraction (3D8)

Scope and Application

Total sand is the sum of the very fine sand (VFS), fine sand (FS), medium sand (MS), coarse sand (CS), and very coarse sand (VCS) fractions. The rationale for five subclasses of sand and the expansion of the texture classes of sand, e.g., sandy loam and loamy sand, is that the sand separates are the most visible to the naked eye and the most detectable to the field soil scientist by "feel."

Total sand is a soil separate that has particle diameter of 0.05 to 2.0 mm and is reported as a weight percentage on a <2-mm basis. The KSSL determines the sand fractions by sieve analysis (3A1a). For more information on the application of these data, refer to Soil Survey Staff (2011).

Ratios and Estimates Related to Particle-Size Analysis, Bulk Density, and Water Retention (3D)
2- to 5-mm Fraction (3D9)

Scope and Application

Coarse fractions that have particle diameter of 2 to 5 mm correspond to the "fine pebbles" rock-fragment division (Soil Survey Division Staff, 1993). The 2- to 5-mm division corresponds to the size of openings in the no. 10 and no. 4 screens (2.0 and 4.76 mm) used in engineering.

The KSSL determines coarse fractions that have particle diameter of 2 to 5 mm by method 3A2. Coarse fractions that have particle diameter of 2 to 5 mm are reported as a weight percentage on a <75-mm basis (3D9). For more information on coarse fractions that have particle diameters >2-mm and on the application of these data, refer to Soil Survey Staff (2011).

Ratios and Estimates Related to Particle-Size Analysis, Bulk Density, and Water Retention (3D)
5- to 20-mm Fraction (3D10)

Scope and Application

Coarse fractions that have particle diameter of 5- to 20-mm correspond to the "medium pebbles" rock fragment division (Soil Survey Division Staff, 1993). The 5- to 20-mm divisions correspond to the size of opening of the no. 4 and ¾-in screens (4.76 and 19.05 mm) used in engineering.

The KSSL determines coarse fractions that have particle diameter of 5 to 20 mm by procedures outlined in method 3A2. Coarse fractions that have particle diameter of 5 to 20 mm are reported as a weight percentage on a <75-mm basis. For more information on these data, refer to Soil Survey Staff (2011).

Ratios and Estimates Related to Particle-Size Analysis, Bulk Density, and Water Retention (3D)
20- to 75-mm Fraction (3D11)

Scope and Application

Coarse fractions that have particle diameter of 20 to 75 mm correspond to the "coarse pebbles" rock fragment division (Soil Survey Division Staff, 1993). The 20- to 75-mm divisions correspond to the size of openings of the ¾-in and 3-in screens (19.05 and 76.1 mm) used in engineering.

The KSSL determines coarse fractions that have particle diameter of 20 to 75 mm by procedures outlined in method 3A2. Coarse fractions that have particle diameter of 20 to 75 mm are reported as a weight percentage on a <75-mm basis (method 3D11). For more information on these data, refer to Soil Survey Staff (2011).

Ratios and Estimates Related to Particle-Size Analysis, Bulk Density, and Water Retention (3D)
0.1 to 75-mm Fraction (3D12)

Scope and Application

These data are listed to assist in taxonomic placement by particle-size class; e.g., to distinguish loamy from silty particle-size classes.

The KSSL determines coarse fractions that have particle diameter of 0.1 to 75 mm by procedures outlined in methods 3A1a and 3A2. The 75-mm division corresponds to the size of opening in the 3-in screen (76.1 mm) used in engineering. Coarse fractions that have particle diameter of 0.1 to 75 mm are reported as a weight percentage on a <75-mm basis (3D12). Refer to Soil Survey Staff (2014, 2011) for additional discussion on particle-size classes.

Ratios and Estimates Related to Particle-Size Analysis, Bulk Density, and Water Retention (3D)
>2-mm Fraction (3D13)

Scope and Application

Coarse fractions that have particle diameter of >2-mm are reported as a weight percent on a whole-soil basis (method 3D13). The KSSL determines coarse fractions that have particle diameter of >2-mm by a procedure outlined in method 3A2. For more information on these data, refer to Soil Survey Division Staff (1993) and Soil Survey Staff (2011, 2014).

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Micromorphology (3E)
Thin Sections (3E1)
Preparation (3E1a)

1. Introduction to Thin Section Preparation

Micromorphology is used to identify fabric types, skeleton grains, weathering intensity, and illuviation of argillans and to investigate genesis of soil or pedological features.

2. Scope and Field of Application

Characteristics that can be identified individually through separate analyses include grain size, organic content, and clay content. Thin-section analysis and the study of micromorphology can provide information on in situ conditions of clay films around grains and permineralization of carbonates or oxides along drainage or root paths. Orientation of the clod is critical during thin sectioning if the project focus concerns redox features or the lateral flow of water through a profile.

3. Principle

A soil clod is impregnated with a polymer resin (Innes and Pluth, 1970). A flat surface of the soil sample is glued to a glass slide, and the sample is cut and ground to a thickness of ≈30 µm. The thin section is examined with a petrographic microscope (Anon., 1987; Cady et al., 1986).

3.1 Interferences

Sample must be completely dry to ensure complete impregnation by the resin. If impregnation is not complete, the sample disintegrates during preparation.

Oven drying at temperatures >40º C can result in shrinkage of soil material and creation of artifacts, especially in soils that have a high content of clay or organic matter.

Air bubbles interfere with petrographic examination. The number of bubbles can be minimized by using proper temperature, pressure, and technique.

Final thickness of the sample needs to be 30 µm to enable accurate mineral identification. To ensure correct thickness, the slide can be examined under polarized light. If the quartz-interference colors are of first order, i.e., white, gray, and pale yellow, the sample is ≈30 µm (Anon., 1987).

Avoid using water in the slurry if the sample contains soluble salts.

4. Apparatus

4.1 Petro-thin, thin sectioning system

4.2 Metallographic polisher with cast-iron laps

4.3 Diamond-edged saw
4.4 Electric oven
4.5 Hot plate with temperature control; or a petrographic slide warmer
4.6 Polarizing microscope
4.7 Vacuum, 0.8-bar (80 kPa)
4.8 Desiccator
4.9 Disposable container with height and width greater than the sample (Tin or paper cup to hold sample during impregnation)
4.10 Porcelain crucibles
4.11 Standard petrographic slides
4.12 Cover glass
4.13 Silicon carbide abrasives
4.14 Squares of thick, rough-textured plate glass, 305-mm
4.15 Metal probes or dissecting needles
4.16 Small forceps
4.17 Art brush
4.18 Razor blade
4.19 Small chisel, probe (ice pick), ordinary hacksaw, or jeweler's hacksaw

5. Chemicals

5.1 Petrographic resin, hardener, and dye if needed (Several commercial choices are available.)
5.2 Ethylene glycol (CAS# 107-21-1)

6. Health and Safety

Personal Protective Equipment (PPE).—Use disposable gloves with appropriate polymer rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Use polymer-appropriate disposable gloves when grinding in oil or glycol. Thoroughly wash hands after handling reagents or samples.

Use adequate ventilation when mixing, heating, and applying resins. Use tongs or heat resistant gloves when handling hot slides or resins.

7. Sample Preparation

7.1 Clods should represent a given horizon and be approximately the size of a fist or a potato (≈250 to 550 cm^3 in volume). They should be carefully preserved in saran, bagged, and boxed for shipment to the KSSL. Additional resources include method 1A1b (Field Sample Collection and Preparation) and the video tutorial "How to Sample Bulk Density in the Field" (https://youtu.be/E7BSZrJ-TDw).

7.2 Mark the top of clod with a thumb tack, staple, or pin to ensure proper orientation. Select clods from bulk samples if orientation is not important. Do not dip clods for thin section in saran; coatings interfere with the grinding after the clod is sectioned.

8. Procedure

8.1 Sample Preparation

8.1.1 Consult the project analysis request to determine the sample size for epoxy impregnation and sectioning. Ideal sample size is approximately 5 cm^3 to no more than 10 cm^3. If the sample is friable, the whole core or clod can be impregnated. Trim the sample; cause as little impact on the soil structure as possible. Ideal tools include a small chisel to wedge sample from the clod (especially for soils that have a high clay content); a jeweler's saw; a small, thin-bladed hacksaw; or a probe (ice pick).

8.1.2 Place the soil sample in a disposable, heat- and chemical-resistant weighing boat or tin. Collect an initial sample weight. Place sample in oven at 40 °C. Weigh sample daily until weight is constant. Time will vary depending on sample size and clay content. Sample could be treated with acetone or freeze-dried as an alternative to being oven-dried.

8.1.3 Connect a glass desiccator to house vacuum and ensure vacuum is closed. Take sample from oven and place in desiccator. Leave sample in tin or paper boat. Evacuate the air from the desiccator, ensuring sample does not absorb ambient moisture.

8.2 Sample Resin Impregnation

8.2.1 Prepare epoxy resin in a fume hood. Follow manufacturer's directions for amounts and proportions of resin to hardener. Do not incorporate bubbles into the epoxy while mixing. Mix resin and hardener until uniform.

8.2.2 Open the desiccator containing the dry samples and slowly add the epoxy resin. Initially add enough epoxy to cover the bottom third of the sample. Slowly apply vacuum and observe the rate of imbibition, which will vary based on soil texture. Do not add more epoxy until sample begins taking in resin. Air bubbles may become trapped in the sample porosity. Repeat adding epoxy until the resin has penetrated the thickness of the sample and the sample is completely enclosed by resin.

8.2.3 Allow sample to cure overnight in the oven at 110 °C. Ensure the oven is vented. Allow samples to cool after curing. Disposable containers can be cut away from sample after cooling.

8.3 Cutting and Rough Grinding

8.3.1 With the thinnest, least aggressive saw blade available, cut the epoxy cured sample block into 13-mm wide sections to fit on a regular petrographic slide.

8.3.2 Using a slurry of successively finer abrasives, grind one surface smooth on the revolving lap until the surface is highly polished. Specific grit-size lap wheels can be used, or a slurry of abrasive can be composed in finer succession.

8.3.2.1 Do not use water in the slurry if the sample contains soluble salts. If the surface of the sample plucks or peels when exposed to water, dry the sample, trim or grind the damaged end smooth, and continue grinding with abrasives while using mineral oil, oil-based solvents, or ethylene glycol as lubricant.

8.3.2.2 Use polymer-correct disposable gloves when grinding in oil or glycol.

8.3.3 Clean the sample free of all abrasive material. An ultrasonic bath is recommended. Dry thoroughly.

8.4 Sample Glass Mounting

8.4.1 Attach the billet to the textured side of the slide using thin section epoxy with a refractive index of 1.54. Follow manufacturer's specifications for mixing.

8.4.2 Apply a thin layer of epoxy to the slide and billet. Slowly lower billet on the slide. Apply slight pressure and adjust the billet on the slide removing any air bubbles or excess epoxy.

8.4.3 Clean the glass of excess cement. Sample can be clamped to slide. Follow manufacturer's guide for epoxy curing time and temperature. Cure billets in vented oven.

8.5 Final Grinding

8.5.1 Before beginning, review manual for proper operation and adjustments of thin section machine.

8.5.2 Remove the excess sample material (cut off excess so sample remaining on the glass is <2 mm). Retain billet for additional sectioning.

8.5.3 Grind the sample to ≈30 µm with the diamond lapidary. Examine the section frequently under a polarizing microscope during the final stages of grinding. If quartz is present in the sample, use it to judge thickness. If the sample is ≈0.030 mm thick, the quartz interference colors are of the first order, i.e., white, gray, and pale (straw) yellow.

8.5.4 If manufacturer's thin sectioning equipment is not available, trim the mounted sample with a diamond-edged saw blade to a thickness of 50 to 100 µm. Begin with the coarse abrasive and lap by hand until

the sample is relatively thin. Use successively finer abrasives. Use the finest abrasive to finish grinding on ground-glass plates. Wash the section free of abrasive and dry thoroughly.

8.5.4.1 Note: Care and considerable practice are needed to handle an almost-finished section without over-grinding. Slides should be made in duplicate if the technician is less experienced or just learning the process.

8.6 Seating Cover Glass

8.6.1 Heat the finished section and the cover slip to ≈40 °C. Spread a small quantity of epoxy over the surface of the thin section and the cover slip. Wait a few seconds for the air bubbles to escape. Place the cover glass obliquely on one end of the section and lower very slowly. If any air bubbles remain, remove them by pressing lightly on the cover glass with a soft eraser or rubber policeman.

8.6.2 As the section cools, but before the plastic hardens, use a razor blade to remove excess epoxy on edge of thin section slide. After the epoxy hardens, remove the final thin film with the razor blade. If the film is too thick, the slide may break when the epoxy is removed.

8.7 In special circumstances, very dense soils and soils that have clay fractions that contain >30% montmorillonite require special handling.

8.7.1 Use oil-based lubricating media only.

8.7.2 Both oven drying and drying with acetone may be required to fully dry sample.

8.7.3 Once sample is impregnated, corundum sandpaper sheets or a lapidary wheel can be used to dry-grind one face of the sample by hand.

8.7.4 Use a figure-eight motion for best results. Use successively finer abrasives and continue to grind until the surface is highly polished. Proceed with the standard mounting technique.

9. Calculations

None. Describe the thin section as outlined in method 3E1b.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Anon. 1987. Petrographic sample preparation for micro-structural analysis. Buehler Digest, Vol. 24, No.1.

Innes, R.P., and D.J. Pluth. 1970. Thin section preparation using an epoxy impregnation for petrographic and electron microprobe analysis. Soil Sci. Soc. Am. Proc. 34:483–485.

Micromorphology (3E)
Thin Sections (3E1)
Interpretation (3E1b)

1. Introduction to Thin Section Interpretation

Micromorphology is defined as the study of soils or regolith samples in their natural undisturbed arrangement using microscopic techniques (Cady et al., 1986; Stoops, 2003). This study uses thin sections of soil fabric to identify types and sequences of active or past processes occurring in soils via identification of coatings, fabric types, skeletal grains, and weathering intensity. It is an ideal tool to investigate genesis of soil or pedological features. It is most useful when combined with other field data, such as landscape and soil morphological descriptions, and laboratory data (Cady, 1965; Stoops et al., 2010).

The science and terminology of microfabric analysis were initially documented by Kubiena in 1938. Since then, important publications documenting terminology and methodological descriptions for producing thin sections have been published. They are sited in the reference section of this method in order to link past and present descriptions.

2. Scope and Field of Application

Thin sections are primarily used to gain information about soil fabric and component arrangement. Sample preparation procedures used for grain studies destroy or eliminate the arrangement of soil components during the separation of sand, silt, and clay, which are key features of micromorphological analysis. Mineral quantification is less important in micromorphology. More focus is directed to recognition of aggregates, grain weathering, secondary pseudomorphs, and pedofeatures, such as coatings, infillings, or nodules.

Examination of sections using a polarizing light microscope can be considered an extension of field morphological studies. Some features, such as depletions and concentrations of redoximorphic features, are observable without magnification. Petrographic microscopy provides additional information, thereby allowing the development of genetic theories of feature formation based on mineralogy, nodule morphology, or characteristics of coatings.

3. Principle

The analyst should be familiar with the project focus and scan the overall features of a thin section to determine those features that require emphasis. Initial scanning should include all thin sections from a soil profile or all those related to a particular problem. Different kinds of illumination should be used with each magnification.

Using current descriptive terminology, address mineral components, groundmass, porosity, coatings, and other features that provide keys to soil development.

The degree and quality of optical effects depend on the purity, continuity, and orientation of the mineral or clay body.

In optical mineralogy, the speed of light that travels in the direction of the crystallographic c-axis vibrates parallel to the a-axis and is almost the same as that of light that vibrates parallel to the b-axis. Therefore, the refractive indices are very close, and the interference effects in cross-polarized light are small (birefringence is weak and interference colors are white, yellow, or brown) when observed along the c-axis (observed when the grain is lying flat on the microscope stage or in the thin section). Light that vibrates parallel to the c-axis travels faster than in other directions. Therefore, the refractive index is lower. If the edge of the crystal or aggregate of crystals is viewed along the a-b plane between crossed polarizers, two straight extinction positions are viewed and interference colors are stronger (high birefringence). If clay-sized grains are concentrated and organized so that most of the plates are parallel, these optical effects can be observed.

3.1 Interferences

Thin sections that are not ground to 30 µm can lead to mineral misidentification and obscure finer features, such as clay coatings. Check thickness by observing quartz interference colors. The section is ≈30 µm if the colors are first order; i.e., white, gray, and pale (straw) yellow.

Grains that are less than 20 µm (fine silt and clay) in diameter appear stacked and cannot be viewed individually. Similarly, pores smaller than 20 to 30 µm cannot be seen clearly.

A thin section is a two-dimensional slice through a three-dimensional body. The shapes of mineral grains and structural features are viewed in one plane, and the true shapes must be inferred.

4. Apparatus

4.1 Petrographic microscope

5. Chemicals

None.

6. Health and Safety

No specialized safety equipment is required for microscope slide interpretation.

7. Sample Preparation

Refer to method 3E1a for thin section preparation. A soil clod is impregnated with a polymer resin. A flat surface of the soil sample is glued to a glass slide, and the sample is cut and ground to a thickness of ≈30 µm.

8. Procedure

8.1 Description of Microfabrics

8.1.1 Terminology has developed for the description of soil fabric and constituents. Micromorphological descriptions commonly contain terminology from different sources to describe properties of the fabric. Historical contributors are included in the Reference section of this method. The terminology emphasized here is from Stoops (2003 and 2010).

8.1.2 The commonly described components of thin section are soil microstructure and porosity, groundmass (mineral and organic constituents), and pedofeatures. Groundmass is considered the base material of coarse and fine materials. Pedofeatures are distinct fabric units that are concentrated and distinct from the groundmass.

8.2 Components of Thin Section Descriptions and Interpretations

8.2.1 Soil Microstructure: Describes the size, shape, and arrangement of particles and voids in soil material. It is applicable to both aggregated and non-aggregated soil material. If aggregates are present, types of peds (spheroidal, blocky, plates, or prisms aggregates) can be described as well as the degree of ped separation, size, accommodation, roughness, and pattern.

8.2.1.1 Voids: The space between solid materials which form a continuum in soil but are treated as individuals and described by morphology.

Types of voids:

- Chambers: Smooth walled voids intersected by channels
- Packing voids: Formed from the loose packing of unaccommodated faces of grains or between peds or other compound individuals (fig. 3E1b–1)
- Vughs: Generally equidimensional voids with irregular shapes (fig. 3E1b–2)
- Vesicles: Spherical voids with smooth perimeters (fig. 3E1b–3)
- Channels: Elongated voids (fig. 3E1b–4)
- Planes: Planer, flat voids (fig. 3E1b–5)

8.2.1.2 In addition to type, other aspects of the voids that may be described include size, abundance, roughness of walls, accommodation, and arrangement.

8.2.1.3 Nomenclature for microstructures has been developed based on ped and void types. The list of microstructure types is fairly extensive. Examples include vughy

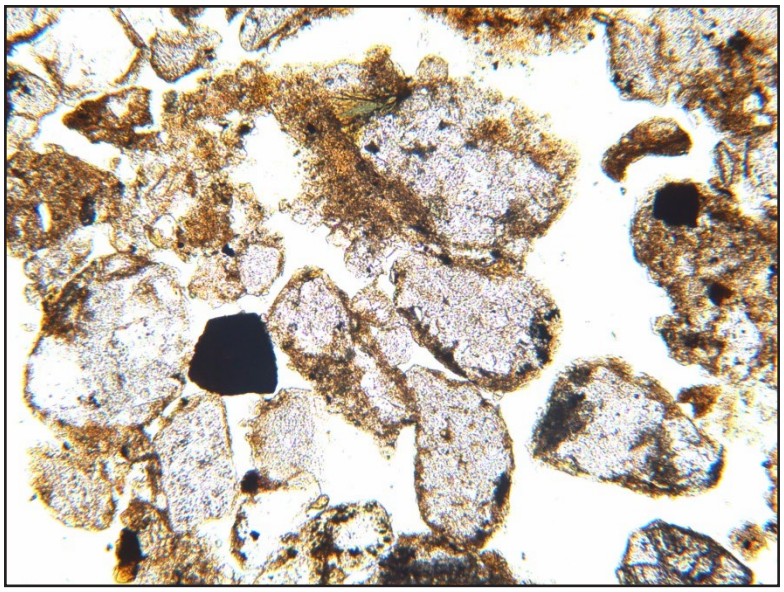

Figure 3E1b–1.—Simple packing voids, partially coated with fine materials, under plane-polarized light. These voids arise from the loose packing of soil components. Material is from a Bt1 horizon in an Endlich soil (pedon 99P0001; Colorado). Frame width is 1.1 mm.

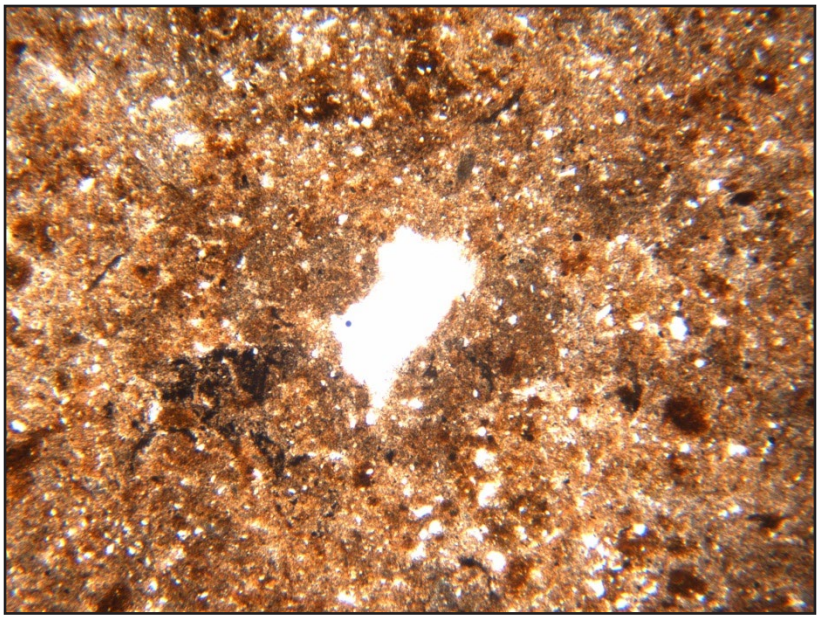

Figure 3E1b–2.—A void described as a vugh. Vughs are semi-equidimensional, irregular voids that are not interconnected with other voids. Material is from a Bkss horizon of a Typic Epiaquert in Brazoria County, Texas (pedon 98P0582). Horizon composition: 52% clay, principally smectite, and 42% silt. COLE is 0.011. Frame width is 2.5 mm. Light is plane-polarized.

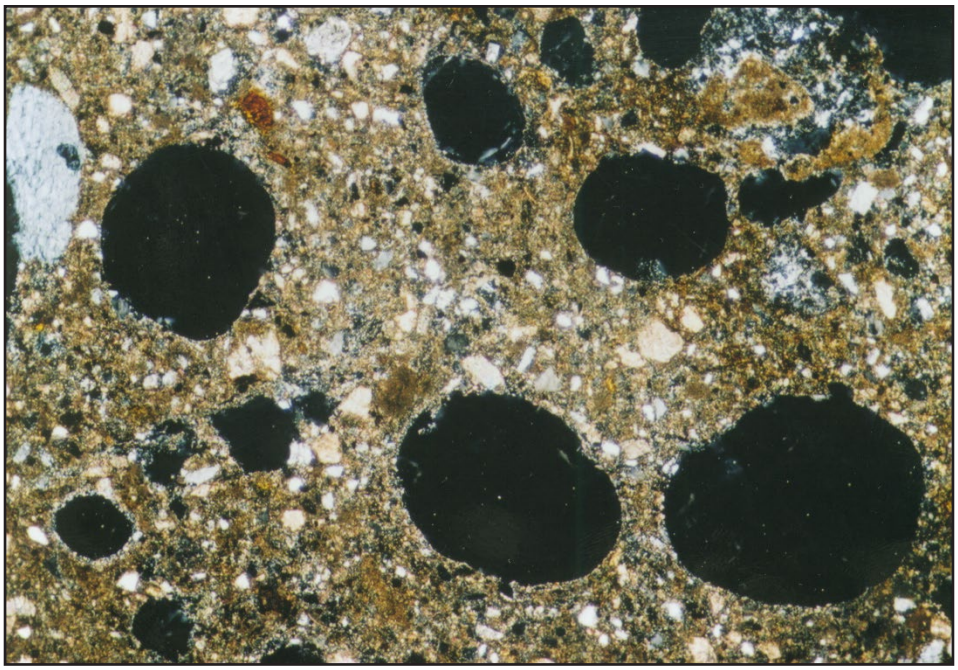

Figure 3E1b–3.—Walls consisting of "smooth, simple curves" indicate that this void is a vesicle. These vesicles formed in the thin surface crust. Material is from an A1 horizon of a Dera soil, which is a Typic Haplargid, in Utah (pedon 81P0610). Frame width is 3.2 mm. Light is cross-polarized.

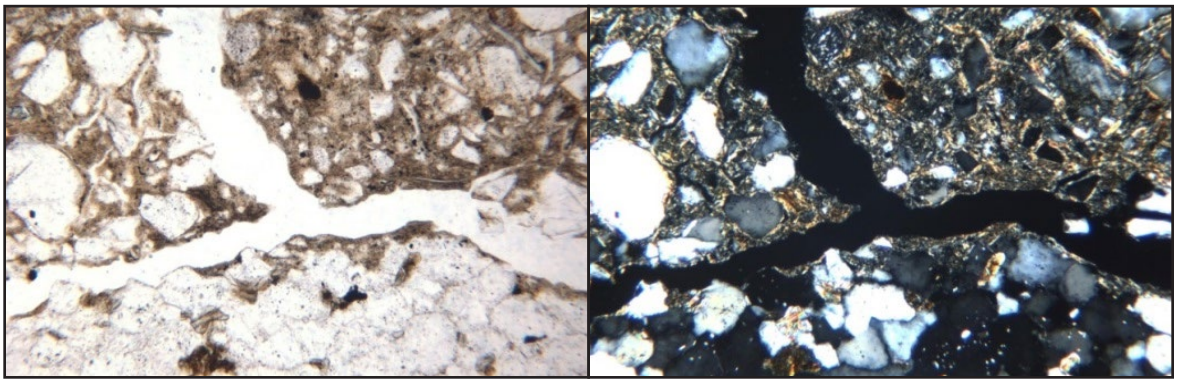

Figure 3E1b–4.—A bifurcated channel. Note the oriented clay around coarse grains (granostriated b-fabric). Material is from a Bt1 horizon in a Brod soil, which is an Ustollic Haplocryalf, in Montana (pedon 03N1014). Frame width is 1.1 mm. Light is plane-polarized on the left and cross-polarized on the right.

microstructure, granular microstructure, and lenticular microstructure. The most common types are listed in Stoops (2003).

8.2.2 Soil Microstructure Interpretation

8.2.2.1 Micromorphological studies can measure porosity and predict soil water content at various suctions and

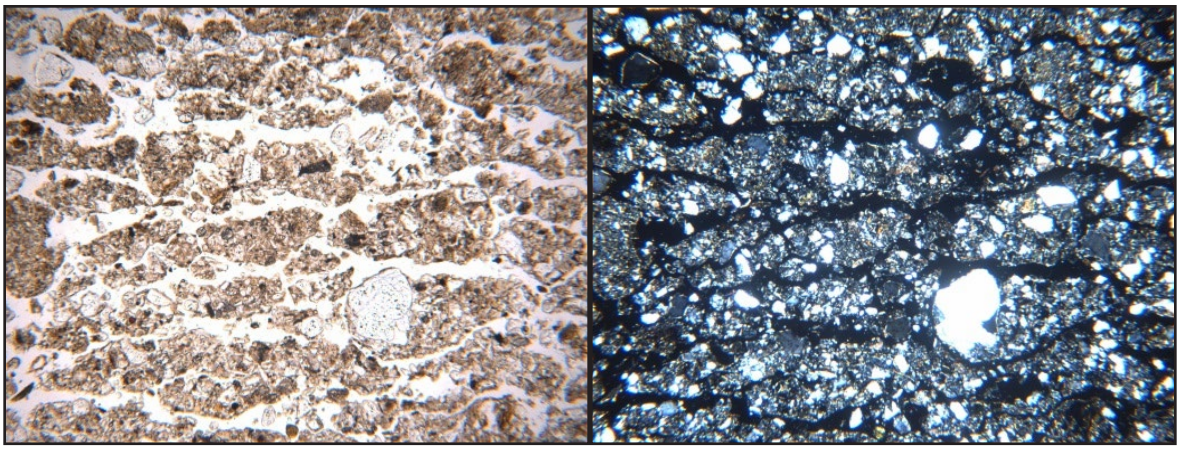

Figure 3E1b–5.—Voids termed "planes," which developed in the platy structure of an A1 horizon in a Frisite soil in Wyoming (pedon 98P0453). Frame width is 2.5 mm. Light is plane-polarized on the left and cross-polarized on the right.

hydraulic conductivity. In thin section studies of voids in sands and sandy soils, there is a close correlation between micromorphology and suction methods (Swanson and Peterson, 1942). However, in those soils in which the volume changes with water content, pore-size distribution is undefined and no constant void-size distribution exists (Brewer, 1976). Furthermore, several invalidated assumptions relating porosity to permeability are common (Nielsen et al., 1972, p. 11). The invalid assumptions that especially relate to soil fabric are "no pores are sealed off," "pores are distributed at random," and "pores are generally uniform in size." Vepraskas et al. (1991) used micromorphology to demonstrate that fractures and veins in saprolite were generally plugged with clay and oxides and that most water flow through the saprolite was via root channels.

8.2.2.2 A study of soil voids may be useful in predicting the clay activity and shrink-swell behavior of soils. In an experimental study of soil microfabrics by anisotropic stresses of confined swelling and shrinking, Jim (1986) showed that an increase in the activity and content of the clay fraction is correlated to a drastic decrease in void volume, especially the >30-µm voids. Furthermore, the void shapes change from compound packing voids to planar voids and vughs. As stress increases from shrink-swell forces, aggregates become flattened at contacts, resulting in more angular aggregates and eventually fused compound units.

8.2.2.3 The size, shape, and arrangement of skeleton grains determine the nature of simple packing voids, but the origin of compound packing voids is not as straightforward. The unaccommodated peds of the compound packing voids may be formed by faunal excreta, shrink-swell action, human activities, or unknown causes.

8.2.2.4 Vughs typically occur in soil materials that have a wide range in size of particles, including silicate clays. Some vughs form by the weathering and removal of carbonate, and others form by faunal activity or the normal packing of plasma and skeleton grains. Blevins et al. (1970) showed that porosity decreased around trees due to root pressure on the surrounding soil. Balbino et al. (2002) found that the loss of porosity on soils cleared of their native savanna vegetation to develop pastures resulted from the loss of earthworms and other fauna rather than from the change in land use. Voids characterized as planes are produced in relatively uniform fine-textured soils by a relatively regular system of cracking upon drying (Brewer, 1976). Once formed, these joint planes tend to open in the same place during successive drying cycles.

8.2.2.5 Vesicular pores are non-connecting spherical pores that typically occur in arid region soils (Nettleton and Peterson, 1983). The process to form these vesicles results from sealing of the soil surface and the entrapment of air during cycles of wetting and drying (Lapham, 1932; McFadden et al., 1998; Turk and Graham, 2011; Williams et al., 2012). This cycle is also responsible for creation of polygonal cracking and the creation of columnar structure. Over time, the vesicles collapse and form planar voids (Turk and Graham, 2011). Laboratory studies verify this phenomenon (Springer, 1958). If soils that have a high content of silt are allowed to dry before each irrigation, the vesicle size increases with the number of irrigations (Miller, 1971). Studies of infiltration rates and sediment production in rangeland in central and eastern Nevada found that the infiltration rates are lowest and the sediment yields are highest on sites that have vesicular surface horizons (Blackburn and Skau, 1974; Rostagno, 1989). The failure of most vesicles to connect to other voids and the low strength of the crust in which vesicles occur help to explain the low infiltration rates and high sediment yields.

8.2.3 Description of Groundmass

8.2.3.1 Groundmass is a general term for the coarse and fine materials present in the soils, inclusive of voids. Groundmass components form the base materials in the soil and reflect the lithology and weathering of the parent material. Groundmass can be considered the materials left after the identification of the pedofeatures, such as nodules and clay coatings. The term "groundmass" is used similarly to Brewer's (1976) term "s-matrix," although some differences exist (Stoops, 2003).

8.2.3.2 A description of groundmass should include the author's designated size limit between coarse (c) and fine (f) materials, c/f-related distribution, and characteristics of coarse material and fine material (micromass). The five "coarse-fine (c/f) related distribution patterns," as described by Stoops (2003), are intended to be broadly defined. There are no restrictions on material type, absolute size, orientation, granulation, or origin. The system may be used to describe the distribution of primary particles, e.g., quartz grains, as well as compound units, e.g., humic micro-aggregates. The size limit between coarse and fine units "floats." The variation is based on the individual soil. The coarser particles may be silt, sand, or gravel; whereas the finer material may be clay, silt, or sand. Figure 3E1b–6 shows the average textures, linear extensibilities (LE), and drained pore to filled pore (DP/FP) ratios of related distribution patterns.

8.2.3.3 The five coarse-fine (c/f) related distribution patterns are: monic, gefuric, chitonic, enaulic, and porphyric.

- Monic distribution: Fabric units of only one size group; e.g., pebbles, sand, lithic fragments (coarse monic), or clay (fine monic).
- Gefuric distribution: Coarser units linked by bridges of, but not surrounded by, finer material.
- Chitonic distribution: Coarser units surrounded by coatings of finer material (fig. 3E1b–7).
- Enaulic distribution: Larger units support one another, and the interstitial spaces are partially filled with aggregates of finer material (fig. 3E1b–8). The enaulic fabric consists of a greater amount of finer material than in either the gefuric or chitonic distributions.

Variable*

C/f Patterns	Chitonic	Enaulic	Close Porphyric	Single-Space Porphyric	Double-Space Porphyric	Open Porphyric
Clay, %	20C**	23BC	20C	25BC	34AB	41A
Silt & Clay, %	37D	50BC	40CD	54B	74A	84A
LE, %	4.4AB	2.2B	2.9AB	2.7AB	4.0AB	6.6A
DP/FP	1.1BC	1.3B	0.7CD	0.6CD	0.5D	0.3D
Nos.	8	26	23	112	53	94

* C/F Patterns are related distribution patterns of coarse and fine constituents, LE, linear extensibility; DP/FP, ratio of drained to filled pores at 33kPa suction.
** Means with the same letter are not significantly different at the 95% confidence level (SAS Institute, 1988).

Figure 3E1b–6.—Types of related distribution patterns and their physical properties. Frame width of each idealized kind of fabric is 0.5 mm. The lower size limit of coarse material in the c/f related distribution patterns was set at about 50 µm for most of the thin sections represented in the figure.

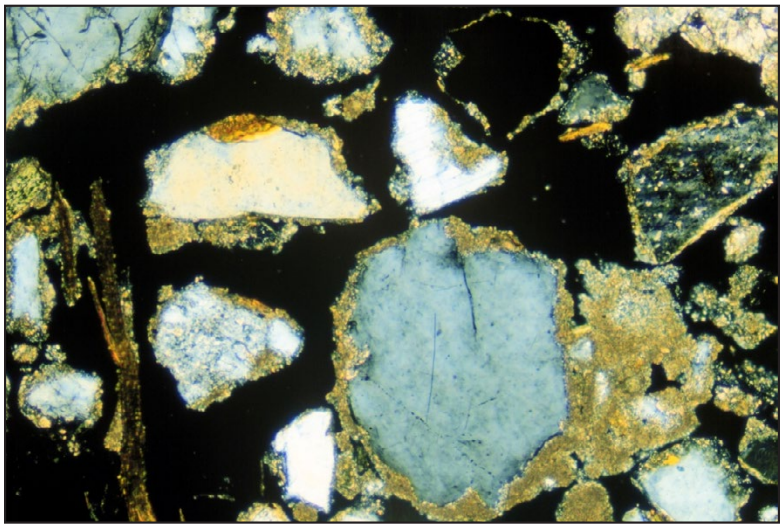

Figure 3E1b–7.—Calcium carbonate around quartz and feldspar grains in a chitonic c/f related distribution pattern. Material is from a Bkq2 horizon of a Cax soil in San Bernardino, California (pedon 97P0420). Frame width is 0.9 mm. Light is cross-polarized.

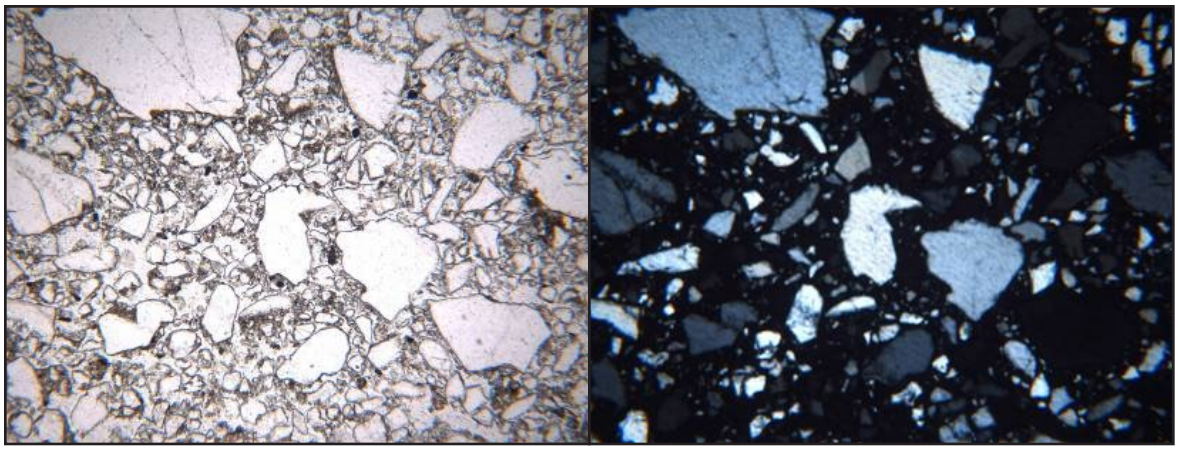

Figure 3E1b–8.—Enaulic c/f related distribution pattern. Material is from an E horizon of a Fuquay soil, which is a Kandiudult, in South Carolina (pedon 06N0830). Frame width is 2.5 mm. Light is plane-polarized on the left and cross-polarized on the right.

- Porphyric distribution: End member of the sequence. This distribution has coarse materials embedded in finer materials, and there is an absence of interstitial pores (fig. 3E1b–9). The porphyric distribution may be divided into types based on the spacing of the coarser units. Additional information about the coarser material can also be recorded; for example, mineralogy (composition), size, abundance, shape, color, roughness, and sorting.

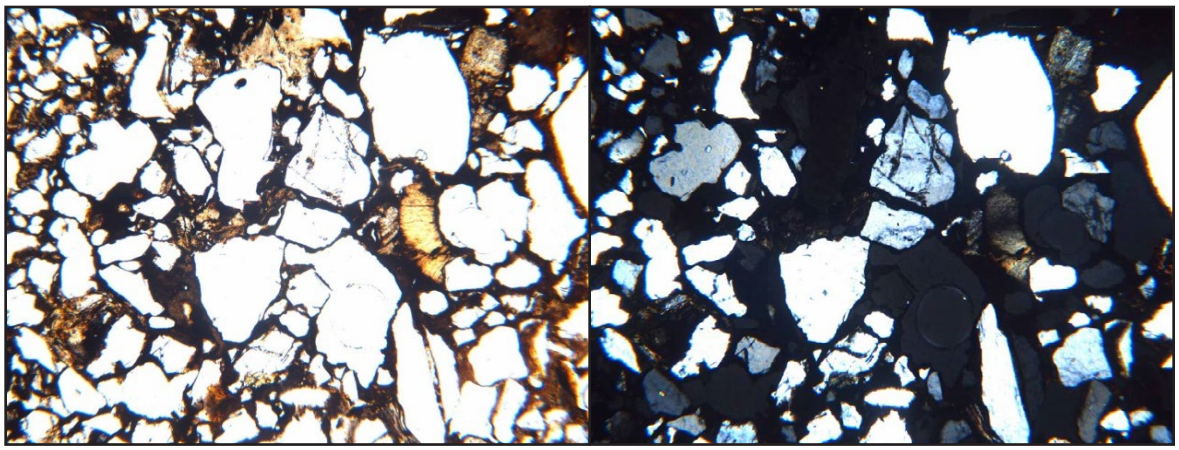

Figure 3E1b–9.—Horizon has close porphyric c/f related distribution and a micromass composed of kaolinite embedded with iron oxides. Note the yellow vermiform kaolinite in the right center of the image. This grain likely forms via in situ weathering of a sand-sized grain. Material is from a Btvx2 horizon of a Dothan soil (06N0831). Frame width is 2.5 mm. Light is plane-polarized on the left and cross-polarized on the right.

8.2.4 Related Distribution Patterns

8.2.4.1 The average properties of some related distributions are shown in figure 3E1b–6 (figure shown earlier in the method for description of groundmass). In an experimental study of soil microfabrics by anisotropic stresses of confined swelling and shrinking, Jim (1986) showed that with an increase in the activity and proportion of the clay fraction, the related distribution patterns alter from dominantly monic to enaulic to porphyric.

8.2.4.2 Some monic fabrics are inherited and include soil fabrics formed in sand dunes, sandy sediments deposited by streams and rivers, beach deposits, and gruss. Fauna can produce monic fabrics that are mostly fecal pellets. Monic fabrics also can form by fracturing and flaking of organic coatings in the upper B horizons of the Spodosols (Flach, 1960) and by freezing and thawing (Brewer and Pawluk, 1975).

8.2.4.3 Several kinds of finer material (micromass) can bridge the coarser particles (skeleton grains) to form gefuric related distribution patterns. Gefuric patterns are common in weakly developed argillic and spodic horizons and in some duripans. Bridges of material form between skeleton grains. Typically, the cement or clay is material that bonds covalently with skeleton grains. As the amount of cementing agent or clay increases, the next progression is the chitonic related distribution pattern (Pawluk, 1983). For example, silicate clays can bridge skeleton grains in some argillic horizons (gefuric c/f related distribution pattern) and subsequently develop complete coatings of clay with increasing illuviation (chitonic c/f related distribution pattern). These cements commonly include silica (fig. 3E1b–10), iron, aluminum, and organic matter (Chadwick and Nettleton, 1990).

8.2.4.4 In spodic horizons, monomorphic Al-Fe organic complexes develop and, with increasing amounts, grade from gefuric to chitonic to close porphyric (Wilson and Righi, 2010; Salem Avad et al., 1982). Even though organic matter has covalent bonds and usually surrounds grains, organic material can form pellets in void spaces between skeleton grains in some spodic horizons. These types of horizons form enaulic c/f related distribution patterns. These pellets are polymorphic materials, consisting of crumbs or granules of several forms of degraded plant materials (De Coninck and Righi, 1983).

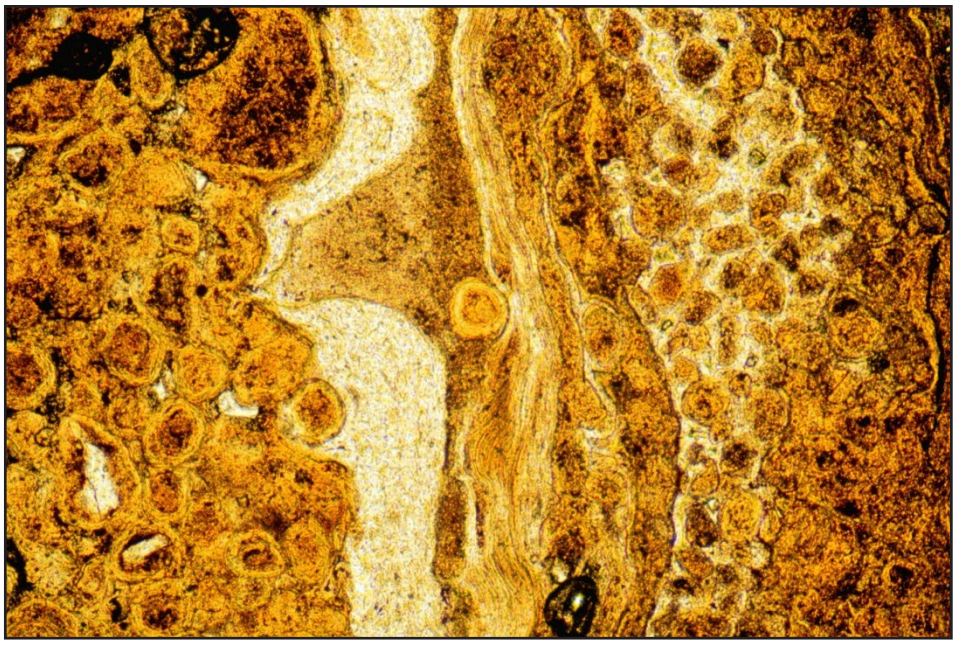

Figure 3E1b–10.—Horizon with duripan exhibiting silica cementation under plane-polarized light. Fabric has an opal and chalcedony laminar cap. The matrix above and below is composed of durinodes (non-crystalline silica) surrounded by moderately-oriented silicate clays. Clay can provide the initial absorption surface for silica in soil solution. The absorption of silica onto established silica phases leads to formation of nodules. Material is from a 2Bkqm horizon of a soil without a designated series name in Jefferson County, Oregon (pedon 87P0513). Frame width is 1.1 mm.

In the lower horizons of Spodosols, monomorphic materials are dominant. These materials are regarded as soluble organic compounds that are water-transported and precipitated. These deposits coat mineral grains and are present on channel pores (Buurman et al., 2005), forming horizons with close porphyric c/f related distribution patterns.

8.2.4.5 The enaulic related distribution patterns are more common in soil material in which the cement bonds to itself more strongly than to skeleton grains. For example, ionic-bonded calcite and gypsum tend to bond to themselves more strongly than to skeleton grains in sandy-textured soils (fig. 3E1b–11), thereby producing enaulic followed by open porphyric c/f related distribution patterns (Chadwick and Nettleton, 1990).

8.2.4.6 Porphyric c/f related distribution patterns are common in loessial soils, especially in argillic and petrocalcic horizons, duripans, and ortstein. This pattern can be the

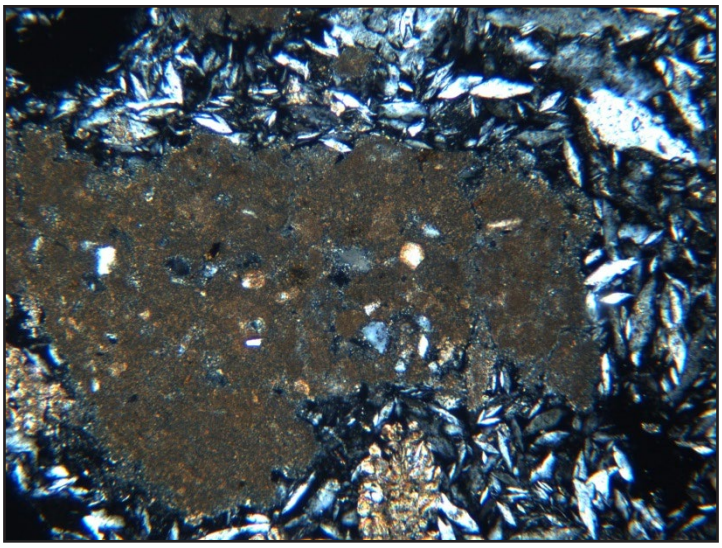

Figure 3E1b–11.—Lenticular gypsum crystals surrounding a micritic calcite mass under cross-polarized light. Material is from a Bym1 horizon of a Drygyp soil in Nevada (pedon 04N0770). Frame width is 2.5 mm.

end member of a progress sequence, or form from normal packing of grains in materials that have a high proportion of fine material. In precursors of the porphyric related distribution patterns, the silt-to-clay ratio is useful for identifying the kind of sequences by which the porphyric pattern develops (Brewer et al., 1983). In porphyric related patterns, there may or may not be skeleton grains of primary minerals, pedorelicts, organics, lithic fragments of shale, sandstone, or other rocks. The micromass consists of silt and clay, and the interstices tend to be filled with minimal formation of coatings.

8.2.5 Micromass

8.2.5.1 The fine materials (micromass) and the characteristics of the fabric are generally described based on optical characteristics (color, limpidity, and birefringence) because the size and shape of the particles are below the resolution of the microscope. Zones or aggregates of oriented clay display interference colors due to the birefringence of clay particles. Thus, a primary descriptive category of the micromass is orientation and distribution of interference colors from birefringence fabric, or b-fabric.

8.2.5.2 The main types of b-fabric are described as follows:

- *Undifferentiated.*—Absence of interference colors.

- *Strial.*—The entire structural unit exhibits birefringence with uniform parallel extinction throughout the unit.
- *Crystallitic.*—Presence of small birefringent mineral grains, e.g., calcite, that result in the color of the b-fabric (seen in fig. 3E1b–7).
- *Speckled.*—Small, randomly arranged domains of oriented clay (fig. 3E1b–12). Speckled materials can be either stipple speckled (fig. 3E1b–13) or mosaic speckled (fig. 3E1b–14).
- *Striated.*—Elongated domains of oriented clay that are generally parallel throughout the structural unit. Striated materials can be subdivided into 10 types, e.g., porostriated, parallel striated (fig. 3E1b–15), monostriated, granostriated (fig. 3E1b–16), or random striated.

8.2.6 Interpretation of Micromass

8.2.6.1 There are at least two origins for oriented clay on coarser sandy soils. One origin is a result of clay illuviation, commonly associated with monic, gefuric, or enaulic

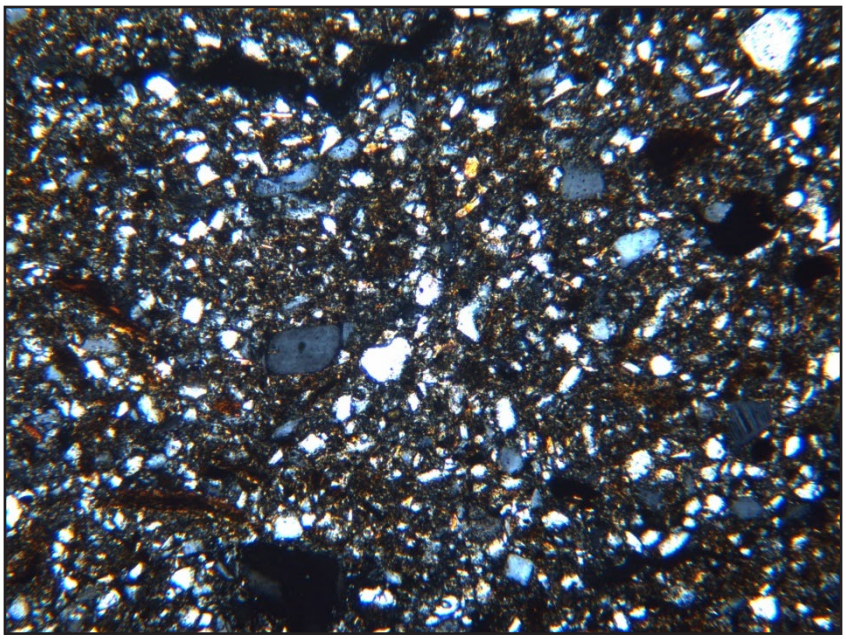

Figure 3E1b–12.—Speckled b-fabric under cross-polarized light. Material is from an Ap horizon of a Southridge soil, which is a Typic Argiudoll, in Allamakee County, Iowa (pedon 87P0075). Horizon composition is 19% clay dominated by vermiculate and smectite. COLE is 0.016. Frame width is 1.3 mm.

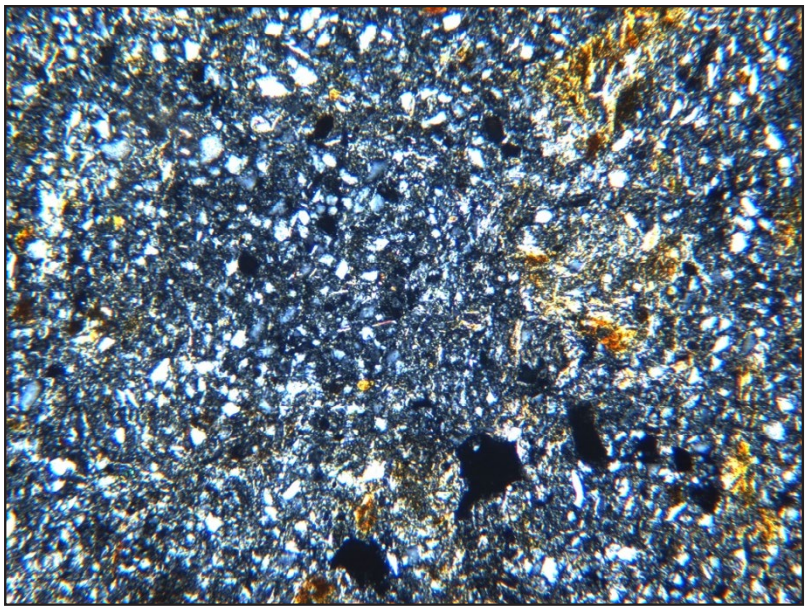

Figure 3E1b–13.—Stipple speckled b-fabric under cross-polarized light. Material is from a BE horizon of an Adco soil, which is a Vertic Albaqualf, in Macon County, Missouri (pedon 87P0771). Horizon composition is 29% clay dominated by smectite with lesser amounts of mica and kaolinite and 63% silt. COLE is 0.026. Frame width is 1.3 mm.

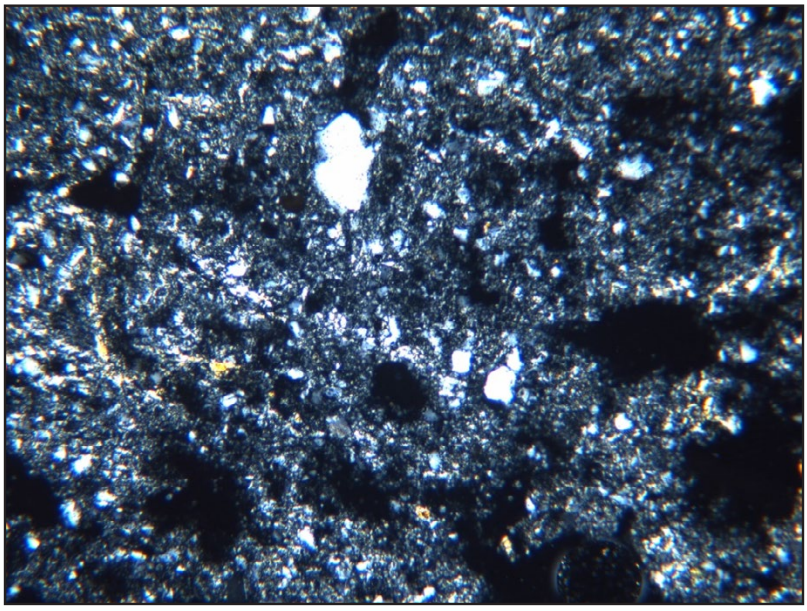

Figure 3E1b–14.—Mosaic speckled b-fabric under cross-polarized light. Material is from a 2Btg3 horizon of a Leonard soil, which is a Chromic Vertic Epiaqualf, in Macon County, Missouri (pedon 87P0770). Horizon composition is 48% clay dominated by smectite. COLE is 0.132. Frame width is 1.1 mm.

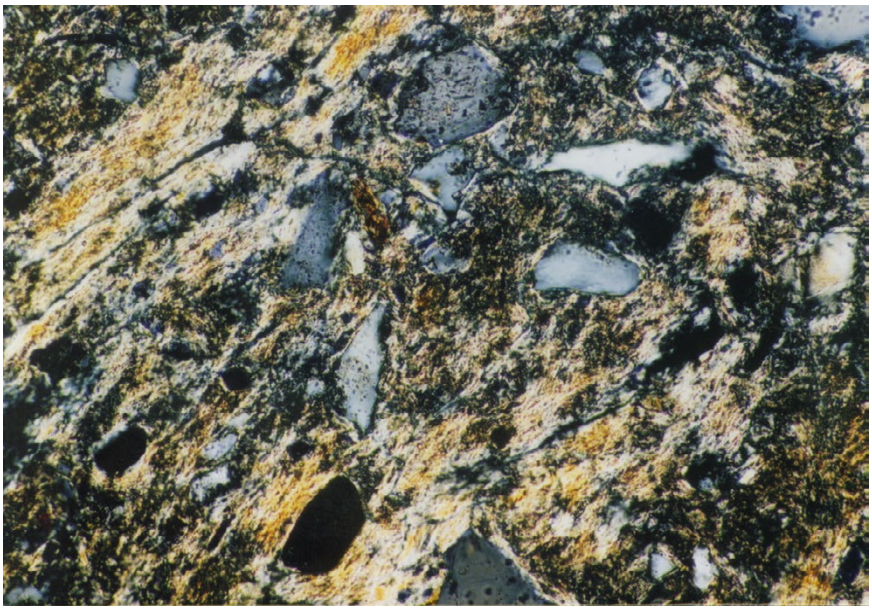

Figure 3E1b–15.—Parallel striated b-fabric under cross-polarized light. Material is from a Bt horizon of a Gloria soil, which is a Durixeralf, in Monterey County, California (pedon 40A2845). Horizon composition is 47% clay dominated by illite with lesser amounts of kaolinite and smectite. COLE is 0.056. Frame width is 1.3 mm.

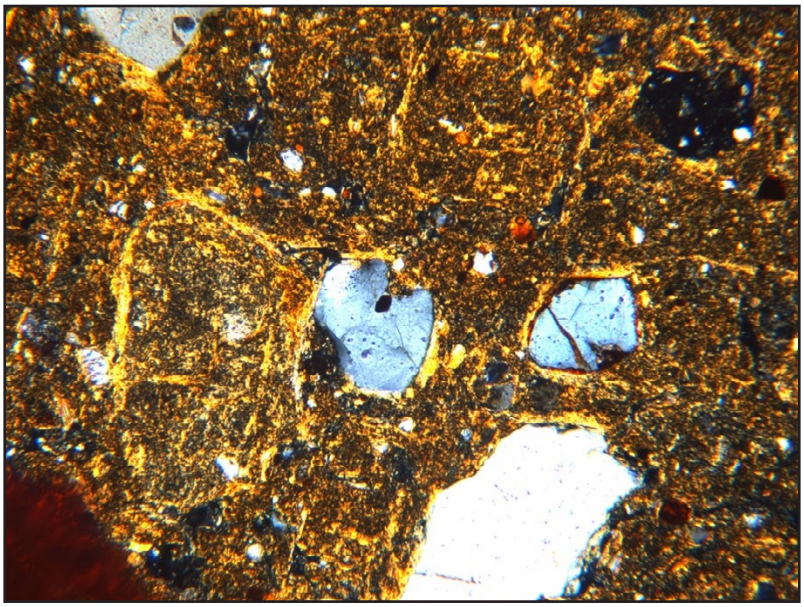

Figure 3E1b–16.—Granostriated b-fabric under cross-polarized light. Material is from a Bt horizon of a Redding soil, which is a Durixeralf, in San Diego County, California (pedon 40A2847). Horizon composition is 60% clay fraction dominated by kaolinite and smectite. COLE is 0.063. Frame width is 1.1 mm.

c/f related distribution patterns. The other origin is shrink-swell processes and is more commonly found in porphyric c/f related distribution patterns that have linear extensibilities >4 % for dryland soils; i.e., soils in aridic, xeric, or ustic soil moisture regimes. The b-fabrics in these latter types of soils are the true granostriated b-fabrics. Shrink-swell forces have been involved in their formation as shown by the relatively few papules or clay coatings remaining and by areas of striated b-fabrics.

8.2.6.2 Speckled or striated b-fabrics have higher clay contents, typically <30% but as much as 70% (Brewer et al., 1983). These b-fabrics are important in many fine-textured B horizons. Parallel, cross, and random striated b-fabrics are evidence of linear extensibilities >4% in dryland soils that have higher clay contents. Clay content is typically >35% in soils with these b-fabrics, but the threshold amount is dependent on the type of clay mineral and the degree of dryness common to the environment. In these three fabrics, clay coatings are rare, but areas of granostriated and porostriated b-fabrics may be present.

8.2.6.3 Deformation experiments indicate that the degree of clay orientation increases with an increase in clay percentage, linear extensibility, and applied stress (Clark, 1970; Edil and Krizek, 1976). In an experimental study of soil microfabrics by anisotropic stresses of confined swelling and shrinking, Jim (1986) showed that with an increase in the activity and content of the clay fraction, there is an increase in the long and narrow plasma separations; i.e., a progression from stippled speckled to mosaic speckled to parallel striated b-fabrics. The b-fabric types can form a sequence relative to increasing linear extensibility in soils from a similar climate. With increasing linear extensibility, the micromass sequence has been shown to progress from stippled speckled to mosaic speckled to random striated to parallel striated (Nettleton et al., 1969; Holzhey et al., 1974).

8.2.6.4 Stippled speckled plasmic b-fabric is very common in finer-grained porphyric B horizons of a wide range of soil groups (Brewer et al., 1983). Soils with this b-fabric generally have a linear extensibility of <4 percent. In some stipple speckled b-fabrics, clay islands are pseudomorphs of some weatherable mineral. In other stipple speckled fabrics, these islands are fragments of clay coatings or eolian sand-size clay aggregates (Butler,

1974). Mosaic speckled b-fabrics commonly contain more islands and therefore have more clay than stipple speckled fabrics. However, in mosaic speckled b-fabrics, linear extensibility also remains low. Shrink-swell forces have not been sufficient or have not operated long enough to have homogenized the islands of clay into the soil matrix.

8.2.6.5 Striated b-fabrics occur in soil horizons that have undergone stress either due to shrink-swell forces or to tillage. Even though root growth has been found to be adequate to increase the percentage of oriented clay near the root-soil interface (Blevins et al., 1970), root growth does not appear adequate to form these highly stressed b-fabrics.

8.2.6.6 Organic matter or iron stains that result in a flecked distribution pattern can mask the birefringence of crystalline clays. A complete absence of interference colors is what characterizes the undifferentiated b-fabric that is common in Spodosols and Andisols. In spodic horizons, the clay is commonly composed of monomorphic organic materials enriched with aluminum (Wilson and Righi, 2010). In Andisols, the b-fabric is undifferentiated due the presence of noncrystalline colloids of allophane or imogolite (Sedov et al., 2010). The water-holding capacities of these soil horizons are relatively high, and some unweathered volcanic ash may be present.

8.2.6.7 Crystallitic b-fabrics are common in B horizons of soils that formed in arid climates. These soils have many small birefringent mineral grains that control the interference colors of the whole (Stoops, 2003). Micaceous soils with fine grained sericite are commonly crystallitic. Arid soils that are rich in microcrystalline (micritic) calcite also exhibit this type of fabric (Durand et al., 2010) compared to soil horizons principally composed of microcrystalline gypsum that have nearly undifferentiated b-fabric (Poch et al., 2010). In soil horizons with large areas of interlocking crystals, soil permeability is restricted, unconfined compressive strength is increased, and particle dispersion is limited, depending on the degree of cementation.

8.2.7 Description of Pedofeatures

8.2.7.1 **“**Pedofeatures” refers to discrete units of material that are present in the fabric and have apparent differences to the groundmass based on concentration. Examples

are clay coatings, nodules, and crystals. The size of a pedofeature has no upper limit. It has a lower limit of about 20 µm, which is the lower limit of resolution with a petrographic microscope.

8.2.7.2 "Intrusive" and "matrix" are terms to describe two main distinctions between pedofeatures. The difference is based on the location of the pedofeature being described.

- Intrusive pedofeatures are those that formed through processes outside the groundmass and formed in voids or appended to the groundmass. Descriptive terms for intrusive pedofeatures are coatings, infillings, crystals, and crystal intergrowths, intercalations, and nodules.
- Matrix pedofeatures are those that formed due to weathering within or intrusion of a feature into the groundmass. Descriptive terms for the types of matrix pedofeatures are hypocoatings, quasicoatings, matrix infillings, intercalations, and matrix nodules. A matrix pedofeature can be:
  - *Fabric pedofeature.*—An alteration in the groundmass only; e.g., disturbed material filling void via bioturbation of earthworm.
  - *Impregnative pedofeatures.*—An infusion of a material (e.g., iron oxides) into the microporosity of the groundmass or preexisting void) (fig. 3E1b–17).

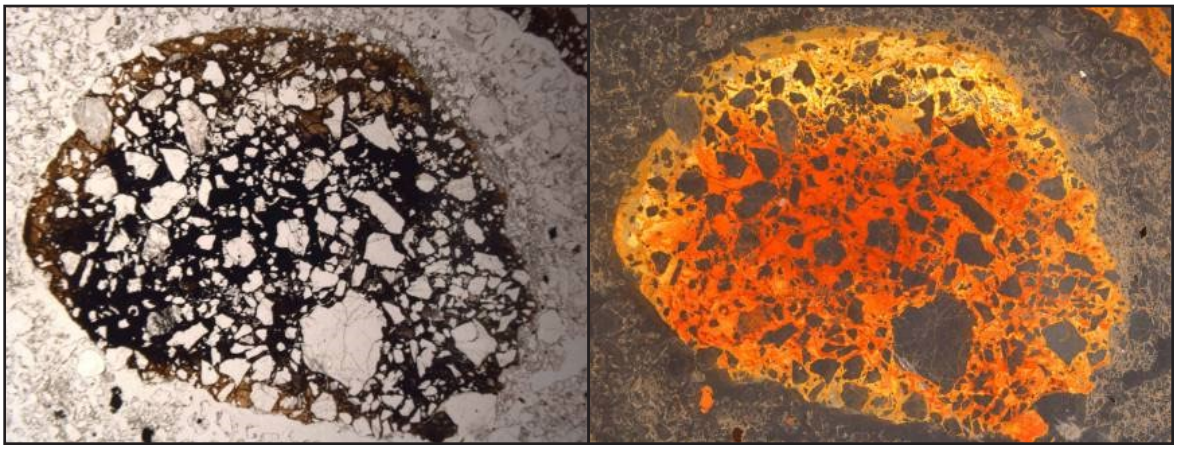

Figure 3E1b–17.—Ironstone nodule (petroplinthite). The core of the nodule is composed of well-crystalline goethite as opposed to plinthite nodules, which are composed of primarily noncrystalline iron oxides. Material is from an E horizon of a Dothan soil. Frame width is 16.7 mm. Light is transmitted and plane-polarized on the left and reflected on the right. Reflected light allows the actual color of the fabric to be seen.

- *Depletion pedofeatures.*—A lower concentration or loss of a substance (e.g., iron oxide) in a zone of the ground mass (fig. 3E1b–18). An example that the size of a pedofeature has no upper limit, as noted with the quarter for scale.

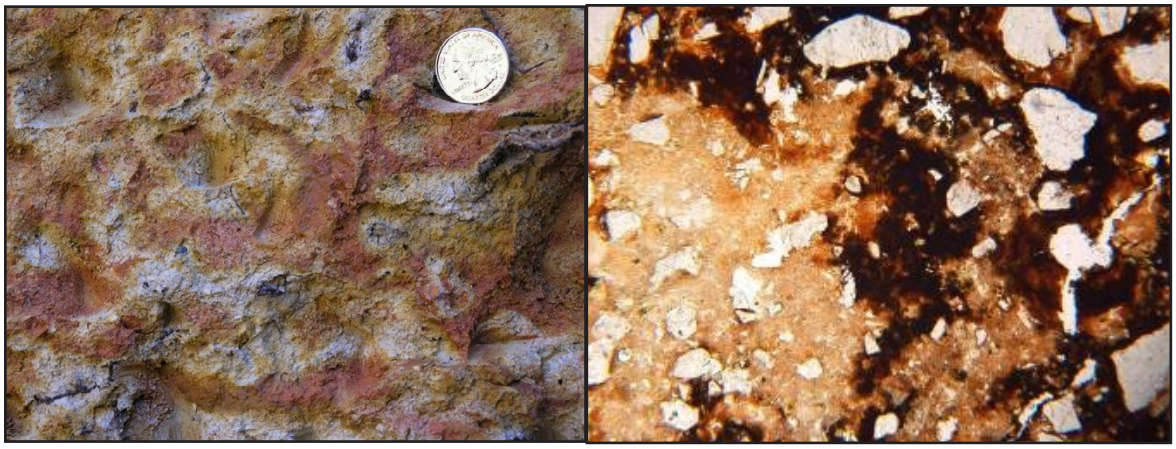

Figure 3E1b–18.—The mottled fabric on the pit face (left) and the thin section of soil fabric from the same horizon (right). These photos illustrate the movement of iron oxides in the soil as it undergoes seasonal saturation and reduction followed by reoxidation. Material is from a Btvx2 horizon of a Fuquay soil.

- Coatings can be textural coatings (composed of sand, silt, or clay), crystalline, cryptocrystalline, or amorphous. Textural coatings can be described as sorted, unsorted, laminated, or layered. The most common coating described in thin sections is composed of clay (fig. 3E1b–19).
- Several terms for clay coatings have been used in the past, including cutans (Brewer, 1964), clay films, and clay skins. Brewer described cutans according to composition, e.g., argillans, neomangans, and calcitans, but this terminology has been replaced by descriptions of the mineral or textural composition of the coating, e.g., calcite coatings and clay coatings.

8.2.7.3 Usually, the basic descriptive terms for soil fabrics do not imply any specific genesis of the feature. However, modifiers can be added when fabric descriptions are complete enough to understand the means of formation. For example, “stress-oriented clay coating” can signify in-

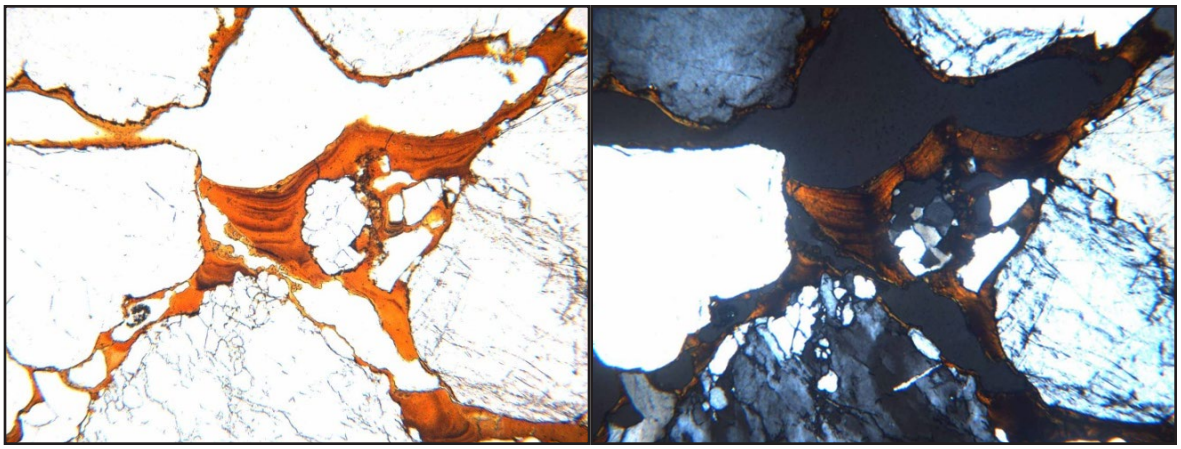

Figure 3E1b–19.—Clay coatings. Note the lamination visible under plane-polarized light (left). Under cross-polarized light (right), the clay coating exhibits birefringence and developed lines of extinction; both are characteristic of a well-oriented illuvial clay deposit. Material is from a 2Btx horizon of a Cowarts soil (pedon 06N0834). Frame width is 2.5 mm.

place plasma modification resulting from differential forces, such as shearing. This can be compared to the description of an "illuviation clay coating," which formed by movement of material in solution or suspension and later deposited.

8.2.8 Pedofeature Interpretations

8.2.8.1 Most clay coatings are formed, in part, by illuviation (fig. 3E1b–19). If clay coatings are present in argillic horizons of dryland soils, the soil linear extensibility is typically <4 percent (Nettleton et al., 1969). In some humid environments, these features may be present even where the linear extensibility is >4 percent because the moisture decreases the extent of shrinking. As soils in humid environments do not dry to the same degree as those in the desert, the clay coatings may survive because only part of the linear extensibility is effective.

8.2.8.2 The content of strongly oriented clay in soils that have argillic horizons is usually <5% of the soil volume. This clay typically consists of clay coatings, but can also include hypocoatings and quasicoatings. In some sandy soils that have a low content of silt, these three coatings may comprise up to 30% of the soil material (Brewer et al., 1983). The measured illuvial clay rarely accounts for the difference in clay content between the A and B horizons, indicating that some of the clay may originate from weathering in place and some from a destruction of the three types of clay coatings.

8.2.8.3 Clay hypocoatings (matrix pedofeatures immediately adjoining a void) and quasicoatings (a pedofeature within the matrix and not adjacent to a void surface) may originate by the weathering of primary minerals, the isolation of clay coatings by the channel, and void migration within the soil matrix (Nettleton et al., 1968; Nettleton et al., 1990) or by the introduction of eolian sands and silts that are composed of clays (Butler, 1974; Brewer and Blackmore, 1976). Internal fabric resemblances, comparison of parent material, and comparison of size and shape of minerals within the hypocoatings and quasicoatings may help to determine if the coatings are pseudomorphs of one of the primary minerals.

8.2.8.4 Nodules of iron oxides and manganese oxides are common in soils that have fluctuating water table levels but do not tend to develop in soils that have long term saturation (Jien et al., 2010). Soluble iron and manganese migrate via diffusion through the soil matrix, precipitating in small pores. As the small pores grow, they commonly envelop small grains that become entrapped in the interior of the nodules (Wilson et al., 2012; Lindbo et al., 2002). Coatings of iron oxides and manganese oxides are common along voids of soils that undergo seasonal saturation (fig. 3E1b–20). The soluble iron moves to the channel or pore, where it precipitates (Ogg et al., 2011). This migration can result in depletion pedofeatures.

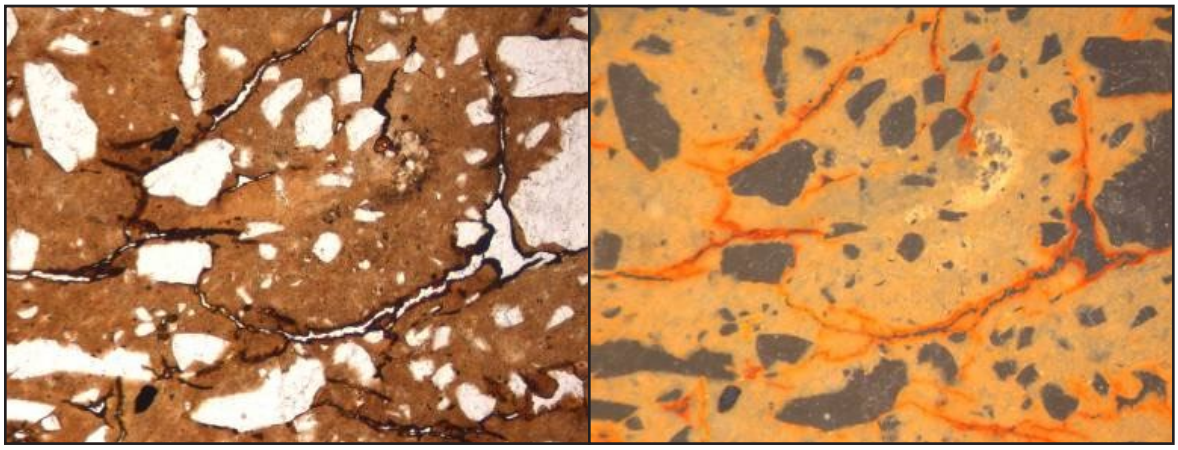

Figure 3E1b–20.—Porphyric c/f related distribution pattern. Micromass between the coarse grains composed of quartz is coated with iron oxides concentrated along the void channels. Material is from a Btvx3 horizon of a Fuquay soil (pedon 06N0830). Frame width is 2.5 mm. Light is plane-polarized and transmitted on the left and reflected on the right. Reflected light allows the actual color of the fabric to be seen.

9. Calculations

No calculations are needed. Results are reported through feature descriptions and observations.

10. Quality Assurance/Quality Control

10.1 Assess plausibility of observations in context of expected soil profile trends.

10.2 Assess plausibility of relationship of observations to other project laboratory analytical data and metadata.

10.3 Assign overall project data to soil data quality specialist.

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Wet Aggregate Stability (3F)
Wet-Sieving (3F1)
Air-Dry, 2- to 1-mm, 2- to 0.5-mm Aggregates Retained (3F1a1a)

1. Introduction to Aggregate Stability

This method was developed for use by the soil survey field offices of the Natural Resources Conservation Service. It provides a measure of aggregate stability following a disruption of initially air-dry aggregates by abrupt submergence followed by wet sieving.

2. Scope and Field of Application

An aggregate is a group of primary particles that cohere to each other more strongly than to other surrounding soil particles (Soil Science Society of America, 1997). Aggregate stability is a function of the capacity of cohesive forces between particles to withstand an applied disruptive force. The analysis of soil aggregation can be used to evaluate or predict the effects of various agricultural techniques; e.g., tillage, additions of organic-matter, and erosion by wind and water (Nimmo and Perkins, 2002). The measurement can serve as a predictor of infiltration and soil erosion potential.

3. Principle

This method measures the retention of air-dry aggregates (2 to 1 mm) on a 0.5-mm sieve after a sample has been submerged in reverse osmosis water overnight and then agitated.

3.1 Interferences

Air bubbles in the sieve can create tension in the water, thereby reducing the percentage of aggregates that are retained on the 0.5-mm sieve. Variation in the moisture content of air-dry soils can affect results. A correction should be made for the content of sand that is >0.5 mm and resistant to dispersion in sodium hexametaphosphate

4. Apparatus

4.1 Bowls, plastic lunch containers or equivalent, 1,800-mL

4.2 Electronic balance, ±0.01-g sensitivity and 500-g capacity

4.3 Sieves, square-hole

- 0.5-mm, stainless steel, no.35, 125-mm diameter, 50-mm height
- 1-mm, brass, 203-mm diameter, 50-mm height
- 2-mm, brass, 203-mm diameter, 50-mm height

4.4 Oven, 110 °C

4.5 Camping plate, stainless steel, 152-mm diameter

4.6 Aluminum foil dish, 57-mm diameter x 15-mm deep, with lifting tab

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Sodium hexametaphosphate $(NaPO_3)_6$ (CAS# 68915-31-1), reagent grade

5.3 Sodium carbonate (Na_2CO_3) (CAS# 497-9-8)

5.4 Sodium hexametaphosphate solution

Components: Sodium hexametaphosphate $(NaPO_3)_6$, sodium carbonate (Na_2CO_3), RO water

- In a 1-L polyethylene bottle, add the following in order:
  - 1 L of RO water
  - 35.7 g of $(NaPO_3)_6$
  - 7.94 g of Na_2CO_3
- Invert to mix.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents, especially concentrated acids and bases, use disposable gloves with appropriate polymer rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use insulated gloves to remove samples from oven. Follow standard laboratory safety precautions.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C and sieved to 1 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage

8. Procedure

8.1 Use natural fabric (NF) samples in pint containers. Assemble a 2-mm sieve on top of a 1-mm sieve. Crush the NF sample by hand or lightly roll with rubber sample roller. Leave sample as intact as possible but able to pass through the 2-mm sieve. Sieve entire NF sample.

8.2 Place the material that is retained on 1-mm sieve in a pint container and discard the remaining material.

8.3 Sieve the material again with 1-mm sieve to remove dust and other small particles. Weigh approximately 3.00 ±0.05-g sample of the 2- to 1-mm material in aluminum foil dishes.

8.4 Place 0.5-mm sieve in plastic bowl and fill bowl so that the water level is at a height of 20-mm above the base of screen. Remove air bubbles with a syringe.

8.5 Distribute 3.00-g of 2- to 1-mm soil sample on the 0.5-mm sieve. Aggregates should not touch. Allow sample to sit overnight.

8.6 Agitate the sample by raising and lowering the sieve in the water bowl 20 times in 40 s. On the upward strokes, drain sieve but do not raise so high that air enters to beneath the sieve.

8.7 Remove sieve from water bowl, place on camping plate, and dry in oven for 2 to 2.5 h at 110 °C. During drying process, the plate retains the soil that drops through the sieve.

8.8 Remove the sample from the oven. Weigh sieve, plate, and sample. Record weight (Wt_1). If no sand (>0.5 mm) is present, discard sample from sieve and plate by brushing. Weigh sieve and plate. Record weight (W_2). Sample is those aggregates retained on 0.5-mm sieve. $W_R = Wt_1 - Wt_2$.

8.9 If sand (>0.5 mm) is present and no particle-size data are available, discard sample on plate and disperse sample that was retained on the sieve with sodium hexametaphosphate solution. Alternatively, place 3 g of Calgon in plastic bowl and stir until dissolved. Place the 0.5-mm sieve with sample in sodium hexametaphosphate (or Calgon) solution so that the solution line is 35 mm above the base of screen. Gently triturate the dispersing solution with fingers to remove soft <0.5-mm material adhering to the ≥0.5-mm particles. Remove sieve from sodium hexametaphosphate (or Calgon) solution and rinse with RO water until all solution has passed through sieve and only the sand (>0.5 mm) is left on sieve. Place sieve on camping plate, place in oven, and dry for 2 to 2.5 h at 110 °C.

8.10 Remove sample from oven. Weigh the sieve, plate, and sample. Record weight (Wt_3). Discard sample and brush sieve and plate. Weigh sieve and plate. Record weight (Wt_4). Sand weight: $SW = Wt_3 - Wt_4$.

8.11 Thoroughly wash sieve and plate with RO water, especially those sieves used with sodium hexametaphosphate solution.

9. Calculations

9.1 $\text{Aggregates (\%)} = \{\{(W_R - S_W) / \{[I_W / (AD/OD)] - S_W\}\} \times 100$

I_W = Initial sample weight (approximately 3 g)

W_R = Total weight of aggregates retained on 0.5-mm sieve

S_W = Weight of 2- to 0.5-mm sand

AD/OD = Air-dry/oven-dry weight (if measured value is not available, use 1.00)

9.2 Report aggregate stability as a percentage of aggregates (2- to 0.5-mm) retained after wet sieving. Do not report determinations if the 2- to 0.5-mm primary particles are ≥50% of the 2- to 1-mm sample.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Nimmo, J.R., and K.S. Perkins. 2002. Aggregate stability and size distribution. p. 317–328. *In* J.H. Dane and G.C. Topp (eds.) Part 4. Physical methods. Soil Sci. Am. Book Series No. 5. ASA and SSSA, Madison, WI.

Soil Science Society of America. 1997. Glossary of soil science terms. Soil Sci. Soc. Am., Madison, WI.

Particle Density (3G)

Pycnometer Gas Displacement (3G1)

Oven-Dry, <2 mm (3G1a1)

Oven-Dry, >2 mm (3G1a2)

1. Introduction to Pycnometer Gas Displacement

Lithic fragments, pararock, and concretions usually possess a greater particle density than the surrounding groundmass. A gas pycnometer for measuring particle density provides accurate measurements because the helium gas accounts for porosity and permeability of fragments. A value of 2.65 g/cm^3 (density of quartz) is a default value if particle density is determined via Archimedes displacement techniques.

2. Scope and Field of Application

Density is defined as mass per unit volume. Particle density refers to the density of the solid particles collectively (Flint and Flint, 2002). Particle density is required for sedimentation analysis; calculating soil volume or mass; and mathematically correcting bulk soil samples containing significant amounts of rock fragments so as to determine fine-soil density, water content, or other soil properties affected by volume displacement of rock fragments (Flint and Childs, 1984).

3. Principle

A sample is placed in a calibrated pycnometer cell. The cell is evacuated of ambient air and is filled with helium gas. A series of measurements are taken and reported by the pycnometer software.

If a pycnometer is not available, more rudimentary measurements can be taken by a calculated displacement of the sample in water using Archimedes' principle of fluid displacement to determine the volume.

3.1 Interferences

Sample should be dry. Displacement gas evaporates water molecules and creates additional partial pressure (Flint and Flint, 2002).

Temperature should be relatively constant because the method uses the ideal gas equation of state.

Instrument should be calibrated when environmental conditions change.

4. Apparatus

4.1 Electronic balance, ±0.01-g sensitivity

4.2 Oven, capable of constant 110 °C

4.3 Gas pycnometer

5. Chemicals

5.1 Compressed helium (minimum purity 99.999%)

6. Health and Safety

Personal Protective Equipment (PPE).—Use disposable gloves with appropriate polymer rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents or samples.

7. Sample Preparation

Particle-size fractions either <2-mm or >2-mm are collected from bulk sample, cores, or clods. Fragments are dried at 110 °C overnight. Biological activity is low.

8. Procedure

8.1 Oven dry the soil sample at 110 °C overnight.

8.2 Allow the pycnometer to warm up for at least 30 min prior to use.

8.3 Set the regulator pressure to slightly over 20 PSIG.

8.4 Validate the calibration by determining the volume of the calibration sphere provided by manufacturer. If volumes are outside specification range, recalibrate the instrument per instruction manual.

8.5 Select appropriate sample cell size (examples: 135 cc, 50 cc, or 10 cc). The sample should fill at least half of the sample cell volume.

8.6 Weigh the sample cell to the nearest 0.01 g. Place sample in the sample cell and reweigh to the nearest 0.01 g. Record the weight: [(Cell wt+sample wt)−cell wt].

8.7 Place the sample cells into pycnometer cell holders. Seal the cell holders with covers.

8.8 Define each cell with sample cell size, weight, and sample number.

8.9 Start sample run with predefined parameters for purge time, pulse cycles, and run time.

8.10 Record the average volume for each sample.

9. Calculations

9.1 Particle density (g/cm^3) = Sample weight (g) / Sample volume

9.2 Report particle density (g/cm^3) to the nearest 0.01 unit on either the <2-mm or >2-mm particle-size fraction.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Flint, A.L., and S.W. Childs. 1984. Physical properties of rock fragments and their effect on available water in skeletal soils. p. 91–103. *In* J.E. Box, Jr. (ed.) Erosion and productivity of soils containing rock fragments. SSSA Spec. Publ. 13. SSSA, Madison, WI.

Flint, A.L., and L.E. Flint. 2002. Particle density. p. 229–240. *In* J.H. Dane and G.C. Topp (eds.) Methods of soil analysis. Part 4. Physical methods. Soil Sci. Am. Book Series No. 5. ASA and SSSA, Madison, WI.

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Atterberg Limits (3H)

Liquid Limit (3H1)

Air-Dry, <0.4 mm (3H1a1)

Field-Moist, <0.4 mm (3H1b1)

Plasticity Index (3H2)

Air-Dry, <0.4 mm (3H2a1)

Field-Moist, <0.4 mm (3H2b1)

1. Introduction to Liquid Limit Atterberg Testing

The liquid limit and plastic limit of soils (along with the shrinkage limit) are often collectively referred to as the Atterberg limits. These limits distinguished the boundaries of the several consistency states of plastic soils (ASTM, 2018).

2. Scope and Field of Application

The liquid limit, plastic limit, and plasticity index of soils are used individually or together with other soil properties to correlate engineering behavior of soils. Examples include compressibility, hydraulic conductivity (permeability), compatibility, shrink-swell potential, and shear strength.

Useful indicators of the engineering behavior of clay soils derived from Atterberg limits are the liquid limit, from which the compressibility of normally consolidated clays can be estimated, and the plasticity index, from which the undrained shearing resistance of normally consolidated clays can be estimated (Perloff and Baron, 1976).

3. Principle

A pat of soil is placed in a standard cup and cut by a standardized grooving tool. The sample flows together at the base of the groove for a distance of 13 mm (½ in) when subjected to 25 shocks from the cup being dropped 10 mm in a standard liquid limit (LL) apparatus operated at a rate of 2 shocks s^{-1}.

3.1 Interferences

Ensure sample format is appropriate for requested test and dried to a constant weight.

4. Apparatus

4.1 Liquid limit device

4.2 Balance capable of ±0.01 g

4.3 Grooving tool

4.4 Gauge block

4.5 Sieves

4.6 Spatula

4.7 Water bottle

4.8 Drying oven

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

6. Health and Safety

Personal Protective Equipment (PPE).—Use disposable gloves with appropriate polymer rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents or samples.

7. Sample Preparation

Field-moist or air-dried samples are processed to <2 mm (method 1B1b2b1). Subsamples are further pressed, crushed, and sieved to <425 µm (method 1B1b1c1). The weight of air-dry soil remains relatively constant. Biological activity is low during storage, and moist samples are refrigerated until analysis.

8. Procedure

8.1 Moist or air-dried sample that is prepared to ≈425 µm is used for testing of Atterberg limits using the American Society for Testing and Materials (ASTM) method D 4318 (ASTM, 2018).

9. Calculations

9.1 Calculate the Liquid Limit (LL):

$$LL_n = W_n(N_n/25)^{0.121}$$

LL_n = one-point liquid limit for given trial “n”, %

N_n = number of drops causing closure of the groove

W_n = water content for given trial, %

9.2 Calculate plasticity index (PI):

PI = LL − PL

LL = liquid limit (whole number)

PL = plastic limit (whole number)

Both LL and PL are whole numbers. If either the liquid limit or plastic limit could not be determined, or if the plastic limit is equal to or greater than the liquid limit, report the soil as non-plastic (NP).

9.3 The LL is reported as percent water on a <0.4-mm basis (40-mesh).

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

American Society of Testing and Materials (ASTM) 2018. Standard test methods for liquid limit, plastic limit, and plasticity index of soils, Designation: D4318 − 17.

Perloff, W., and W. Baron. 1976. Soil mechanics principles and applications. Ronald Press Co.

SOIL AND WATER CHEMICAL EXTRACTIONS AND ANALYSES (4)

Acid Standardization (4A)

1. Introduction to Acid Standardization

Standardization is the technique used to determine the exact concentration of a prepared solution (Dean,1995) by titrating with a high purity, primary standard. Ideally, the primary standard should be a stable, pure substance (<0.1 to 0.2% impurities) that is non-hygroscopic and has a reasonably high equivalent weight (Day and Underwood, 1980).

2. Scope and Field of Application

For acid-base standardizations, prepare solutions that approximate the desired concentration, then titrate to calculate the exact concentration. Standardization is necessary when using one solution to precisely measure the concentration of an unknown solution. Some widely used primary standards are listed in table 4A–1. For common acids and bases, refer to table 4A–2.

3. Principle

Dissolve a known amount of the primary standard in reverse osmosis deionized (RODI) water. Prepare 10 primary-standard solutions plus 8 blanks. Titrate with the acid to be standardized. Calculate the normality of the acid from the mean of the blanks and titers. Report the normality and standard deviation for the acid standardization. The method outlined below uses a sodium carbonate (Na_2CO_3) primary standard and hydrochloric acid (HCl) as a common example of acid standardization.

3.1 Interferences

Wiping the electrode dry with a cloth, laboratory tissue, or similar material may cause electrode polarization and deterioration. Clean the glass electrode by rinsing with distilled water.

Slow electrode response may cause the end point to be overshot. Proper cleaning with only RODI water and appropriate storage are critical for electrode accuracy. If damage or contamination is suspected, replace the electrode.

Primary standards hydrate due to ambient conditions. Oven dry the primary standards and store them in a desiccator to prevent hydration.

Contamination of the primary standard can occur when drying, storing, or weighing the reagent. Use gloves when weighing the primary standard in the weighing vessel.

4. Apparatus

4.1 Electronic balance, ±0.10-mg sensitivity
4.2 Oven, 110 °C
4.3 Weighing vessel, 40 x 50 mm
4.4 Desiccator
4.5 Automatic titrator with control unit, sample changer, dispenser, and software
4.6 Combination pH-reference electrode
4.7 Titration beakers, 250-mL, borosilicate glass

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water
5.2 pH buffers: 4.00, 7.00, and 9.18
5.3 Sodium carbonate (Na_2CO_3) (CAS# 497-9-8), anhydrous, 99.8% pure
5.4 Desiccator: Calcium sulfate (anhydrous) (CAS# 7778-18-9) or equivalent desiccant
5.5 Primary standards: Refer to table 4A–1 for a list of standards and CAS #.

Table 4A–1.—Examples of Primary Standards.

Reagent	CAS#	Molecular Wt.	Preparation and Indicators
Benzoic acid ($C_6H_5CO_2H$)	65-85-0	122.123	Dissolve about 0.5 g in 50% ethanol and titrate to phenolphthalein end point.
Borax ($Na_2B_4O_7•10H_2O$)	1303-96-4	381.360	Use methyl red indicator. Dissolve in water. Borax forms a weak acid.
Mercuric oxide (HgO)	21908-53-2	216.599	Use bromthymol blue indicator. Dissolve 0.5 g HgO with 15 g of KBr in 25 mL of reverse osmosis deionized (RODI) water, excluding CO_2.
Potassium bicarbonate ($KHCO_3$)	298-14-6	100.116	Use bromcresol green indicator. The first tint of green is the end point.
Potassium biiodate ($KH(IO_3)_2$)	13455-24-8	389.912	Bromthymol blue end point. Strong acid. Low solubility.
Potassium biphthalate ($KHC_8H_4O_4$)	877-24-7	204.224	Use phenolphthalein indicator. Potassium biphthalate forms a weak acid.

Table 4A–1.—Examples of Primary Standards—Continued

Reagent	CAS#	Molecular Wt.	Preparation and Indicators
Potassium bitartrate ($KHC_4H_4O_6$)	868-14-4	188.178	Phenolphthalein indicator. Solutions of potassium bitartrate are susceptible to mold growth.
Sodium carbonate (Na_2CO_3)	497-9-8	105.988	Use bromocresol green indicator. The end point is the first green.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Dispense concentrated acids in a fume hood. Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids. Follow the manufacturer's safety precautions when using the automatic titrator.

Review safety data sheets (SDS) for reagents.

7. Sample Preparation

A weighing vessel containing ≈10 g of the Na_2CO_3 is placed in an oven at 110 °C for a minimum of 2 hours. Cool in a desiccator to room temperature (≈30 min).

8. Procedure

8.1 Make a copy of "Table 4A–3: Bench Sheet for Acid Standardization." Weigh the vessel containing the oven-dried Na_2CO_3. Record the weight to the nearest 0.1 mg in table 4A–3. This is Vessel Weight 1a (VW_{1a})

8.2 Tare a 250-mL titration beaker on the electronic balance. Add 0.15 to 0.55 g Na_2CO_3 to the beaker. Record the sample weight of the Na_2CO_3 to the nearest 0.1 mg in table 4A–3. This is Standard Weight 1 (SW_1).

8.3 Reweigh vessel containing the oven-dried Na_2CO_3. Record the weight to the nearest 0.1 mg in table 4A–3. This is Vessel Weight 1b (VW_{1b})

8.4 Verify the weighed SW_1 as follows: $SWC_1 = VW_{1a} - VW_{1b}$

8.4.1 If SWC_1 calculated weight is within 0.5 g of the weighed SW_1 weight, continue through the procedure. If weights are >0.5 g, begin weighing process over.

8.5 Prepare nine more Na_2CO_3 solutions (SW_2 …SW_{10}).

Table 4A–2.—Common Commercial Strengths of Acids and Bases.

Name	Molecular Weight	Moles per Liter	Grams per Liter	Percent by Weight	Specific Gravity
Acetic acid	60.05	17.4	1,045	99.5	1.05
Glacial acetic acid	60.05	6.27	376	36	1.045
Butyric acid	88.1	10.3	912	95	0.96
Formic acid	46.02	23.4 5.75	1,080 264	90 25	1.20 1.06
Hydriodic acid	127.9	7.57 5.51 0.86	969 705 110	57 47 10	1.70 1.50 1.1
Hydrobromic acid	80.92	8.89 6.82	720 552	48 40	1.50 1.38
Hydrochloric acid	36.5	11.6 2.9	424 105	36 10	1.18 1.05
Hydrocyanic acid	27.03	25 0.74	676 19.9	97 2	0.697 0.996
Hydrofluoric acid	20.01	32.1 28.8	642 578	55 50	1.167 1.155
Hydrofluosilicic acid	144.1	2.65	382	30	1.27
Hypophosphorous acid	66.0	9.47 5.14 1.57	625 339 104	50 30 10	1.25 1.13 1.04
Lactic acid	90.1	11.3	1,020	85	1.2
Nitric acid	63.02	15.99 14.9	1,008 938 837	71 67 61	1.42 1.40 1.37
Perchloric acid	100.5	11.65 9.2	1,172 923	70 60	1.67 1.54
Phosphoric acid	98	14.7	1,445	85	1.70
Sulfuric acid	98.1	18.0	1,766	96	1.84
Sulfurous acid	82.1	0.74	61.2	6	1.02
Ammonia water	17.0	14.8	252	28	0.898
Potassium hydroxide	56.1	13.5 1.94	757 109	50 10	1.52 1.09
Sodium carbonate	106.0	1.04	110	10	1.10
Sodium hydroxide	40	19.1 2.75	763 111	50 10	1.53 1.11

8.6 Add 100 mL of RODI water to each of the SW_1.....SW_{10} standard samples and to eight empty beakers for Blanks (B_1....B_8). Gently swirl to facilitate dissolution of the salt.

8.7 Prepare the titration system according to the manufacturer's instructions. Calibrate the pH electrode with 4.00, 7.00, and 9.18 pH buffers. Recalibrate electrode if R^2 <0.950.

8.8 Set-up the automatic titrator to set end point titration mode. The "Set" pH parameters are listed as follows:

Parameter	Value
Measured value	pH
Titration rate	normal
Stop volume	100.0 mL
Stop end point	9
Stop potential	4.2 pH
Sensitivity	High
Fixed end point	4.6 pH
Signal drift	25
Equilibration time	5 s

8.9 Titrate each of SW_1.....SW_{10} and B_1.....B_8. Record the titers in table 4A–3.

9. Calculations

9.1 Determine the Blank Mean (mL).

$B_{mean} = B_{sum} / n$

- B_{sum} = Sum of blank titers (mL) as recorded in column 5 of table 4A–3
- n = Number of blanks (n = 8)

9.2 Determine Corrected Sample Titer (mL).

$TCS_{1.....10} = TS_{1.....10} - Bm$

- $TS_{1 .....10=}$ Sample titer (mL) as recorded for a given sample in column 4
- Bm = Blank Mean (mL)

9.3 Determine the normality of the acid calculated from the titer (number of equivalents of solute per liter).

$N_{1.....10=}[(SW_{1.....10} \times 0.0188698 \text{ mole HCl/g } Na_2CO_3) / (TCS_{1.....10} \times 10^{-3} \text{ L mL}^{-1})] = (SW_{1....10} \times 18.8698) / TCS_{1.....10}$

- $SW_{1.....10=}$ Weight of Na_2CO_3 (g) in the standard sample

9.4 Determine the Normality Mean (N_{mean})

$N_{mean} = N_{sum} / n$

- N_{sum} = Sum of normalities determined for each sample
- n = Number of samples (n = 10)

9.5 Calculate standard deviation (Std) for N_{mean}. If $N_{Std} \leq 0.0005$, record N_{mean} to four places to right of decimal point. If $N_{Std} > 0.0005$, discard no more than two suspicious values and weigh fresh standards for titration until 10 (n=10) are achieved.

9.6 Report the mean normality of acid (N_{mean}), standard deviation, and date of standardization.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assign overall project data to soil data quality specialist.

11. References

Day, R.A., Jr., and A.L. Underwood. 1980. Quantitative analysis. Prentice-Hall, Inc., Englewood Cliffs, NJ.

Dean, J.A. 1995. Analytical chemistry handbook. McGraw Hill, Inc., New York, NY.

Table 4A–3.—Bench Sheet for Acid Standardization

Acid:		Date:	Technician:			
Standard Samples		**Vessel Weight**	**Sample Weight**	**Sample Titer**	**Blanks**	**Corrected Sample Titer**
#1 Beginning weight		VW_{1a}	SW_{1}	TS_{1}	B_{1}	TCS_{1}
Ending weight		VW_{1b}			B_{2}	
#2 Beginning weight		VW_{2a}	SW_{2}	TS_{2}	B_{3}	TCS_{2}
Ending weight		VW_{2b}			B_{4}	
#3 Beginning weight		VW_{3a}	SW_{3}	TS_{3}	B_{5}	TCS_{3}
Ending weight		VW_{3b}			B_{6}	
#4 Beginning weight		VW_{4a}	SW_{4}	TS_{4}	B_{7}	TCS_{4}
Ending weight		VW_{4b}			B_{8}	
#5 Beginning weight		VW_{5a}	SW_{5}	TS_{5}	B_{sum}	TCS_{5}
Ending weight		VW_{5b}			B_{mean}	
#6 Beginning weight		VW_{6a}	SW_{6}	TS_{6}		TCS_{6}
Ending weight		VW_{6b}				
#7 Beginning weight		VW_{7a}	SW_{7}	TS_{7}		TCS_{7}
Ending weight		VW_{7b}				
#8 Beginning weight		VW_{8a}	SW_{8}	TS_{8}		TCS_{8}
Ending weight		VW_{8b}				
#9 Beginning weight		VW_{9a}	SW_{9}	TS_{9}		TCS_{9}
Ending weight		VW_{9b}				
#10 Beginning weight		VW_{10a}	SW_{10}	TS_{10}		TCS_{10}
Ending weight		VW_{10b}				
					$N_{1....10}$	
					N_{Std}	

Ion Exchange and Extractable Cations (4B)

Ion exchange is a reversible process by which one cation or anion held on the solid phase is exchanged with another cation or anion in the liquid phase. If two solid phases are in contact, ion exchange may also take place between two surfaces (Tisdale et al., 1985). In most agricultural soils, the cation exchange capacity (CEC) is generally considered to be more important than anion exchange (AEC). The anion molecular retention capacity of these soils is typically much smaller than the CEC (Tisdale et al., 1985). Some soils with abundant goethite and gibbsite, such as in some oxic horizons or subsoils of Oxisols (Soil Survey Staff, 2014), may have a CEC to AEC ratio approaching 1.0 (net charge of zero) or a small positive charge (Foth and Ellis, 1988).

Soil mineral and organic colloidal particles have negative valence charges that hold dissociable cations and thus are “colloidal electrolytes” (Jackson, 1958). The CEC is a measure of the quantity of readily exchangeable cations that neutralize negative charges in the soil (Rhoades, 1982). Cation exchange is a reversible reaction in soil solution, dependent upon negative charges of soil components arising from permanently charged or pH-dependent sites on organic matter and mineral colloid surfaces. The mechanisms for these negative charges are isomorphic substitution within layered silicate minerals; broken bonds at mineral edges and external surfaces; dissociation of acidic functional groups in organic compounds; and preferential adsorption of certain ions on particle surfaces (Rhoades, 1982). Isomorphic substitution produces permanent charge. The other charge mechanisms produce variable charge that is dependent on the soil solution phase as affected by soil pH, electrolyte level, valence of counter-ions, dielectric constant, and nature of anions (Rhoades, 1982). As a result of the variable charge in soils, the measurement of CEC is dependent on the method and conditions of determination.

CEC is a measure of the total quantity of negative charges per unit weight of the material and is commonly expressed in units of centimoles per kg of soil (cmol(+) kg^{-1}) or milliequivalents per 100 g of soil (meq 100 g^{-1}). The KSSL reports cmol(+) kg^{-1} on a <2-mm air-dry basis. CEC can range from less than 1.0 to greater than 100 cmol(+) kg^{-1} soil. The term “equivalent” is defined as “1 gram atomic weight of hydrogen or the amount of any other ion that will combine with or displace this amount of hydrogen.” The milliequivalent weight of a substance is one thousandth of its atomic weight. Because the equivalent weight of hydrogen is about 1 gram, the term *milliequivalent* may be defined as “1 milligram of hydrogen or the amount of any other ion that will combine with or displace it” (Tisdale et al., 1985).

Common CEC values for some soil components (NSSL Staff, 1975) are as follows:

Soil component	cmol(+) kg−1
Organic matter	200 to 400
“Amorphous” clay	160 (at pH 8.2)
Vermiculite	100 to 150
Montmorillonite	60 to 100
Halloysite•4H_2O	40 to 50
Illite	20 to 40
Chlorite	10 to 40
Kaolinite	2 to 16
Halloysite•2H_2O	5 to 10
Sesquioxides	0

These very broad CEC ranges are intended only as general guidelines. More narrow groupings of CEC values are possible as data are continually collected and correlated. For example, the CEC of organic matter in Mollisols in the western United States ranges from 100 to 300 cmol (+) kg^{-1} (average 200), and the CEC of organic matter in Histosols ranges from 125 to 185 cmol (+) kg^{-1} and increases with decomposition of the organic matter (NSSL Staff, 1975).

Many procedures have been developed to determine CEC. These CEC measurements vary according to the nature of the cation employed, concentration of salt, and the equilibrium pH. The CEC measurement should not be thought of as highly exact but rather as an equilibrium measurement under the selected conditions (Jackson, 1958). Knowledge of the operational definition (procedure, pH, cation, and concentration) is necessary before evaluating the CEC measurement (Sumner and Miller, 1996). The more widely adopted methods of CEC determination are classified (Rhoades, 1982) as follows:

1. Cation summation
2. Direct displacement
3. Displacement after washing
4. Radioactive tracer

The most commonly reported methods by the KSSL are CEC–7 (4B1a1a1a1), CEC–8.2 (4B4b1), and effective cation exchange capacity (ECEC) (4B4b2). As a general rule, CEC–8.2 > CEC–7 > ECEC. Refer to Soil Survey Staff (2014) for the use and application of these CEC values in U.S. Soil Taxonomy.

Cation Exchange Capacity: NH_4OAc, pH 7.0 (CEC–7)

CEC–7 (method 4B1a1a1a1) has become a standard reference to which other methods are compared (Peech et al., 1947). Displacement after washing is the basis for this procedure. This CEC is determined by saturating the exchange sites with an index cation (NH_4^+) by using a mechanical vacuum extractor (Holmgren et al., 1977); washing the soil free of excess saturated salt; displacing the index

cation (NH_4^+) adsorbed by the soil; and measuring the amount of the index cation (NH_4^+). An advantage of using this method is that the extractant is highly buffered and therefore the extraction is performed at a constant and known pH (pH 7.0). In addition, the NH_4^+ on the exchange complex is easily determined. CEC–7 is an analytically determined value and is usually used for the calculation of CEC–7/clay ratios. Primary Characterization Data Sheets predating 1975 show CEC–8.2/clay.

Cation Exchange Capacity: Sum of Cations (CEC–8.2)

Cation summation is the basis for this procedure. CEC–8.2 is calculated as follows:

CEC–8.2 = NH_4OAc extractable bases + Extractable acidity

CEC–8.2 minus CEC–7 is considered the pH dependent charge from pH 7.0 to pH 8.2.

CEC–8.2 is not reported if carbonates, gypsum, or soluble salts are present in the soil because the NH_4OAc extracts cations from the dissolution of these soil constituents. Method codes are CEC–8.2 (method 4B4b1), NH_4OAc extractable bases (4B1a1b1-4), and $BaCl_2$-TEA extractable acidity (4B2b1a1).

Effective Cation Exchange Capacity: NH_4OAc Extractable Bases + Aluminum

CEC can be measured by extraction with an unbuffered salt. The unbuffered salt solution, such as 1 *N* KCl, only affects the soil pH one unit or less. The extraction is determined at or near the soil pH and extracts only the cations held at active exchange sites at the particular pH of the soil. This measures the effective cation exchange capacity (ECEC); i.e., CEC at the normal soil pH (Coleman et al., 1958).

ECEC can be determined by extracting one soil sample with neutral normal NH_4OAc to determine the exchangeable basic cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) and by extracting another sample of the same soil with 1.0 *N* KCl to determine the exchangeable Al. Neutral NH_4OAc extracts the same amounts of Ca^{2+}, Mg^{2+}, Na^+, and K^+ as KCl and therefore the method of extractable bases by NH_4OAc is used at the KSSL in place of KCl-extractable bases.

The 1 *N* KCl-extractable Al method approximates exchangeable Al and is a measure of “active” acidity present in soils with a 1:1 pH <5.5. Aluminum is non-exchangeable at pH >5.5 due to hydrolysis, polymerization, and precipitation. For soils with pH <7.0, the ECEC should be less than the CEC measured with a buffered solution at pH 7.0. ECEC (method 4B4b2a) is calculated by summing the NH_4OAc bases (method 4B1a1b1-4) plus the KCl extractable Al (method 4B3a1a1) as follows:

ECEC = NH_4OAc extractable bases + KCl-extractable Al

Effective Cation Exchange Capacity: NH_4Cl (ECEC)

The CEC method (4B1b1a1a1) that uses a neutral unbuffered salt (NH_4Cl)

provides an estimate of the ECEC of the soil (Peech et al., 1947). For a soil with a pH of <7.0, the ECEC value should be less than the CEC measured with a buffered solution at pH 7.0. The NH_4Cl CEC is about equal to the NH_4OAc extractable bases plus the KCl extractable Al for noncalcareous soils. This ECEC method is used less commonly at the KSSL.

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Ion Exchange and Extractable Cations (4B)

Displacement after Washing, NH_4OAc, pH 7 (4B1a)

Automatic Extractor, 2 *M* KCl Rinse (4B1a1a)

Flow Injection Analyzer (4B1a1a2a)

Cation Exchange Capacity (CEC–7) (4B1a1a2a1)

Air-dry or Field-Moist, <2 mm (4B1a1a2a1a-b1)

1. Introduction to Ion Exchange and Extractable Cations

Ammonium acetate (NH_4OAc) is used to displace cations from negatively charged exchange sites of the soil, replacing them with ammonium (NH_4^+). Ethanol is used to wash excess NH_4^+ from the soil. Adsorbed NH_4^+ is displaced by a potassium chloride (KCl) solution. The displaced NH_4^+ is collected and measured by flow injection spectrophotometry.

2. Scope and Field of Application

Cation exchange capacity is important in soil taxonomy. It is used to classify CEC activity of mixed and siliceous mineralogy classes of clayey soils. Additionally, CEC values can be used to interpret nutrient holding capacity and productivity of a soil. Cation-exchange capacity can be thought of as the quantity of readily exchangeable cations in the soil (Rhoades, 1982a).

Cation exchange capacity is a measure of the negative charges per unit weight of soil material expressed in units of centimoles per kg of soil (cmol(+) kg^{-1}). The CEC measurement should not be thought of as highly exact but rather as an equilibrium measurement under the conditions selected (Jackson, 1958).

3. Principle

A solution of NH_4OAc at pH 7 is used to displace extractable bases (Ca_2^+, Mg_2^+, K^+, and Na^+) from soil exchange sites, replacing them with NH_4^+. The samples are then washed with ethanol to remove excess NH_4OAc. A KCl solution is used to displace adsorbed NH_4^+. The solution is collected and analyzed by a flow injection spectrophotometer to determine cation exchange capacity.

3.1 Interferences

This method overestimates the “field” CEC of soils with pH <7 (Summer and Miller, 1996).

Incomplete saturation of the soil with NH_4^+ and insufficient removal of NH_4^+ are the greatest interferences to this method.

Ethanol may remove adsorbed NH_4^+ from the exchange sites of some soils.

Soils that contain large amounts of vermiculite can irreversibly “fix” ammonium.

Soils that contain large amounts of soluble carbonates can change the pH of the NH_4OAc, can contribute to erroneously high cation levels in the extract, or both.

4. Apparatus

4.1 Electronic balance, ±1.0 mg-sensitivity

4.2 Mechanical vacuum extractor, custom equipment. (The KSSL can be contacted for more information.)

4.3 O-Ring, 70A, Buna, size 217

4.4 Filter adapter, custom equipment. (The KSSL can be contacted for more information.) (fig. 4B1a1a–1)

4.5 Frits, ultra-high-density polyethylene, 25 mm diameter, $^1/_{16}$" thickness, 0.45-µm porosity

4.6 Filter pad, polyester white needled felt, ⅛" thickness, 25 mm diameter

4.7 Tubes, 60-mL, polypropylene, syringe barrels, with 23-mm diameter hole bored in the bottom (SET in fig. 4B1a1a–2)

4.8 Barrel of syringe, 60-mL, polypropylene, with adapter, to serve as reservoir (RT in fig. 4B1a1a–2)

4.9 Syringe, 60-mL, polypropylene, tared (ET_{NH_4OAc} in fig. 4B1a1a–2) and (ET_{KCl} in fig. 4B1a1a–2)

4.10 Rubber tubing, 3.2 ID x 1.6 OD x 12.7 mm (⅛" ID x $^1/_{16}$" OD x ½") for connecting syringe barrel with filter adapter

4.11 Flow injection spectrophotometer

4.12 Centrifuge tubes, 50-mL, disposable

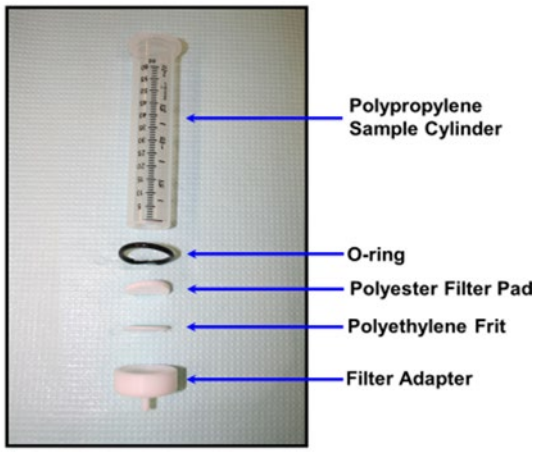

Figure 4B1a1a–1.—Sample tube and filter assembly.

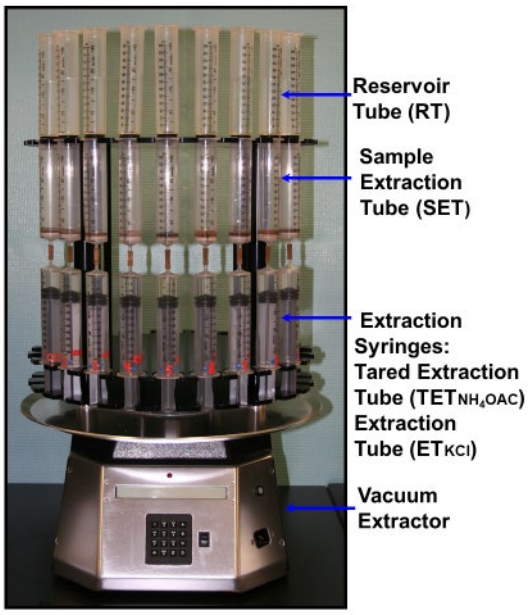

Figure 4B1a1a–2.—Vacuum extractor, 24 samples. (The KSSL can be contacted for more information.)

4.13 Wash bottles

4.14 15-mL plastic test tubes with caps

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade, reagent water

5.2 Ethanol (CH_3CH_2OH) (CAS# 64-17-5) 95%, U.S.P.

5.3 Glacial acetic acid (CH_3CO_2H) (CAS# 64-19-7)

5.4 Potassium iodide (KI) (CAS# 7681-11-0)

5.5 Mercuric iodide (HgI_2) (CAS# 7774-29-0)

5.6 Potassium chloride (KCl) (CAS# 7447-40-7)

5.7 Ammonium hydroxide (NH_4OH) (CAS# 1336-21-6), reagent-grade, S.G. 0.90

5.8 Sodium hypochlorite solution (6%) NaOCl (CAS# 7681-52-9)

5.9 Sodium hydroxide (NaOH) (CAS# 1310-73-2)

5.10 Sodium salicylate (HOC_6H_4COONa) (CAS# 54-21-7)

5.11 Sodium nitroferricyanide (III) dihydrate ($Na_2[Fe(CN)_5NO]\cdot 2H_2O$) (CAS# 13755-38-9)

5.12 Brij L23 solution (30%), commercially prepared surfactant

5.13 Ammonium 1,000 µg/mL, commercially prepared

5.14 Cation exchange solutions

5.14.1 Ammonium acetate solution, 1 N, pH 7.0

Components: Glacial acetic acid (CH_3CO_2H), ammonium hydroxide (NH_4OH), RODI water

- To an 18-L polyethylene carboy, add the following in order:
  - 15 L of RODI water
  - 1,066 mL of glacial acetic acid (CH_3COOH)
  - 1,222 mL of 15 *N* ammonium hydroxide (NH_4OH)
- Allow to stand 24 hours to equilibrate to room temperature.
  - Mix and adjust to pH 7.0 with glacial acetic acid (typically, ≈40 mL) or ammonium hydroxide as needed.
  - Fill to volume (18 L) with RODI water.

5.14.2 Nessler's reagent

Components: Potassium iodide (KI), mercuric iodide (HgI_2), sodium hydroxide (NaOH), RODI water

Note: This reagent is made in two parts

5.14.2.1 K-Hg-I solution

- To a 50-mL glass beaker, add the following in order:

- 30 mL of RODI water.
- 4.56 g of KI
- 5.68 g of HgI_2

- Stir until dissolved.

5.14.2.2 NaOH solution

- In a separate 250-mL volumetric flask, add the following in order:
  - 200 mL of RODI water
  - 10 g of NaOH
- Slowly add K-Hg-I solution to NaOH solution.
  - Fill to volume with RODI water and thoroughly mix.
- Nessler's reagent can be used immediately after preparation.
- Store in an amber bottle to protect from light.
- If a precipitate forms, the solution needs to be re-made.

5.14.3 Potassium chloride (KCl) solution, 2 M

Components: Potassium chloride (KCl), RODI water

- To a 10-L polyethylene carboy, add the following in order:
  - 8.0 L of RODI water
  - 1,341.9 g of KCl
- Allow solution to equilibrate to room temperature.
  - Dilute to 9.0 L with RODI water.
- Swirl to mix.

5.15 Flow injection analysis solutions

5.15.1 Hypochlorite solution

Components: 6% sodium hypochlorite, sodium hydroxide, Brij L23, RODI water

- To a 1-L polyethylene volumetric, add the following in order:
  - 700 mL of RODI water
  - 50 mL of 6% sodium hypochlorite
  - 3 mL of Brij L23
  - Fill to volume with RODI water.
- Invert to mix; solution may be slightly hazy.

5.15.2 Salicylate Stock Solution (Reagent A)

Components: Sodium salicylate, sodium hydroxide, Brij L23, RODI water

- To a 1-L glass bottle, add the following in order:

- 700 mL of RODI water
- 110 g of sodium salicylate
- 5.5 g of sodium hydroxide
- 3.3 mL of Brij L23
- Fill to volume with RODI water.

- Invert to mix.
- Prepare fresh weekly.

5.15.3 Nitroferricyanide stock solution (Reagent B)

Components: Sodium nitroferricyanide (III) dihydrate, RODI water

- To a 100-mL glass volumetric, add the following in order:
  - 75 mL of RODI water
  - 2.0 g of sodium nitroferricyanide (III) dihydrate
  - Fill to volume with RODI water.
- Invert to mix; solution will be orange.
- Prepare fresh weekly.

5.15.4 Salicylate/catalyst solution

Components: Salicylate stock solution, nitroferricyanide stock solution

- To a 1-L dark glass bottle, add the following in order:
  - 9 parts salicylate stock solution
  - 1 part nitroferricyanide stock solution
- Invert to mix.

5.15.5 Probe wash solution

Components: Brij L23, RODI water

- To a 1-L polyethylene bottle, add the following in order:
  - 800 mL of RODI water
  - 3.3 mL of Brij L23
  - Fill to volume with RODI water.
- Invert to mix.

5.15.6 Primary stock standard; 100 ppm Ammonium

Components: Ammonium; 1,000 µg/mL, 2 *M* KCl solution

- To a 250-mL glass volumetric, add the following in order:
  - 25 mL of Ammonium; 1,000 µg/mL
  - Dilute to volume with 2 *M* KCl.
- Invert to mix.

5.15.7 Standard ammonium calibration and verification solutions

Components: Primary stock standard, 2 *M* KCl solution

- Refer to table 4B1a1a–1 for mixing instructions.
- Invert to thoroughly mix.
- Make fresh weekly.
- Table 4B1a1a–2 lists solution concentrations.

5.15.7.1 Ammonium blank

- To a 100-mL polyethylene volumetric, add 100 mL of 2 *M* KCl solution

5.15.7.2 Ammonium standard 1

- To a 100-mL polyethylene volumetric, add the following in order:
  - 0.10 mL of primary stock standard
  - Fill to volume with 2 *M* KCl.
- Invert to mix.

5.15.7.3 Ammonium standard 2

- To a 100-mL polyethylene volumetric, add the following in order:
  - 1.00 mL of primary stock standard
  - Fill to volume with 2 *M* KCl.
- Invert to mix.

5.15.7.4 Ammonium standard 3

- To a 100-mL polyethylene volumetric, add the following in order:
  - 5.00 mL of primary stock standard
  - Fill to volume with 2 *M* KCl.
- Invert to mix.

5.15.7.5 Ammonium standard 4

- To a 100-mL polyethylene volumetric, add the following in order:
  - 10.00 mL of primary stock standard
  - Fill to volume with 2 *M* KCl.
- Invert to mix.

5.15.7.6 Ammonium standard 5

- To a 100-mL polyethylene volumetric, add the following in order:
  - 20.00 mL of primary stock standard
  - Fill to volume with 2 *M* KCl.
- Invert to mix.

5.15.7.7 Ammonium standard 6

- To a 100-mL polyethylene volumetric, add the following in order:
  - 30.00 mL of primary stock standard
  - Fill to volume with 2 *M* KCl.
- Invert to mix.

Table 4B1a1a–1.—Preparation for Ammonium Standards S1–S6. (Prepare in 100-mL volumetrics.)

Standard	Primary Stock Standard	2 *M* KCl
	(mL)	
Ammonium blank	0	Bring to volume with 2 *M* KCl
S1	0.10	
S2	1.00	
S3	5.0	
S4	10.0	
S5	20	
S6	30	

Table 4B1a1a–2.—Concentrations of Ammonium Calibration Standards S1–S6.

Standard	NH_4^+
	(mg/kg)
Blank	0
S1	0.1
S2	1
S3	5
S4	10
S5	20
S6	30

5.15.8 Quality control solution

- To a 100-mL polyethylene volumetric, add the following in order:
  - 12.5 mL of primary stock standard

- Fill to volume with 2 *M* KCl.
- Invert to mix.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Nessler's reagent contains mercury, which is toxic. Proper disposal of the Nessler's reagent and clean-up of equipment in contact with the reagent are necessary.

Ethanol is flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers.

Sodium hydroxide and sodium nitroferricyanide (III) dihydrate have the potential to be highly toxic or highly hazardous. The toxicity and carcinogenicity of all reagents used in this method must be considered and handled accordingly.

Dispense concentrated acids and bases in a fume hood. Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids.

Follow the manufacturer's safety precautions when using the vacuum extractors and the flow injection analyzer.

7. Sample Preparation

For CEC analysis, the field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

The extractors (fig. 4B1a1a–2) use three tiers of tubes and syringes: reservoir tubes, sample extraction tubes, and extraction syringes.

- Reservoir Tube (RT) is the reservoir for reagent only. It allows for metered administration of reagent to sample over a given extraction period.
- Sample Extraction Tube (SET) is a tube with sample and filter. It remains in place for the entirety of the analysis. See figure 4B1a1a–1 for tube and filter assembly.
- Extraction Syringes (two types): Extraction Tube (ET_{NH_4OAc}) and Extraction Tube (ET_{KCl}) are extraction syringes that contain filtrate collected from the sample over the course of an extraction period.

8.1 Extraction of Bases

8.1.1 To the nearest mg, weigh 2.5 g of <2-mm air-dry, mineral soil into the sample extraction tubes (SET). If sample is organic, weigh 1.0 g (to the nearest mg). Include one process-control sample and one blank sample per batch of 22 test samples.

8.1.2 Record the empty syringe weight, minus the rubber tubing, of each extraction syringe (ET_{NH_4OAc}).

8.1.3 Place sample extraction tubes on extractor and connect to corresponding ET_{NH_4OAc} with rubber tubing.

8.1.4 Rinse down the walls of the tube while filling SET to the 20-mL mark with 1 *N,* pH 7 NH_4OAc (≈10 mL). All of the sample should be wetted, and no air bubbles should be present. Shaking, swirling, stirring, or tapping may be required to wet organic samples.

8.1.5 Secure RT to top of SET and let stand for 30 minutes. Extract the NH_4OAc solution at a rate of 60 mL/30 min until 2 mL of NH_4OAc remains above the top of the soil. Do not let the soil dry.

8.1.6 Add 35.0 mL of NH_4OAc solution to the RT. Extract at a rate of 60 mL/12h.

8.1.7 After extraction is complete, remove RT from extractor. Carefully remove ET_{NH_4OAc}. Leave the rubber tubing on the SET. Weigh each ET_{NH_4OAc} containing the NH_4OAc extract to the nearest mg.

8.1.8 Mix the extract in each ET_{NH_4OAc} by manually shaking. Fill a 5-mL plastic test tube with extract solution and cap. Discard the excess properly.

Note:

- The solution in the vial is reserved for analyses of extracted cations using ICP–MS.
- Some samples may be cloudy and need to be filtered prior to analysis.
- If extracts are not to be analyzed immediately after collection, then store extracts at 4 °C in plastic tubes.

8.2 Removal of Excess Ammonium Acetate

8.2.1 Re-connect the ET_{NH_4OAc} with paired SET. Use a wash bottle to rinse the sides of the SET with ethanol to remove any remaining NH_4OAc or soil particles adhering to the SET. All soil should be wetted, and no air bubbles should be present. Fill SET to the 20-mL mark with ethanol. Secure RT to top of SET and let stand for 30 minutes.

8.2.2 Extract the ethanol solution at a rate of 60 mL/30 min until 2 mL of the solution remains above the soil level. Turn off extractor. Do not let the soil dry.

8.2.3 Add 40 mL of ethanol to the RT. Extract the ethanol at a rate of 60 mL/45 min until 2 mL of this solution remains above the soil level. Turn off the extractor. Do not let the soil dry. Disconnect the ET_{NH_4OAc} from the SET and discard the ethanol properly.

8.2.4 Re-connect the ET_{NH_4OAc} to the SET and add 50 mL of ethanol to the RT. Extract the ethanol at a rate of 60 mL/45 min. Turn off the

extractor. Remove the ET_{NH_4OAc}, leaving the tubing connected to the ET. Discard the ethanol properly.

8.2.5 Collect a few drops of ethanol extract from each SET on a spot plate. Test for NH_4^+ by using Nessler's reagent. A yellow, red, or reddish-brown precipitate indicates a positive test for NH_4^+. If the test is positive, additional ethanol washes are required. Repeat step 8.2.4 until a negative Nessler's test is obtained.

8.3 Potassium Chloride Rinse

8.3.1 Record the empty syringe weight of each extraction tube minus the rubber tubing (ET_{KCl}).

8.3.2 Connect the new labeled extraction tube (ET_{KCl}) with the rubber tubing to SET on extractor.

8.3.3 Fill SET to the 20-mL mark with 2 *M* KCl solution using a wash bottle to rinse down any remaining ethanol or soil particles adhering to the SET. All soil should be wetted, and no air bubbles should be present. Let stand for 30 minutes.

8.3.4 Extract the KCl solution at a rate of 60 mL/30 min until 2 mL of the solution remains above soil level. Turn off extractor. Do not let soil dry.

8.3.5 Secure RT to top of SET tube. Add 40 mL of KCl solution to RT and set the extractor for a rate of 60 mL/45 min. Remove the SET and ET_{KCl} from the extractor.

8.3.6 Weigh each ET_{KCl} containing the NH_4OAc extract, minus the rubber tubing, to the nearest mg.

8.4 Quantifying Ammonium (NH_4^+) in extracts from 8.3.4

8.4.1 Transfer the contents of the ET_{KCl} to a 50-mL centrifuge tube. If extracts are not to be analyzed immediately after collection, then store samples at 4 °C.

8.4.2 Refer to the manufacturer's manual for operation of the flow injection analyzer.

8.4.3 Analyze samples by flow injection spectrophotometry.

9. Calculations

9.1 Determine cmol(+) kg^{-1} = (A*[(B1−B2)/B3]*C*R*1)/(E*F)

A = Analyte ($NH4^+$) concentration in extract (mg L^{-1})

B1 = Weight of extraction syringe and extract (g)

B2 = Weight of tared extraction syringe (g)

B3 = Density of 2 *N* KCl at 20 °C (1.087 g mL^{-1})

C = Dilution factor

R = Air-dry/oven-dry ratio (method 3D1) or field-moist/oven-dry ratio (method 3D2), unitless

1 = Net conversion factor to produce units of cmol (+) kg^{-1}

E = Soil sample weight (g)

F = Equivalent weight (mg $cmol(+)^{-1}$)

NH_4^+ = 180.399.2

9.2 Report CEC to the nearest 0.1 (cmol (+) kg^{-1})

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist for final review.

10.6 Compare individual results to method detection limits (MDL) and practical quantitation limits (PQL) before reporting analysis results.

10.6.1 Report numerical values for results that are above the PQL.

10.6.2 Report “trace” for results that are between the MDL and PQL.

10.6.3 Report “non-detect” for results that are below the MDL.

MDL and PQL in Reporting Units

Analyte	MDL	PQL
	(mg kg^{-1} of oven-dried soil)	*(mg kg^{-1} of oven-dried soil)*

11. References

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Ion Exchange and Extractable Cations (4B)

Displacement after Washing, NH_4Cl (4B1b)

Automatic Extractor, 2 *M* KCl Rinse (4B1b1a)

Flow Injection Analyzer (4B1b1a2a)

Cation Exchange Capacity (4B1b1a2a1)

Air-dry or Field-Moist, <2 mm (4B1b1a2a1a-b1)

1. Introduction to CEC Ammonium Chloride (NH_4Cl)

The cation exchange capacity (CEC) determined in an unbuffered system with a pH neutral salt, e.g., 1 *N* NH_4Cl, is an estimate of the "effective" CEC (ECEC) of the soil (Peech et al., 1947). For a soil with a pH of <7.0, the ECEC values should be <CEC measured with a buffered solution at pH 7.0. The NH_4Cl CEC is approximately equal to the NH_4OAc extractable bases plus the KCl extractable Al for non-calcareous soils.

2. Scope and Field of Application

In most agricultural soils, the cation exchange capacity (CEC) is generally considered to be more important than anion exchange (AEC). The anion molecular retention capacity of these soils is typically much smaller than the CEC (Tisdale et al., 1985).

3. Principle

Displacement after washing is the basis for this procedure. The CEC is determined by:

- Saturating the exchange sites with an index cation (NH_4^+),
- Washing the soil free of excess saturated salt,
- Displacing the index cation (NH_4^+) adsorbed by the soil, and
- Measuring the amount of the index cation (NH_4^+).

A sample is leached using 1 *N* NH_4Cl and a mechanical vacuum extractor. The extract is weighed and saved for analyses of the cations. The NH_4^+ saturated soil is rinsed with ethanol to remove the NH_4^+ that was not adsorbed. The soil is then rinsed with 2 *M* KCl. This leachate is analyzed by flow injection analysis to determine the NH_4^+ adsorbed on the soil exchange complex. The CEC by NH_4Cl is reported as meq 100 g^{-1} or (cmol (+) kg^{-1}) soil.

3.1 Interferences

Incomplete saturation of the soil with NH_4^+ and insufficient removal of NH_4^+ are the greatest interferences to this method.

Ethanol removes some adsorbed NH_4^+ from the exchange sites of some soils. Isopropanol rinses have been used for some soils in which ethanol removes adsorbed NH_4^+.

Soils that contain large amounts of vermiculite can irreversibly "fix" NH_4^+. Soils that contain large amounts of soluble carbonates can change the extractant pH, can contribute to erroneously high cation levels in the extract, or both.

4. Apparatus

4.1 Electronic balance, ±1.0 mg-sensitivity

4.2 Mechanical vacuum extractor, custom equipment. (The KSSL can be contacted for more information.)

4.3 O-Ring, 70A, Buna, size 217

4.4 Filter adapter, custom equipment. (The KSSL can be contacted for more information.) (fig. 4B1b1a–1)

4.5 Frits, ultra-high-density polyethylene, 25 mm diameter, $^1/_{16}$" thickness, 0.45-µm porosity

4.6 Filter pad, polyester white needled felt, ⅛" thickness, 25 mm diameter

4.7 Tubes, 60-mL, polypropylene, syringe barrels, with 23-mm diameter hole bored in the bottom (SET in fig. 4B1b1a–2)

4.8 Barrel of syringe, 60-mL, polypropylene, with adapter, to serve as reservoir (RT in fig. 4B1b1a–2)

4.9 Syringe, 60-mL, polypropylene, tared (TET_{NH_4Cl} in fig. 4B1b1a–2) and (ET_{KCl} in fig. 4B1b1a–2)

4.10 Rubber tubing, 3.2 ID x 1.6 OD x 12.7 mm (⅛" ID x $^1/_{16}$" OD x ½") for connecting syringe barrel with filter adapter

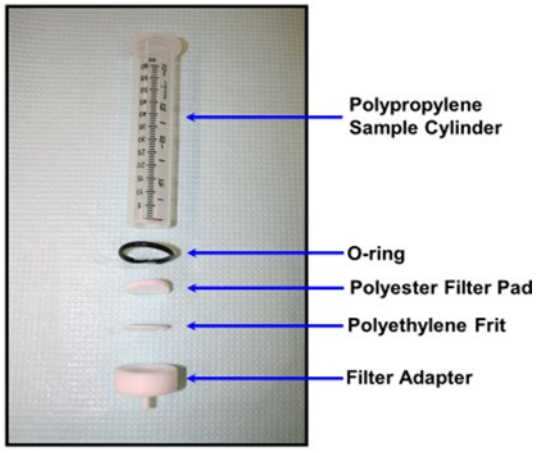

Figure 4B1b1a–1.—Sample tube and filter assembly.

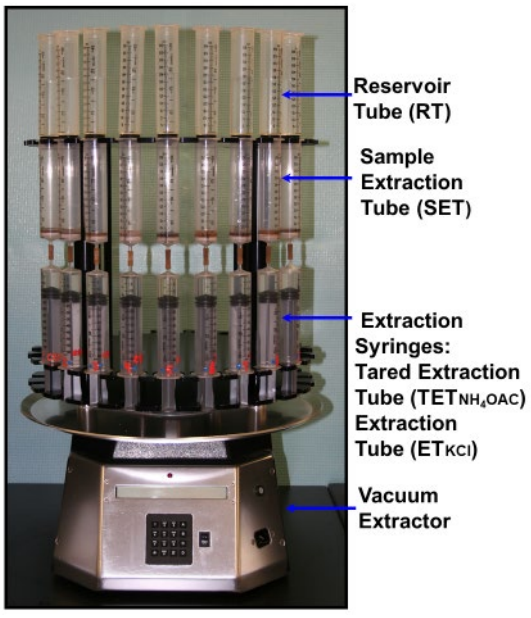

Figure 4B1b1a–2.—Vacuum extractor, 24 samples. (The KSSL can be contacted for more information.)

4.11 Flow injection spectrophotometer
4.12 Centrifuge tubes, 50-mL, disposable
4.13 Wash bottles
4.14 15-mL plastic test tubes with caps

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water
5.2 Concentrated hydrochloric acid (HCl) (CAS# 7647-01-0), 12 *N,* trace pure grade
5.3 Ethanol (CH_3CH_2OH) (CAS# 64-17-5), 95%, U.S.P.
5.4 Ammonium chloride (NH_4Cl) (CAS# 12125-02-9)
5.5 Sodium hydroxide (NaOH) (CAS# 1310-73-2), manufactured 50% solution
5.6 Potassium chloride (KCl) (CAS# 7447-40-7)
5.7 Mercuric iodide (HgI_2) (CAS# 7774-29-0)
5.8 Potassium iodide (KI) (CAS# 7681-11-0)
5.9 Ammonium; 1,000 µg/mL, commercially prepared
5.10 Ammonium chloride solution, 1 *N*

Components: Ammonium chloride (NH_4Cl), RODI water

- To a 10-L polyethylene carboy, add the following in order:
  - 7 L of RODI water
  - 535 g of NH_4Cl
- Fill to 10 L volume with RODI water.

5.11 Nessler's reagent

Components: Potassium iodide (KI), mercuric iodide (HgI_2), sodium hydroxide (NaOH), RODI water

- Note: This solution is made in two parts and then combined.
- To a 100-mL glass volumetric flask, add the following in order:
  - 50 mL of RODI water
  - 4.56 g of potassium iodide
  - 5.68 g of mercuric iodide
- Stir until dissolved.
- In a separate 250-mL glass volumetric flask, add the following in order:
  - 150 mL of RODI water
  - 10 g of sodium hydroxide
  - Slowly add K-Hg-I solution to NaOH solution
  - Fill to 250-mL volume with RODI water.
- Invert to mix.

- Solution should not contain a precipitate.
- Store in brown bottle to protect from light.

5.12 Potassium chloride solution, 2 N

Components: Potassium chloride (KCl), RODI water

- To a 10-L polyethylene carboy, add the following in order:
  - 8 L of RODI water
  - 1,341.9 g of KCl
  - Fill to 9 L volume with RODI water.
- Allow solution to equilibrate to room temperature.

5.13 Flow injection analysis solutions

5.13.1 Hypochlorite solution

Components: 6% sodium hypochlorite, sodium hydroxide, Brij L23, RODI water

- To a 1-L polyethylene volumetric, add the following in order:
  - 700 mL of RODI water
  - 50 mL of 6% sodium hypochlorite
  - 3 mL of Brij L23
  - Fill to volume with RODI water.
- Invert to mix; solution may be slightly hazy.

5.13.2 Salicylate stock solution (Reagent A)

Components: Sodium salicylate, sodium hydroxide, Brij L23, RODI water

- To a 1-L glass bottle, add the following in order:
  - 700 mL of RODI water
  - 110 g of sodium salicylate
  - 5.5 g of sodium hydroxide
  - 3.3 mL of Brij L23
  - Fill to volume with RODI water.
- Invert to mix.
- Prepare fresh weekly.

5.13.3 Nitroferricyanide stock solution (Reagent B)

Components: Sodium nitroferricyanide (III) dihydrate, RODI water

- To a 100-mL glass volumetric, add the following in order:
  - 75 mL of RODI water
  - 2.0 g of sodium nitroferricyanide (III) dihydrate
  - Fill to volume with RODI water.
- Invert to mix; solution will be orange.
- Prepare fresh weekly.

5.13.4 Salicylate/Catalyst solution

Components: Salicylate stock solution, nitroferricyanide stock solution

- To a 1-L dark glass bottle, add the following in order:
  - 9 parts salicylate stock solution
  - 1 part nitroferricyanide stock solution
- Invert to mix.

5.13.5 Probe wash solution

Components: Brij L23, RODI water

- To a 1-L polyethylene bottle, add the following in order:
  - 800 mL of RODI water
  - 3.3 mL of Brij L23
  - Fill to volume with RODI water.
- Invert to mix.

5.13.6 Primary stock standard; ammonium

Components: Ammonium; 1,000 µg/mL, 2 *M* KCl solution

- To a 250-mL glass volumetric, add the following in order:
  - 25 mL ammonium; 1,000 µg/mL
  - Dilute to volume with 2 *M* KCl.
- Invert to mix.

5.13.7 Standard ammonium calibration and verification solutions

Components: Primary stock standard, 2 *M* KCl solution

- Refer to table 4B1b1a–1 for mixing instructions.
- Invert to thoroughly mix.
- Make fresh weekly.
- Table 4B1b1a–2 lists solution concentrations.

5.13.7.1 Ammonium blank

- To a 100-mL polyethylene volumetric, add 100 mL of 2 *M* KCl solution.

5.13.7.2 Ammonium standard 1

- To a 100-mL polyethylene volumetric, add the following in order:
  - 0.10 mL primary stock standard
  - Fill to volume with 2 *M* KCl.
- Invert to mix.

5.13.7.3 Ammonium standard 2

- To a 100-mL polyethylene volumetric, add the following in order:
  - 1.00 mL primary stock standard

- Fill to volume with 2 *M* KCl.
- Invert to mix.

5.13.7.4 Ammonium standard 3

- To a 100-mL polyethylene volumetric, add the following in order:
  - 5.00 mL of primary stock standard
  - Fill to volume with 2 *M* KCl.
- Invert to mix.

5.13.7.5 Ammonium standard 4

- To a 100-mL polyethylene volumetric, add the following in order:
  - 10.00 mL of primary stock standard
  - Fill to volume with 2 *M* KCl.
- Invert to mix.

5.13.7.6 Ammonium standard 5

- To a 100-mL polyethylene volumetric, add the following in order:
  - 20.00 mL of primary stock standard
  - Fill to volume with 2 *M* KCl.
- Invert to mix.

5.13.7.7 Ammonium standard 6

- To a 100-mL polyethylene volumetric, add the following in order:
  - 30.00 mL of primary stock standard
  - Fill to volume with 2 *M* KCl.
- Invert to mix.

Table 4B1b1a–1.—Preparation of Ammonium Standards S1–S6. (Prepare in 100-mL volumetrics.)

Standard	Primary Stock Standard	2 *M* KCl
	(mL)	
Ammonium blank	0	Bring to volume with 2 *M* KCl
S1	0.10	
S2	1.00	
S3	5.0	
S4	10.0	
S5	20	
S6	30	

Table 4B1b1a–2.—Concentrations of Ammonium Calibration Standards S1–S6.

Standard	NH_4^+
	(mg/kg)
Blank	0
S1	0.1
S2	1
S3	5
S4	10
S5	20
S6	30

5.13.8 Quality control solution

- To a 100-mL polyethylene volumetric, add the following in order:
  - 12.5 mL of primary stock standard
  - Fill to volume with 2 *M* KCl.
- Invert to mix.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Dispense concentrated acids and bases in a fume hood. Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids.

Nessler's reagent contains mercury, which is toxic. Proper disposal of the Nessler's reagent and clean-up of equipment in contact with the reagent are necessary.

Ethanol is flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use if necessary.

Follow the manufacturer's safety precautions when using the vacuum extractors and the flow injection analyzer.

7. Sample Preparation

For CEC analysis, the field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

The extractors (fig. 4B1b1a–2) use three tiers of tubes and syringes: reservoir tubes, sample extraction tubes, and extraction syringes.

- Reservoir Tube (RT) is a reservoir for reagent only. It allows for metered administration of reagent to sample over a given extraction period.
- Sample Extraction Tube (SET) is a tube with sample and filter. It remains in place for the entirety of the analysis. See figure 4B1b1a–1 for tube and filter assembly.
- Extraction syringes (two types). Extraction Tube (ET_{NH_4Cl}) and Extraction Tube (ET_{KCl}) are extraction syringes that contain filtrate collected from the sample over the course of an extraction period.

8.1 Extraction of Bases

8.1.1 To the nearest mg, weigh out 2.5 g of <2-mm air-dry, mineral soil into the sample extraction tubes (SET). If sample is organic, weigh 1.0 g to the nearest mg. Include one process-control sample and one blank sample per batch of 22 test samples.

8.1.2 Record the empty syringe weight, minus the rubber tubing, of each ET_{NH_4Cl}.

8.1.3 Place sample extraction tubes on extractor and connect to corresponding ET_{NH_4CL} with rubber tubing.

8.1.4 Rinse down the walls of the tube while filling SET to the 20-mL mark with 1 *N* NH_4Cl (≈10 mL). All soil should be wetted, and no air bubbles should be present. Shaking, swirling, stirring, or tapping may be required to wet organic samples.

8.1.5 Secure RT to top of SET and let stand for 30 minutes. Extract the NH_4Cl solution at a rate of 60 mL/30 min until 2 mL of NH_4Cl remains above the top of the soil. Do not let soil dry.

8.1.6 Add 35.0 mL of NH_4Cl solution to the RT. Extract at a rate of 60 mL/12h.

8.1.7 After extraction is complete, remove RT from extractor. Carefully remove ET_{NH_4Cl}. Leave the rubber tubing on the SET. Weigh each ET_{NH_4Cl} containing the NH_4Cl extract to the nearest mg.

8.1.8 Mix the extract in each ET_{NH_4Cl} by manually shaking. Fill a 5-mL plastic test tube with extract solution and cap. Discard the excess properly. Note:

- The solution in the vial is reserved for analyses of extracted cations using ICP–MS.
- Some samples may be cloudy and need to be filtered prior to analysis.
- If extracts are not to be analyzed immediately after collection, then store extracts at 4 °C in plastic tubes.

8.2 Removal of Excess Ammonium Chloride

8.2.1 Re-connect the ET_{NH_4Cl} with paired SET. Use a wash bottle to rinse the sides of the SET with ethanol to remove any remaining NH_4Cl or soil particles adhering to the SET. All soil should be wetted, and no air bubbles should be present. Fill SET to the 20-mL mark with ethanol. Secure RT to top of SET and let stand for 30 minutes.

8.2.2 Extract the ethanol solution at a 60 mL/30 min rate until 2 mL of the solution remains above the soil level. Turn off extractor. Do not let the soil dry.

8.2.3 Add 40 mL of ethanol to the RT. Extract the ethanol at a rate of 60 mL/45 min until 2 mL of this solution remains above the soil level. Turn off the extractor. Do not let the soil dry. Disconnect the ET_{NH_4Cl} from the SET and discard the ethanol properly.

8.2.4 Re-connect the ET_{NH_4Cl} to the SET and add 50 mL of ethanol to the RT. Extract the ethanol at a rate of 60 mL/45 min. Turn off the extractor. Remove the ET_{NH_4Cl}, leaving the tubing connected to the ET. Discard the ethanol properly.

8.2.5 Collect a few drops of ethanol extract from each SET on a spot plate. Test for NH_4+ by using Nessler's reagent. A yellow, red, or reddish-brown precipitate indicates a positive test for NH_4+. If the test is positive, additional ethanol washes are required. Repeat step 8.2.4 until a negative Nessler's test is obtained.

8.3 Potassium Chloride Rinse

8.3.1 Record the empty syringe weight of each extraction tube minus the rubber tubing (ET_{KCl}).

8.3.2 Connect the new labeled extraction tube (ET_{KCl}) with the rubber tubing to SET on extractor.

8.3.3 Fill SET to the 20-mL mark with 2 *M* KCl solution using a wash bottle to rinse down any remaining ethanol or soil particles adhering to the SET. All soil should be wetted, and no air bubbles should be present. Let stand for 30 minutes.

8.3.4 Extract the KCl solution at a rate of 60 mL/30 min until 2 mL of the solution remains above soil level. Turn off extractor. Do not let soil dry.

8.3.5 Secure RT to top of SET tube. Add 40 mL KCl solution to RT and set the extractor for a rate of 60 mL/45 min. Remove the SET and ET_{KCl} from the extractor.

8.3.6 Weigh each ET_{KCl} containing the NH_4Cl extract, minus the rubber tubing, to the nearest mg.

8.4 Quantifying Ammonium (NH_4+) in extracts

8.4.1 Transfer the contents of the ET_{KCl} to a 50-mL centrifuge tube. If extracts are not to be analyzed immediately after collection, then store samples at 4 °C.

8.4.2 Refer to the manufacturer's manual for operation of the flow injection analyzer.

8.4.3 Analyze samples by flow injection spectrophotometry.

9. Calculations

9.1 Determine cmol(+) kg^{-1} = (A*[(B1−B2)/B3]*C*R*1) / (E*F)

A = Analyte (NH_4^+) concentration in extract (mg L^{-1})

B1 = Weight of extraction syringe and extract (g)

B2 = Weight of tared extraction syringe (g)

B3 = Density of 2 *N* KCl at 20 °C (1.087 g mL^{-1})

C = Dilution factor

R = Air-dry/oven-dry ratio (method 3D1) or field-moist/oven-dry ratio (method 3D2), unitless

1 = Net conversion factor to produce units of cmol (+) kg^{-1}

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist for final review.

10.6 Compare individual results to method detection limits (MDL) and practical quantitation limits (PQL) before reporting analysis results.

10.6.1 Report numerical values for results that are above the PQL.

10.6.2 Report "trace" for results that are between the MDL and PQL.

10.6.3 Report "non-detect" for results that are below the MDL.

MDL and PQL in Reporting Units

Analyte	MDL	PQL
	(mg kg^{-1} of oven-dried soil)	*(mg kg^{-1} of oven-dried soil)*

11. References

Holmgren, G.G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Am. J. 41:1207–1208.

Peech, M., L.T. Alexander, L.A. Dean, and J.F. Reed. 1947. Methods of soil analysis for soil fertility investigations. USDA. Agric. Circular 757, 25 p.

Ion Exchange and Extractable Cations (4B)

Displacement after Washing, NH_4OAc, pH 7 (4B1a)

Automatic Extractor (4B1a1)

Inductively Coupled Plasma Mass Spectrometer (4B1a1c)

Calcium, Magnesium, Potassium, and Sodium (4B1a1c1-4)

Air-dry or Field-moist, <2-mm (4B1a1c1-4a-b1)

1. Introduction

Ammonium acetate (NH_4OAc) is used to displace extractable bases (Ca^{2+}, Mg^{2+}, K^+, and Na^+), which are generally assumed to be the exchangeable cations on the exchange sites of the soil. NH_4OAc-extracted analytes are measured using an inductively coupled plasma mass spectrometer (ICP–MS). Ca^{2+}, Mg^{2+}, K^+, and Na^+ are reported in units of cmol(+) kg^{-1}.

2. Scope and Field of Application

Soil mineral particles and organic colloidal particles have negative valence charges that hold dissociable cations (exchangeable bases) and thus are “colloidal electrolytes” (Jackson, 1958). Ammonium acetate (NH_4OAc) is used to displace the extractable bases (Ca^{2+}, Mg^{2+}, K^+, and Na^+), which are generally assumed to be the exchangeable cations on the exchange sites of the soil. The typical abundance order of these plant-essential nutrients is $Ca^{2+} > Mg^{2+} > K^+ > Na^+$. The term “extractable” is used rather than “exchangeable” because additional sources of water-soluble salts can potentially influence reported concentrations. The presence of calcium carbonate; gypsum; serpentine (high Mg^{2+}); mica or vermiculite (K^+); or natric material (high Na^+) may alter the typically observed abundance of extracted cations (Thomas, 1982).

3. Principle

An NH_4OAc solution is used to displace extractable bases Ca^{2+}, Mg^{2+}, K^+, and Na^+ from soil exchange sites. The solution containing the extracted bases is collected for analysis by an Inductively Coupled Plasma Mass Spectrometer (ICP–MS).

3.1 Interferences

Analyte-specific interferences using ICP–MS are corrected or minimized by using internal standards, collision/reaction cell technology, and careful selection of specific masses for data reporting.

Do not use sodium borosilicate glass tubes for extracts. Such tubes can result in sodium contamination.

4. Apparatus

4.1 Inductively coupled plasma spectrometer
4.2 Digital diluter/dispenser with 10,000-µL and 1,000-µL syringes
4.3 Pipettes, electronic (digital), 250-µL, 1-mL, and 10-mL
4.4 Vortexer, mini
4.5 1-L polyethylene volumetric flasks
4.6 Polymer test tubes, 15-mL
4.7 Containers, polyethylene
4.8 Centrifuge tubes, 50-mL, disposable, polyethylene, with caps

5. Chemicals

5.1 Compressed argon (minimum purity 99.99%)
5.2 Compressed hydrogen (minimum purity 99.999%)
5.3 Compressed helium (minimum purity 99.999%)
5.4 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water
5.5 Concentrated hydrochloric acid (HCl) (CAS# 7647-01-0), 12 *N*, trace pure grade
5.6 Glacial acetic acid (CH_3COOH) (CAS# 64-19-7), 99.5%
5.7 Ammonium hydroxide (NH_4OH) (CAS# 1336-21-6), 15 *N*, reagent-grade, specific gravity 0.90
5.8 Ammonium acetate solution (NH_4OAc), 1 *N*, pH 7.0

Components: Glacial acetic acid (CH_3COOH)**;** ammonium hydroxide (NH_4OH), reagent-grade, specific gravity 0.90; RODI water

- To an 18-L polyethylene carboy, add the following in order:
  - 15 L of RODI water
  - 1,066 mL of glacial acetic acid (CH_3COOH)
  - 1,222 mL of 15 *N* ammonium hydroxide (NH_4OH)
- Allow to stand 24 hours to equilibrate to room temperature.
- Mix and adjust to pH 7.0 with glacial acetic acid (typically ≈40 mL) or ammonium hydroxide as needed.
- Fill to volume (18 L) with RODI water.

5.9 High purity concentrated elements

Individual high purity elemental standards, commercially prepared. Individual solutions containing:

1,000 mg/L Ca, Calcium Standard
1,000 mg/L Mg, Magnesium Standard
1,000 mg/L K, Potassium Standard
1,000 mg/L Na, Sodium Standard

1,000 mg/L Li^6, Lithium Standard

1,000 mg/L Ge, Germanium Standard

1,000 mg/L Tb, Terbium Standard

5.10 ICP–MS calibration standards and calibration verification standard (CVS)

Components: High purity standards: Ca, Mg, K, Na**;** 1.0 *N* ammonium acetate (NH_4OAc) solution; RODI water

- Refer to table 4B1a1c–1 for mixing instructions.
- Date all standards. Working shelf life is 1 month.
- Store calibration standards in polyethylene containers. Do not use glass.
- Table 4B1a1c–2 lists solution concentrations.

5.10.1 CEC 2 (High)

- To a 1-L polyethylene volumetric flask, add the following in order:
  - Approximately 200 mL of RODI water.
  - 5.0 mL of 1.0 *N* NH_4OAc
  - 2.0 mL of 1,000 mg/L Ca, Calcium Standard
  - 0.50 mL of 1,000 mg/L Mg, Magnesium Standard
  - 0.25 mL of 1,000 mg/L K, Potassium Standard
  - 0.75 mL of 1,000 mg/L Na, Sodium Standard
- Fill to volume with RODI and mix thoroughly.

5.10.2 CEC 1 (Low)

- To a 1-L polyethylene volumetric flask, add the following in order:
  - Approximately 200 mL of RODI water.
  - 5.0 mL of 1.0 *N* NH_4OAc
  - 100 mL of CEC 2 High
- Fill to volume with RODI and mix thoroughly.

5.10.3 CEC CVS

- To a 1-L polyethylene volumetric flask, add the following in order:
  - Approximately 200 mL of RODI water.
  - 5.0 mL of 1.0 *N* NH_4OAc
  - 1.0 mL of 1,000 mg/L Ca, Calcium Standard
  - 0.275 mL of 1,000 mg/L Mg, Magnesium Standard
  - 0.125 mL of 1,000 mg/L K, Potassium Standard
  - 0.50 mL of 1,000 mg/L Na, Sodium Standard

- Fill to volume with RODI and mix thoroughly.

5.10.4 CEC Blank

- To a 1-L polyethylene volumetric flask, add the following in order:
  - Approximately 200 mL of RODI water.
  - 5.0 mL of 1.0 *N* NH_4OAc
- Fill to volume with RODI and mix thoroughly.

Table 4B1a1c–1.—Preparation of Calibration Standards and Calibration Verification Standard. (Prepare in 1-L polyethylene volumetric flasks.)

Element or Reagent	CEC 2 High	CEC 1 Low	CEC CVS	CEC Blank
	(mL)	*(mL)*	*(mL)*	
1 *N* NH_4OAc	5 mL			
Ca	2.00	100 mL of CEC 2 High	1.00	---
Mg	0.500		0.275	---
K	0.250		0.125	---
Na	0.750		0.500	---
RODI water	Bring to volume with RODI water			

Table 4B1a1c–2.—Concentrations of Calibration Standards and Calibration Verification Standard.

Reagent	CEC 2 High	CEC 1 Low	CEC CVS	Blank
	(mg L^{-1})	*(mg L^{-1})*	*(mg L^{-1})*	
Ca	2.00	0.200	1.00	---
Mg	0.50	0.050	0.275	---
K	0.250	0.0250	0.125	---
Na	0.750	0.0750	0.500	---

5.10.5 Internal standard solution

Components: High purity standards: Ge, Tb, Li^6; ammonium acetate (NH_4OAc) solution, 1.0 *N*; RODI water

- To a 1-L polyethylene volumetric flask, add the following in order:
  - Approximately 200 mL of RODI water.
  - 5.0 mL of 1.0 *N* NH_4OAc
  - 0.50 mL of 1,000 mg/L Li^6, Lithium Standard
  - 0.50 mL of 1,000 mg/L Ge, Germanium Standard
  - 0.50 mL of 1,000 mg/L Tb, Terbium Standard
- Fill to volume with RODI and mix thoroughly.
- Refer to table 4B1a1c–3 below.

Table 4B1a1c–3.—Concentration for Internal Standard Solution. (Prepare in 1-L volumetric flasks.)

Element or Reagent	Internal Standard
	(mL)
1 *N* NH_4OAc	5.0
Li^6	0.50
Ge	0.50
Tb	0.50
RODI water	Bring to volume with RODI water

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids. Dispense concentrated acids and bases in fume hood.

Dewars of liquefied argon should be maintained in an upright position following standard KSSL laboratory safety procedures.

Follow the manufacturer's safety precautions when using the ICP–MS.

7. Sample Preparation

For CEC analysis, the field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Dilution of sample extracts: Set the digital diluter for a 1:200 dilution. Dilute samples with RODI into 15-mL polymer tubes. Vortex to mix.

8.2 ICP–MS set-up and operation: Refer to the manufacturer's manual. General instrument set-up parameters: Meinhardt nebulizer, cyclonic spray chamber, 1,600 watts, neb flow 1 L/min, aux flow 1.2 L/min, plasma flow 18 L/min. See table 4B1a1c–4 for reported masses, internal standards, and cell gas.

Table 4B1a1c–4.—General Instrument Set-Up and Analysis Conditions.

Analyte	Mass Measured	Internal Standard	Cell Gas
Ca	43	Tb	H_2
Mg	24	Ge	He
K	39	Li^6	He
Na	23	Li^6	He

8.3 Calibrate the ICP–MS using calibration standards from table 4B1a1c–1. Analyze CVS once after calibration and then every 12 test samples. If the CVS fails, recalibrate and re-analyze test samples from the last passing CVS. Recalibrate every 24 samples.

8.4 Analyze a process-control sample with every batch of 24 samples.

If results from process-control sample are outside the acceptable range, re-analyze the process-control sample to confirm the results. If confirmed, re-analyze all associated test samples from beginning of method.

If a test sample analyte exceeds three times the high calibration standard concentration, dilute sample 1:20 and then 1:50 with RODI for a total dilution of 1:1,000.

Record analyte readings to 0.1 unit. The instrument readings for analyte concentration are measured in units of mg L−1, which are converted to a soil basis.

9. Calculations

9.1 Determine extractable base concentration (cmol(+) kg^{-1})

$$\text{cmol(+) kg}^{-1} = (A*[(B1-B2)/B3]*C*R*1)/(E*F)$$

A = Analyte (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}) concentration in extract (mg L^{-1})

B1 = Weight of extraction syringe and extract (g)

B2 = Weight of tared extraction syringe (g)

B3 = Density of 1 *N* NH_4OAc at 20 °C (1.0124 g mL^{-1})
C = Dilution factor; 200 (or 1,000, if needed under step 8.4)
R = Air-dry/oven-dry ratio (method 3D1) or field-moist/oven-dry ratio
1 = Net conversion factor to produce units of cmol(+) kg^{-1}
E = Soil sample weight (g)
F = Equivalent weight (mg $cmol(+)^{-1}$)
Ca^{2+} = 200.4
Mg^{2+} = 121.5
K^{+} = 391.0
Na^{+} = 229.9

9.2 Report the extractable Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} to the nearest 0.1 cmol(+) kg^{-1}.

Table 4B1a1c–5.—Method Detection Limits (MDL) and Practical Quantitation Limits (PQL).

Analyte	MDL	PQL
	(cmol(+) kg^{-1})	*(cmol(+) kg^{-1})*
Ca	0.06	0.30
K	0.06	0.30
Mg	0.01	0.05
Na	0.04	0.20

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist for final review.

10.6 Compare individual results to method detection limits (MDL) and practical quantitation limits (PQL) before reporting analysis results.

10.6.1 Report numerical values for results that are above the PQL.

10.6.2 Report “trace” for results that are between the MDL and PQL.

10.6.3 Report “non-detect” for results that are below the MDL.

MDL and PQL in Reporting Units

Analyte	MDL	PQL
	(mg kg^{-1} of oven-dried soil)	*(mg kg^{-1} of oven-dried soil)*

11. References

Bates, T.E. 1993. Soil handling and preparation. p. 19–24. *In* M.R. Carter (ed.) Soil sampling and methods of analysis. Can. Soc. Soil Sci., Lewis Publ., CRC Press, Boca Raton, FL.

Jackson, M.L. 1958. Soil chemical analysis. Prentice-Hall, Inc., Englewood Cliffs, NJ.

Thomas, G.W. 1982. Exchangeable cations. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Ion Exchange and Extractable Cations (4B)

Displacement after Washing, NH_4Cl (4B1b)

Automatic Extractor (4B1b1)

Inductively Coupled Plasma Mass Spectrometer (4B1b1c)

Calcium, Magnesium, Potassium, and Sodium (4B1b1c1-4)

Air-dry or Field-Moist, <2-mm (4B1b1c1-4a-b1)

1. Introduction

To estimate the "effective" cation exchange capacity (ECEC), the cation exchange capacity (CEC) is determined using an unbuffered, neutral cation salt; i.e., 1 *N* NH_4Cl (Peech et al., 1947). For soils with a pH of <7.0, the ECEC values should be <CEC as measured with a buffered pH 7 NH_4OAc solution. The NH_4Cl CEC is approximately equal to the NH_4OAc extractable bases plus the potassium chloride (KCl) extractable aluminum for non-calcareous soils. NH_4Cl-extracted analytes are measured using an inductively coupled plasma mass spectrometer (ICP–MS). Ca^{2+}, Mg^{2+}, K^+, and Na^+ are reported in units of cmol(+) kg^{-1}.

2. Scope and Field of Application

Soil mineral particles and organic colloidal particles have negative valence charges that hold dissociable cations (exchangeable bases) and thus are "colloidal electrolytes" (Jackson, 1958). Ammonium chloride (NH_4Cl) is used to displace the extractable bases (Ca^{2+}, Mg^{2+}, K^+, and Na^+), which are generally assumed to be the exchangeable cations on the exchange sites of the soil. The typical abundance order of these plant-essential nutrients is $Ca^{2+} > Mg^{2+} > K^+ > Na^+$. The term "extractable" is used rather than "exchangeable" because additional sources of water-soluble salts can potentially influence reported concentrations. The presence of calcium carbonate; gypsum; serpentine (high Mg^{2+}); mica or vermiculite (K^+); or natric material (high Na^+) may alter the typically observed abundance of extracted cations (Thomas, 1982).

3. Principle

An NH_4Cl solution is used to displace extractable bases Ca^{2+}, Mg^{2+}, K^+, and Na^+ from soil exchange sites. The solution containing the extracted bases is collected for analysis by ICP–MS.

3.1 Interferences

Analyte-specific interferences using ICP–MS are corrected or minimized by using internal standards, collision/reaction cell technology, and careful selection of specific masses for data reporting.

Do not use sodium borosilicate glass tubes for extracts. Such tubes can result in sodium contamination

4. Apparatus

4.1 Inductively coupled plasma spectrometer
4.2 Digital diluter/dispenser, with syringes 10,000-µL and 1,000-µL
4.3 Pipettes, electronic digital, 250-µL, 1-mL, and 10-mL
4.4 Vortexer, mini
4.5 1-L polyethylene volumetric flasks
4.6 Plastic test tubes, 15-mL
4.7 Containers, polyethylene
4.8 Centrifuge tubes, 50-mL, disposable, polyethylene, with caps

5. Chemicals

5.1 Compressed argon (minimum purity 99.99%)
5.2 Compressed hydrogen (minimum purity 99.999%)
5.3 Compressed helium (minimum purity 99.999%)
5.4 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water
5.5 Ammonium chloride (NH_4Cl) (CAS# 12125-02-9)
5.6 High purity concentrated elements

Individual high purity elemental standards, commercially prepared.

Individual solutions containing**:**

1,000 mg/L Ca, Calcium Standard
1,000 mg/L Mg, Magnesium Standard
1,000 mg/L K, Potassium Standard
1,000 mg/L Na, Sodium Standard
1,000 mg/L Li^6; Lithium Standard
1,000 mg/L Ge, Germanium Standard
1,000 mg/L Tb, Terbium Standard

5.7 Ammonium chloride solution, 1 *N*

Components: Ammonium chloride (NH_4Cl), RODI water

- To a 10-L polyethylene carboy, add the following in order:
  - 7 L of RODI water
  - 535 g of NH_4Cl
  - Fill to volume with RODI water.
- Swirl to mix.

5.8 ICP–MS calibration standard solutions

Components: High purity standards: Ca, Mg, Ka, Na; ammonium chloride solution, 1.0 N; RODI water

Refer to table 4B1b–1 for mixing instructions.

- Table 4B1b–2 lists solution concentrations.
- Date all standards.
- Working shelf life is 1 month.
- Store calibration standards in polyethylene containers. Do not use glass.

5.8.1 CEC 2 high

- To a 1-L polyethylene volumetric flask, add the following in order:
  - ≈200 mL of RODI water.
  - 5.0 mL of 1.0 *N* NH_4Cl
  - 2.0 mL of Ca primary stock standards (1,000 mg/L^{-1})
  - 0.5 mL of Mg primary stock standards (1,000 mg/L^{-1})
  - 0.25 mL of K primary stock standards (1,000 mg/L^{-1})
  - 0.75 mL of Na primary stock standards (1,000 mg/L^{-1})
  - Fill to volume with RODI water.
- Invert to mix.

5.8.2 CEC 1 low

- To a 1-L polyethylene volumetric flask, add the following in order:
  - ≈200 mL of RODI water.
  - 5.0 mL of 1.0 *N* NH_4Cl
  - 100 mL of CEC 2 High
  - Fill to volume with RODI water.
- Invert to mix.

5.8.3 CEC CVS

- To a 1-L polyethylene volumetric flask, add the following in order:
  - ≈200 mL of RODI water.
  - 5.0 mL of 1.0 *N* NH_4Cl
  - 1.0 mL of Ca primary stock standards (1,000 mg/L^{-1})
  - 0.275 mL of Mg primary stock standards (1,000 mg/L^{-1})
  - 0.125 mL of K primary stock standards (1,000 mg/L^{-1})
  - 0.5 mL of Na primary stock standards (1,000 mg/L^{-1})
  - Fill to volume with RODI water.
- Invert to mix.

5.8.4 CEC blank

- To a 1-L polyethylene volumetric flask, add the following in order:

- ≈200 mL of RODI water.
- 5.0 mL of 1.0 *N* NH_4Cl
- Fill to volume with RODI water.

- Invert to mix.

Table 4B1b–1.—Preparation of Calibration Standards and Calibration Verification Standards. (Prepare in 1-L polymer volumetric flasks.)

Element or Reagent	CEC 2 High	CEC 1 Low	CEC CVS	CEC Blank
	(mL)	*(mL)*	*(mL)*	
1 *N* NH_4Cl	5 mL			
Ca	2.00	100 mL of CEC 2 High	1.00	---
Mg	0.500		0.275	---
K	0.250		0.125	---
Na	0.750		0.500	---
RODI water	Bring to volume with RODI water			

Table 4B1b–2.—Concentrations of Calibration Standards and Calibration Verification Standard.

Reagent	CEC 2 High	CEC 1 Low	CEC CVS	Blank
	(mg L^{-1})	*(mg L^{-1})*	*(mg L^{-1})*	
Ca	2.00	0.200	1.00	---
Mg	0.50	0.050	0.275	---
K	0.250	0.0250	0.125	---
Na	0.750	0.0750	0.500	---

5.9 Internal standard solution

Components: High purity concentrated elements: Ge, Tb, Li^6; ammonium chloride (NH_4Cl) solution, 1.0 *N;* RODI water

- To a 1-L polyethylene volumetric flask, add the following in order:
  - Approximately 200 mL of RODI water.
  - 5.0 mL of 1.0 *N* NH_4Cl
  - 0.50 mL of 1,000 mg/L Li^6, Lithium Standard
  - 0.50 mL of 1,000 mg/L Ge, Germanium Standard

- 0.50 mL of 1,000 mg/L Tb, Terbium Standard
- Fill to volume with RODI water.

- Mix thoroughly.
- Refer to table 4B1b–3 below.

Table 4B1b–3.—Preparation of Internal Standard Solutions. (Prepare in 1-L volumetric flasks.)

Element or Reagent	Internal Standard
	(mL)
1 *N* NH_4Cl	5
Li^6	0.5
Ge	0.5
Tb	0.5
RODI water	Bring to volume with RODI water

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids. Dispense concentrated acids and bases in fume hood.

Dewars of liquefied argon should be maintained in an upright position following standard KSSL laboratory safety procedures.

Follow the manufacturer's safety precautions when using the ICP–MS.

7. Sample Preparation

For CEC analysis, the field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Set the digital diluter for a 1:200 dilution. Dilute samples 1:200 with RODI into 15-mL polymer tubes. Vortex to mix. Note: Do not use sodium borosilicate glass tubes because of the risk of sodium contamination.

8.2 ICP–MS set-up and operation: Refer to the manufacturer's manual. General instrument set-up parameters are: Meinhardt nebulizer, cyclonic

spray chamber, 1,600 watts, neb flow 1 L/min, aux flow 1.2 L/min, plasma flow 18 L/min. See table 4B1b–4 for reported masses, internal standards, and cell gas.

Table 4B1b–4.—General Instrument Set-Up and Analysis Conditions.

Analyte	Mass Measured	Internal Standard	Cell Gas
Ca	43	Tb	H_2
Mg	24	Ge	He
K	39	Li^6	He
Na	23	Li^6	He

8.3 Calibrate the instrument using calibration standards from table 4B1b–1. Analyze CVS once after calibration and then every 12 test samples. Recalibrate every 24 samples.

8.4 If a test sample analyte exceeds three times the high calibration standard concentration, dilute sample 1:20 and then 1:50 with RODI for a total dilution of 1:1,000.

8.5 Record analyte readings to 0.01 unit.

9. Calculations

9.1 Determine extractable base concentration (cmol(+) kg^{-1})

$$cmol(+)\ kg^{-1} = (A*[(B1-B2)/B3]*C*R*1)/(E*F)$$

A = Analyte (Ca^{2+}, Mg^{2+}, K^+, Na^+) concentration in extract (mg L^{-1})

B1 = Weight of extraction syringe and extract (g)

B2 = Weight of tared extraction syringe (g)

B3 = Density of 1 *N* NH_4Cl at 20 °C (1.01 g mL^{-1})

C = Dilution factor; 200 (or 1,000, if needed under step 8.4)

R = Air-dry/oven-dry ratio (method 3D1) or field-moist/oven-dry ratio

1 = Net conversion factor to produce units of cmol(+) kg^{-1}

E = Soil sample weight (g)

F = Equivalent weight (mg $cmol(+)^{-1}$)

Ca^{2+} = 200.4

Mg^{2+} = 121.5

K^+ = 391.0

Na^+ = 229.9

9.2 Report the extractable Ca^{2+}, Mg^{2+}, Na^+, and K^+ to the nearest 0.1 cmol(+) kg^{-1}.

Table 4B1b–5.—Method Detection Limits (MDL) and Practical Quantitation Limits (PQL).

Analyte	MDL	PQL
	(cmol(+) kg^{-1})	*(cmol(+) kg^{-1})*
Ca	0.06	0.30
K	0.06	0.30
Mg	0.01	0.05
Na	0.04	0.20

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist for final review.

10.6 Compare individual results to method detection limits (MDL) and practical quantitation limits (PQL) before reporting analysis results.

10.6.1 Report numerical values for results that are above the PQL.

10.6.2 Report “trace” for results that are between the MDL and PQL.

10.6.3 Report “non-detect” for results that are below the MDL.

MDL and PQL in Reporting Units

Analyte	MDL	PQL
	(mg kg^{-1} of oven-dried soil)	*(mg kg^{-1} of oven-dried soil)*

11. References

Thomas, G.W. 1982. Exchangeable cations. p. 159–165. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Ion Exchange and Extractable Cations (4B)

$BaCl_2$-Triethanolamine, pH 8.2 Extraction (4B2)

Centrifuge (4B2b)

Automatic Titrator (4B2b1)

Back Titration with HCl (4B2b1a)

Extractable Acidity (4B2b1a1)

Air-Dry or Field-Moist, <2 mm (4B2b1a1a-b1)

1. Introduction to Barium Chloride/TEA Extraction

Extractable acidity is the acidity released from the soil by a barium chloride-triethanolamine ($BaCl_2$-TEA) solution buffered at pH 8.2. The Natural Resources Conservation Service uses a pH of 8.2, which approximates the calculated pH of a soil containing free $CaCO_3$ in equilibrium with the normal CO_2 content (0.03%) of the atmosphere. A pH of 8.2 also closely corresponds to the pH of complete neutralization of soil hydroxy-Al compounds. Extractable acidity includes all the acidity generated by replacement of the H and Al from permanent exchange sites and pH-dependent exchange sites.

2. Scope and Field of Application

Extractable acidity by $BaCl_2$-TEA, pH 8.2, is routinely determined by the KSSL for samples that show very slight or no effervescence after treatment with 1 *N* HCl. The $BaCl_2$-TEA pH 8.2 method may not always accurately reflect the nature of soils in situ. Regardless, this method has become a standard reference to which other methods are compared.

3. Principle

A soil sample is leached overnight with a $BaCl_2$-TEA solution buffered at pH 8.2. The sample is shaken, centrifuged, and the extract is back-titrated with HCl. The difference between a blank and the extract is the extractable acidity. Extractable acidity is reported in cmol (+) kg^{-1}.

3.1 Interferences

The buffer capacity of the $BaCl_2$-TEA solution may be exceeded for some very acid soils. In this case, re-analysis will be required using a smaller sample.

4. Apparatus

4.1 Electronic balance, ±1.0-mg sensitivity

4.2 Pipettes or dispenser, adjustable volume to 40 mL

4.3 Vortexer, mini

4.4 Centrifuge tubes, 50-mL, disposable, polyethylene

4.5 Centrifuge capable of 2,000 rpm

4.6 Titration beakers, 250-mL, borosilicate glass or HDPE

4.7 Automatic titrator, with control unit, sample changer, dispenser, and software

4.8 Combination pH-reference electrode

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.2 Hydrochloric acid (HCl) (CAS# 7647-01-0), concentrated 12 *N,* trace pure grade

5.3 Barium chloride ($BaCl_2$) (CAS# 10361-37-2), anhydrous

5.4 Barium hydroxide [$Ba(OH)_2$] (CAS 17194-00-2)

5.5 Triethanolamine (TEA) ($C_6H_{15}NO_3$) (CAS# 102-71-6)

5.6 Hydrochloric acid solution, 0.25 *N,* standardized

Components: Concentrated hydrochloric acid (HCl), RODI water

- In a 20-L polyethylene carboy, add the following in order:
  - 15 L of RODI water
  - 400 mL of concentrated HCl
  - Fill to volume with RODI water.
- Standardize HCl solution using method 4A: standardization of acids.

5.7 $BaCl_2$ (TEA) buffer solution, pH 8.2

Components: Barium chloride ($BaCl_2$), anhydrous; triethanolamine (TEA); hydrochloric acid (HCl) or barium hydroxide [$Ba(OH)_2$]; RODI water

Note: This solution is made in two parts and then combined.

- In a 20-L polyethylene carboy, add the following in order:
  - 8 L of RODI water
  - 977 g of $BaCl_2$
- Swirl to mix.
- In a separate 5-L polyethylene container, add the following in order:
  - 4-L of RODI water
  - 477 g of TEA
- Swirl to mix.
- Pour the TEA solution into the $BaCl_2$ solution.
  - Fill to slightly less than 16 L volume with RODI water.
  - Adjust to pH 8.2 with ≈33 mL of concentrated HCl or barium hydroxide
  - Fill to 16 L volume with RODI water.
- Result: $BaCl_2$ = 0.5 *N*, TEA = 0.2 *N*

5.8 Replacement solution

Components: Barium chloride ($BaCl_2$), TEA buffer solution, RODI water

- In a 20-L polyethylene carboy, add the following in order:
  - 8 L of RODI water
  - 977 g of $BaCl_2$
  - 80 mL of buffer
  - Fill to 16 L volume with RODI water.
- Swirl to mix.

5.9 Buffers for titrator calibration: pH 9.18, 7.00, and 4.00

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Dispense concentrated acids in a fume hood. Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Weigh 5 g of <2-mm air-dry, mineral soil to the nearest mg into a labeled centrifuge tube. If sample is moist, weigh enough soil to achieve ≈5 g of air-dry soil. For every 21 samples, prepare at least two reagent blanks and one quality control sample.

8.2 Add 40.00 mL of $BaCl_2$-TEA buffer solution to each sample. Cap the tube and shake to ensure all soil is wetted.

8.3 Place tube rack on its side and gently shake to stratify the mixture lengthwise along the tube. Allow to stand overnight on its side.

8.4 Use mini vortexer to homogenize the soil and solution.

8.5 Centrifuge samples at 2,000 rpm for 5 minutes.

8.6 Decant extracts into numbered titration beakers.

8.7 Add 40 mL of replacement solution (chemical **5.8** above) to each sample.

8.8 Cap tube and use mini vortexer to homogenize the soil and solution.

8.9 Centrifuge sample tubes at 2,000 rpm for 5 min.

8.10 Decant extract into numbered titration beakers.

8.11 Repeat steps 8.7–8.10. The resulting total volume in each titration beaker should be ≈120 mL.

8.12 Titrate samples.

8.13 Refer to the manufacturer's manual for operation of the automatic titrator.

8.14 Calibrate the titrator meter with pH 9.18, 7.00, and 4.00 buffers.

8.15 Titrate samples to an end point of pH 4.60.

8.16 If pre-titration pH is 0.3 units lower than the average pH of the blanks, rerun sample using a 0.5-g sample.

9. Calculations

9.1 Determine extractable acidity:

$$\text{Extractable acidity cmol (+) kg}^{-1} = [((B-T)/1{,}000)*N*R*]/(E*10)$$

B = Average reagent blank titer (mL)

T = Sample titer (mL)

1,000 = units conversion from mL to L

N = Normality of HCl

R = Air-dry/oven-dry ratio (method 3D1) or field-moist/oven-dry ratio (method 3D2), unitless

E = Sample mass (g)

10 = Net conversion factor to produce units of cmol (+) kg^{-1}

9.2 Report extractable acidity to the nearest 0.1 cmol (+) kg^{-1}.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

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Ion Exchange and Extractable Cations (4B)

1 *N* KCl Extraction (4B3)

Reciprocating Shaker (4B3b)

Inductively Coupled Plasma Atomic Emission Spectrophotometer (4B3b1)

Axial Mode (4B3b1b)

Al (4B3b1b1)

Air-Dry or Field-Moist, <2 mm (4B3b1b1a1-b1)

1. Introduction to KCl Extraction

Aluminum extracted by 1 *N* potassium chloride (KCl) approximates exchangeable Al at the pH of the soil and is a measure of the "active" acidity present. Extractable Al is routinely determined by the KSSL when pH is <5.05 by 1:2 0.01 *M* $CaCl_2$. KCl extractable Al is related to the immediate lime requirement and existing CEC of the soil.

2. Scope and Field of Application

The 1 *N* KCl-extractable Al method approximates exchangeable Al and is a measure of "active" acidity present in soils with a 1:1 pH <5.5 by 1:1 in RO water. Aluminum is non-exchangeable at pH >5.5 due to hydrolysis, polymerization, and precipitation. For soils with pH <7.0, the ECEC should be less than the CEC measured with a buffered solution at pH 7.0. ECEC is calculated by summing the NH_4OAc bases plus the KCl extractable Al as follows:

ECEC = NH_4OAc extractable bases + KCl-extractable Al

3. Principle

Aluminum is leached from the sample using 1 *N* KCl. The leachate is measured by an inductively coupled plasma atomic emission spectrophotometer (ICP–AES). Aluminum in the soil reported as cmol (+) kg^{-1}.

3.1 Interferences

ICP–AES interferences are element dependent and are minimized or eliminated through wavelength selection, background correction, matrix matching, and use of internal standards as appropriate.

4. Apparatus

4.1 Electronic balance, ±1.0-mg sensitivity

4.2 Pipettes, electronic digital, 50-mL, 10,000-µL, and 1,000-µL

4.3 Centrifuge, capable of 3,700 rpm

4.4 Containers, polyethylene

4.5 Inductively coupled plasma atomic emission spectrophotometer (ICP–AES)
4.6 Test tubes, 5-mL and 15-mL (16 mm x 100)
4.7 Centrifuge tubes, 50-mL, disposable
4.8 Vortexer, mini
4.9 Mechanical reciprocating shaker, 200 oscillations min^{-1}, 1½-in strokes

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water
5.2 Argon gas, purity 99.9%
5.3 Nitrogen, purity 99.9%
5.4 Concentrated hydrochloric acid (HCl) (CAS# 7647-01-0), 12 *N,* trace pure grade
5.5 Potassium chloride (KCl) (CAS# 7447-40-7) crystalline
5.6 Hydrochloric acid solution, 0.5 N

Components: Hydrochloric acid (HCl), RODI water

- To a 1-L glass volumetric, add the following in order:
  - 500 mL of RODI water
  - 41.67 mL of HCl
  - Fill to volume with RODI water.
- Invert to mix well.

5.7 Potassium chloride solution, 1.0 N

Components: Potassium chloride (KCl), RODI water

- To an 18-L polyethylene carboy, add the following in order:
  - 16 L of RODI water
  - 1,341.9 g of KCl
- Allow solution to equilibrate to room temperature.
  - Dilute to 18 L with RODI water.
- Swirl to mix thoroughly.

5.8 High purity primary standards: 1,000 mg L^{-1}, concentrated elements, individual high purity elemental standard, commercially prepared. Individual solution containing:

- 1,000 mg/L Al, Aluminum Standard
- 1,000 mg/L Lu, Lutetium Standard

5.9 Internal standard

Components: 1,000 mg/L Lu, Lutetium Standard; RODI water

- To a 500 mL glass volumetric flask, add the following in order:
  - 300 mL of RODI water

- 5 mL of 1,000 mg/L Lu, Lutetium Standard
- Fill to volume with RODI water.

- Invert to mix.

5.10 KCl1–KCl4: Elemental calibration and calibration verification standard solutions

Components: Hydrochloric acid (HCl); 1 *N* KCL solution; 1,000 mg/L Al, Aluminum Standard; RODI water

- Refer to table 4B3b–1 for preparation.
- Table 4B3b–2 lists solution concentrations.
- Prepare blank fresh daily.
- Date all standards.

5.10.1 KCl blank

- To a 1-L glass volumetric flask, add the following in order:
  - 200 mL of 1 *N* KCl
  - 33.3 mL of concentrated HCl
  - Fill to volume with RODI water.
- Invert to mix thoroughly.

5.10.2 KCl 1 (Low)

- To a 1-L glass volumetric flask, add the following in order:
  - 200 mL of 1 *N* KCl
  - 33.3 mL of concentrated HCl
  - 10 mL of 1,000 mg/L Al, Aluminum Standard
  - Fill to volume with RODI water.
- Invert to mix thoroughly.

5.10.3 KCl 2 (Medium)

- To a 1-L glass volumetric flask, add the following in order:
  - 200 mL of 1 *N* KCl
  - 33.3 mL of concentrated HCl
  - 20 mL of 1,000 mg/L Al, Aluminum Standard
  - Fill to volume with RODI water.
- Invert to mix thoroughly.

5.10.4 KCl 3 (High)

- To a 1-L glass volumetric flask, add the following in order:
  - 200 mL of 1 *N* KCl
  - 33.3 mL of concentrated HCl
  - 40 mL of 1,000 mg/L Al, Aluminum Standard
  - Fill to volume with RODI water.
- Invert to mix thoroughly.

5.10.5 KCl 4 (CVS)

- To a 1-L glass volumetric flask, add the following in order:
  - 200 mL of 1 *N* KCl
  - 33.3 mL of concentrated HCl
  - 10 mL of 1,000 mg/L Al, Aluminum Standard
  - Fill to volume with RODI water.
- Invert to mix thoroughly.

Table 4B3b–1.—Preparation of Aluminum Calibration Standards and Calibration Verification Standard. (Prepare in 1-L volumetric flasks.)

Component or High Purity Standard	KCl Blank	KCl 1 Low	KCl 2 Medium	KCl 3 High	KCl 4 CVS
	(mL)	*(mL)*	*(mL)*	*(mL)*	*(mL)*
Al	N/A	10	20	40	10
1 *N* KCl	200	200	200	200	200
12 *N* HCl	33.3	33.3	33.3	33.3	33.3
RODI water	Bring to 1 L volume with RODI water				

Table 4B3b–2.—Concentrations of Aluminum Calibration Standards and Calibration Verification Standard.

Element	KCl 1 Low	KCl 2 Medium	KCl 3 High	KCl 4 CVS
	(mg L^{-1})	*(mg L^{-1})*	*(mg L^{-1})*	*(mg L^{-1})*
Al	10	20	40	10

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids. Dispense concentrated acids and bases in fume hood.

Gas cylinders should be chained or bolted in an upright position following standard KSSL laboratory safety procedures.

Follow the manufacturer's safety precautions when using the ICP–AES.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Extraction of Al

8.1.1 Weigh 1.25 g of <2-mm, air-dry soil to the nearest mg and place in a labeled 50-mL centrifuge tube. If sample is moist, weigh enough soil to achieve ≈1.25 g of air-dry soil. Prepare one quality control and one blank per 24 samples.

8.1.2 Using a 50-mL pipette, add 30 mL of 1 *N* KCl solution to each sample.

8.1.3 Cap the tubes, ensure the samples are thoroughly wetted. Shaking, swirling, or stirring may be required to wet organic samples.

8.1.4 Shake samples 1 hour at 200 oscillations/minute.

8.1.5 After shaking, tap down samples to knock soil from the cap of the tube.

8.1.6 Centrifuge, 15 minutes at 3,700 rpm.

8.1.7 Fill a 5 mL disposable tube with extract solution. This solution is reserved for determination of aluminum. If extracts will not be analyzed immediately after collection, then store samples at 4 °C.

8.2 Dilution of Sample Extracts for ICP–AES Analysis

8.2.1 Dilute KCl sample extracts (1:5 dilution) with 0.5 *N* HCl. Add 4 mL of 0.5 *N* HCl to 1 mL sample extract. Use vortexer to mix sample.

8.3 Refer to the manufacturer's manual for operation of the ICP–AES.

Analyte Data Reporting Wavelength

Element	Reporting Wavelength
	(nm)
Al	396.15

8.4 Calibrate the ICP–AES according to the instrument method. Analyze a CVS (calibration verification standard) after calibrating and every 12 samples. If the CVS falls within the range of the method (±10%), proceed with sample analysis. If the CVS is outside the range, recalibrate and re-analyze from the last CVS that passed. If Al concentration of the sample exceeds the high calibration standard by 5 times or more, an additional dilution is required. Dilute samples 1:10 (1 part KCl sample extract and 9 parts 1 *N* HCl). Record analyte readings to 0.01 mg L^{-1}.

9. Calculations

9.1 Determine the aluminum (cmol (+) kg^{-1})

$$(\text{cmol (+) kg}^{-1}) = (A \times (B1/B2) \times C \times R \times 1)/(E \times F)$$

A = Al concentration in extract (mg L^{-1})

B1 = Mass of 30 mL, 1 *N* KCl (g)

B2 = Density of 1 *N* KCl at 20 °C (1.0412 g mL^{-1})

C = Dilution factor; 5 (or 10, if needed under step 8.4)

R = Air-dry/oven-dry (AD/OD) ratio (method 3D1) or field-moist/oven-dry ratio (method 3D2)

1 = Net conversion factor to produce units of cmol(+) kg^{-1}

E = Soil sample weight (g)

F = Equivalent weight mg $cmol(+)^{-1}$

$Al^{3+} = 89.9$

9.2 Report KCl extractable Al to the nearest 0.1 cmol(+) kg^{-1}.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist for final review.

10.6 Compare individual results to method detection limits (MDL) and practical quantitation limits (PQL) before reporting analysis results.

10.6.1 Report numerical values for results that are above the PQL.

10.6.2 Report “trace” for results that are between the MDL and PQL.

10.6.3 Report “non-detect” for results that are below the MDL.

MDL and PQL in Reporting Units

Analyte	MDL	PQL
	(mg kg^{-1} of oven-dried soil)	*(mg kg^{-1} of oven-dried soil)*

11. References

Bertsch, P.M., and P.R. Bloom. 1996. Aluminum. p. 517–530. *In* D.L. Sparks (ed.) Methods of soil analysis. Part 3. Chemical methods. No. 5. ASA and SSSA, Madison, WI.

Lee, R., B.W. Bache, M.J. Wilson, and G.S. Sharp. 1985. Aluminum release in relation to the determination of cation exchange capacity of some podzolized New Zealand soils. J. Soil Sci. 36:239–253.

Thomas, G.W. 1982. Exchangeable cations. p. 159–165. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Ion Exchange and Extractable Cations (4B)
Ratios and Estimates Related to Ion Exchange and Extractable Cations (4B4)

Refer to Soil Survey Staff (2014) for the use and application of these ratios and estimates in U.S. Soil Taxonomy.

Ion Exchange and Extractable Cations (4B)
Ratios and Estimates Related to Ion Exchange and Extractable Cations (4B4)

Sum of Extractable Bases (4B4a)

Sum of Extractable Bases by NH_4OAc, pH 7 (4B4a1)

Sum of Extractable Bases by NH_4OAc, pH 7, Calculated (4B4a1a)

Sum of the NH_4OAc, pH 7, extractable bases (Ca^{2+}, Mg^{2+}, K^+, and Na^+) (4B4a1a) obtained by method 4B1a1 and analyzed in methods 4B1a1c1-4

This value is reported as cmol (+) kg^{-1} or meq 100 g^{-1}.

Ion Exchange and Extractable Cations (4B)
Ratios and Estimates Related to Ion Exchange and Extractable Cations (4B4)

Sum of Extractable Bases (4B4a)

Sum of Extractable Bases by NH_4Cl (4B4a2)

Sum of Extractable Bases by NH_4Cl, Calculated (4B4a2a)

Sum of the NH_4Cl extractable bases (Ca^{2+}, Mg^{2+}, K^+, and Na^+) (4B4a2a) obtained by method 4B1b1 and analyzed in methods 4B1b1c1-4

This value is reported as cmol (+) kg^{-1} or meq 100 g^{-1}.

Ion Exchange and Extractable Cations (4B)
Ratios and Estimates Related to Ion Exchange and Extractable Cations (4B4)

Cation Exchange Capacity (CEC) (4B4b)

CEC–8.2 (Sum of Cations) (4B4b1)

CEC–8.2, Reported (4B4b1a)

CEC–8.2, Not Reported (4B4b1b)

CEC–8.2 = NH_4OAc Bases + $BaCl_2$-TEA Acidity

Calculate the CEC–8.2 (4B4b1a) by adding the sum of the NH_4OAc extractable bases (4B4a1) plus the $BaCl_2$-TEA extractable acidity (method 4B2a1a1 or 4B2b1a1). Cation summation is the basis for this procedure.

This value is reported as cmol (+) kg^{-1} or meq 100 g^{-1}.

The CEC–8.2 minus the CEC–7 is considered the pH dependent charge from pH 7.0 to pH 8.2. The CEC–8.2 is not reported (method 4B4b1b) if carbonates, gypsum, or soluble salts are present in the soil because the NH_4OAc extracts cations from the dissolution of these soil constituents.

Ion Exchange and Extractable Cations (4B)

Ratios and Estimates Related to Ion Exchange and Extractable Cations (4B4)

Cation Exchange Capacity (CEC) (4B4b)

Effective Cation Exchange Capacity (ECEC) (4B4b2)

Sum of NH_4OAc Extractable Bases+1 *N* KCl Extractable Aluminum, Reported (4B4b2a)

Sum of NH_4OAc Extractable Bases+1 *N* KCl Extractable Aluminum, Not Reported (4B4b2b)

ECEC = NH_4OAc Bases + 1 *N* KCl Al

Calculate the ECEC (method 4B4b2a) by adding the sum of the NH_4OAc extractable bases (4B4a1) plus the 1 *N* KCl extractable Al (method 4B3b1b1).

This value is reported as cmol (+) kg^{-1} or meq 100 g^{-1}.

The ECEC is not reported (method 4B4b2b) if carbonates, gypsum, or significant quantities of soluble salts are present in the soil because the NH_4OAc extracts cations from the dissolution of these soil constituents.

Ion Exchange and Extractable Cations (4B)

Ratios and Estimates Related to Ion Exchange and Extractable Cations (4B4)

Base Saturation (4B4c)

Base Saturation by NH_4OAc, pH 7 (CEC–7) (4B4c1)

Base Saturation by CEC–7, Reported (4B4c1a)

Base Saturation by CEC–7, Set to 100% (4B4c1b)

Base Saturation (%) = (NH_4OAc Bases/CEC–7) x 100

Calculate the base saturation (method 4B4c1a) by dividing by the sum of NH_4OAc extractable (4B4a1) bases by CEC–7 (method 4B1a1a1a1) and multiplying by 100.

This value is reported as cmol (+) kg^{-1} or meq 100 g^{-1}.

If a soil has carbonates, gypsum, or significant quantities of soluble salts, this value is set to 100% (method 4B4c1b).

References

Soil Survey Staff. 2014. Keys to soil taxonomy. 12th ed. USDA–NRCS.

Ion Exchange and Extractable Cations (4B)

Ratios and Estimates Related to Ion Exchange and Extractable Cations (4B4)

Base Saturation (4B4c)

Base Saturation by NH_4Cl (4B4c2)

Base Saturation by NH_4Cl, Reported (4B4c2a)

Base Saturation by NH_4Cl, Set to 100% (4B4c2b)

Base Saturation (%) = (NH_4Cl Bases/CEC by NH_4Cl) x 100

Calculate the base saturation (method 4B4c2a) by dividing the sum of the NH_4Cl extractable (4B4a2) bases by CEC NH_4Cl (method 4B1b1a1a1) and multiplying by 100. If a soil has carbonates, gypsum, or soluble salts, this value is set to 100% (method 4B4c2b).

This value is reported as cmol (+) kg^{-1} or meq 100 g^{-1}.

Ion Exchange and Extractable Cations (4B)

Ratios and Estimates Related to Ion Exchange and Extractable Cations (4B4)

Base Saturation (4B4c)

Base Saturation by CEC–8.2 (Sum of Cations) (4B4c3)

Base Saturation by CEC–8.2, Reported (4B4c3a)

Base Saturation by CEC–8.2, Set to 100% (4B4c3b)

Base Saturation (%) = [NH_4OAc Bases / (NH_4OAc Bases + $BaCl_2$-TEA Acidity)] x 100

Calculate the base saturation (method 4B4c3a) by dividing the sum of the NH_4OAc extractable bases (4B4a1) by CEC–8.2 (method 4B4b1a) and multiplying by 100. This value is reported as cmol (+) kg^{-1} or meq 100 g^{-1}. If a soil has carbonates, gypsum, or soluble salts, this value is set to 100% (method 4B4c3b).

References

Soil Survey Staff. 2014. Keys to soil taxonomy. 12th ed. USDA–NRCS.

Ion Exchange and Extractable Cations (4B)
Ratios and Estimates Related to Ion Exchange and Extractable Cations (4B4)
Base Saturation (4B4c)
Base Saturation by Effective Cation Exchange Capacity (ECEC) (4B4c4)
Base Saturation by Sum of NH_4OAc Extractable Bases+1 *N* KCl Extractable Aluminum, Reported (4B4c4a)
Base Saturation by Sum of NH_4OAc Extractable Bases+1 *N* KCl Extractable Aluminum, Not Reported (4B4c4b)

Base Saturation (%) = [NH_4OAc Bases / (NH_4OAc Bases + 1 *N* KCl Al)] x 100

Calculate the base saturation (method 4B4c4a) by dividing the sum of NH_4OAc extractable bases (method 4B4a1) by the ECEC (method 4B4b2a) and multiplying by 100. If a soil has carbonates, gypsum, or significant quantities of soluble salts, this value is not reported (4B4c4b).

Ion Exchange and Extractable Cations (4B)
Ratios and Estimates Related to Ion Exchange and Extractable Cations (4B4)
Aluminum Saturation (4B4d)
Aluminum Saturation by Effective Cation Exchange Capacity (ECEC) (4B4d1)
Aluminum Saturation by Sum of NH_4OAc Extractable Bases+1 *N* KCl Extractable Aluminum, Reported (4B4d1a)
Aluminum Saturation by Sum of NH_4OAc Extractable Bases+1 *N* KCl Extractable Aluminum, Not Reported (4B4d1b)

Al Saturation (%) = [1 *N* KCl Al / (NH_4OAc Bases + 1 *N* KCl Al)] x 100

Calculate the Al saturation (method 4B4d1a) by dividing the 1 *N* KCl extractable Al (method 4B3b1b1) by ECEC (method 4B4b2a) and multiplying by 100. If a soil has carbonates, gypsum, or significant quantities of soluble salts, this value is not reported (method 4B4d1b).

Ion Exchange and Extractable Cations (4B)
Ratios and Estimates Related to Ion Exchange and Extractable Cations (4B4)
Activity (4B4e)
CEC–7/Clay (4B4e1)

Divide the CEC–7 (method 4B1a1a1a1) by the total clay (method 3A1a). This ratio is reported as a dimensionless value. In the past, the ratios of CEC to clay

were reported as meq g^{-1}. For more detailed information on the application of this ratio, refer to Soil Survey Staff (2011, 2014).

References

Soil Survey Staff. 2014. Keys to soil taxonomy. 12th ed. USDA–NRCS.

Soil Survey Staff. 2011. Soil survey laboratory information manual. Version 2.0. USDA–NRCS. Soil Survey Investigations Report No. 45. U.S. Govt. Print. Office, Washington, DC.

Introduction to Hydrogen Ion Activity

Hydrogen-Ion Activity (4C)
Soil Suspensions (4C1)
Electrode (4C1a)
Standard Glass Body Combination (4C1a1)
Digital pH/Ion Meter (4C1a1a)

Soil pH is one of the most frequently performed determinations and one of the most indicative measurements of soil chemical properties (McLean, 1982). Soil pH provides more information about a soil than merely indicating whether it is acidic or basic. The availability of essential nutrients and toxicity of other elements can be estimated because of their known relationship with pH (Thomas, 1996). Soil pH is affected by many factors; e.g., nature and type of inorganic and organic matter, amount and type of exchangeable cations and anions, soil-to-solution ratio, salt or electrolyte content, and CO_2 content (McLean, 1982). The acidity, neutrality, or basicity of a soil influences the solubility of various compounds, the relative ion bonding to exchange sites, and microbial activities. Depending on the predominant clay type, the pH may be used as a relative indicator of base saturation (Mehlich, 1943). Soil pH is also a critical factor affecting the availability of most essential elements for plants.

The KSSL performs several pH determinations. These methods include, but are not limited to:

- NaF (1 *N* pH 7.5 to 7.8) (4C1a1a1);
- Saturated paste pH (4C1a1a2);
- Oxidized pH (4C1a1a3);
- 1:1 water and 1:2 $CaCl_2$ pH (final solution: 0.01 *M* $CaCl_2$) (4C1a2a1-2);
- 1 *N* KCl pH (4C1a2a3); and
- Organic materials, $CaCl_2$ (final solution ≈0.01 *M* $CaCl_2$) (4C1a1a4).

NaF pH may be used as an indicator that amorphous material dominates the soil exchange complex.

Saturated paste pH is measured using the same sample used to derive the extract for salt analysis. The saturated paste pH is the pH and dilution at which sodium adsorption ratio (SAR) is computed (method 4E4b). The saturated paste pH method is popular in regions that have soils with soluble salts. This method may be more indicative of the saturated, irrigated soil pH rather than the soil pH measurement at a constant soil-to-water ratio; the water content varies with the water storage characteristics of the soil.

Oxidized pH may be used to assess the activities of soil microorganisms.

The methods for 1:1 water and 1:2 $CaCl_2$ pH are used to distinguish two family reaction classes in Histosols (Soil Survey Staff, 2014).

The pH determined by the 1 *N* KCl method indicates the pH at which Al is extracted. It is an index of soil acidity. This method is more popular in those regions that have extremely acid soils and in which KCl is used as an extractant of exchangeable Al. Similarly to the 1:2 $CaCl_2$ pH, the 1 *N* KCl pH readings tend to be uniform regardless of time of year.

An increase in the soil-to-water ratio or the presence of salts generally results in a decrease in the soil pH. The soluble salt content of the soil can be overcome by using dilute salt solutions, e.g., $CaCl_2$ or KCl, instead of distilled water. The use of dilute salt solutions is a popular method for masking seasonal variation in soil pH. The pH readings are usually less with dilute salt solutions than with distilled water but may be equal to or greater than the readings in highly weathered tropical soils; i.e., soils with a high anion exchange capacity. When the pH values of various soils are compared, determination by the same method is important (Foth and Ellis, 1988).

References

Foth, H.D., and B.G. Ellis. 1988. Soil fertility. John Wiley and Sons. New York, NY.

McLean, E.O. 1982. Soil pH and lime requirement. p. 199–224. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Mehlich, A. 1943. The significance of percentage of base saturation and pH in relation to soil differences. Soil Sci. Soc. Am. Proc. 7:167–174.

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Hydrogen-Ion Activity (4C)

Soil Suspensions (4C1)

Electrode (4C1a)

Standard Glass Body Combination (4C1a1)

Digital pH/Ion Meter (4C1a1a)

1 *N* NaF, pH 7.5–7.8 (4C1a1a1)

Air-Dry or Field-Moist, <2 mm (4C1a1a1a-b1)

1. Introduction to Sodium Fluoride pH

Sodium fluoride reacts with non-crystalline/amorphous soil material to release hydroxide ions (OH^-) thereby causing an increase in solution pH. Although not a selective test (NaF releases OH^- ions from any form of reactive hydroxyl aluminum), NaF is useful to identify andic and weathered pyroclastic materials and is a diagnostic criterion for the isotic mineralogy class.

2. Scope and Field of Application

The action of NaF upon noncrystalline (amorphous) soil material releases hydroxide ions (OH^-) to the soil solution and increases the pH of the solution. The amount of amorphous material in the soil controls the release of OH^- and the subsequent increase in pH (Fields and Perrott, 1966). The following reactions illustrate this action and form the basis of this procedure.

$$Al(OH)_3 + 3\ F^- \rightarrow AlF_3 + 3\ OH^-$$

$$Si(OH)_4 + 4\ F^- \rightarrow SiF_4 + 4\ OH^-$$

Results of the NaF pH analysis are not reliable for soils with a 1:1 water pH >8.2. Free carbonates in a soil result in a high NaF pH. Soils with a 1:1 water pH <7.0 are not affected.

A NaF pH ≥9.4 is a strong indicator that amorphous material dominates the soil exchange complex.

3. Principle

A 1-g sample is mixed with 50 mL of 1 *N* NaF and stirred for 2 minutes. While the sample is being stirred, the pH is read at exactly 2 min in the upper ⅓ of the suspension.

3.1 Interferences

To maintain uniformity in pH determination, measure the pH just above the soil sediment. The difference in the sediment and supernatant pH is called the suspension effect (McLean, 1982).

Wiping the electrode dry with a cloth, laboratory tissue, or similar material may cause electrode polarization. Clean the pH electrode by rinsing with reverse osmosis (RO) water.

4. Apparatus

4.1 Electronic balance, ±1.0-mg sensitivity

4.2 Plastic cup, 150-mL (5 fl. oz.), disposable

4.3 Automatic titrator, with control unit, sample changer, dispenser, and software

4.4 Combination pH-reference electrode

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.2 Buffers, pH 7.00, 9.18, and 13.0

5.3 Sodium fluoride (NaF) (CAS# 7681-49-4), 99%, high purity

5.4 Sodium hydroxide (NaOH) (CAS# 1310-73-2)

5.5 Hydrofluoric acid (HF) (CAS# 7664-39-3)

5.6 Sodium fluoride solution, 1.0 *N*

Components: Sodium fluoride (NaF); sodium hydroxide (NaOH) or hydrofluoric acid (HF); RO water

- In a 10-L polyethylene carboy, add the following in order:
  - 8 L of RODI water
  - 400 g of NaF
- Let stand for 3 days.
- On day 3, measure 50 mL of the solution and read pH. The pH should be between 7.5 and 7.8.
- If pH is outside the 7.5 and 7.8 range, adjust pH with either HF or NaOH.

6. Health and Safety

Warning.—NaF is poisonous. Avoid eye contact, skin contact, and ingestion. Do not eat or drink while using NaF. Review safety data sheets (SDS) for NaF before conducting analysis. Use the fume hood when using NaF. Follow standard laboratory safety practices.

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Weigh 1 g of <2-mm or fine-grind, air-dry soil to the nearest 1 mg and place in a 150-mL (5-oz) plastic cup. If sample is moist, weigh enough soil to achieve ≈1 g of air-dry soil.

8.2 Calibrate the titrator with pH 7.00, 9.18, and 13.00 buffer solutions.

8.3 Titrator parameters are created to execute the following sequence of steps:

- The sample is lifted so that the pH electrode is positioned above the soil sediment. Stirring begins immediately and is maintained during each sample cycle.
- 50 mL of NaF solution is added to sample.
- After 2 min, NaF pH is read and recorded to the nearest 0.01 unit.
- Once sample analysis is complete, the electrode and stirrer are rinsed with RO water.
- Sample changer proceeds to the next sample positioned for analysis.
- The cycle is repeated until all samples have been analyzed.

8.4 NaF is highly corrosive. Discard the solution and cup in safe containers within 2 hours of analysis completion. Failure to complete this step could lead to a chemical spill that requires clean up.

9. Calculations

Report NaF pH to the nearest 0.1 pH unit. No calculations are required for this procedure.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

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Hydrogen-Ion Activity (4C)
Soil Suspensions (4C1)
Electrode (4C1a)
Standard Glass Body Combination (4C1a1)
Digital pH/Ion Meter (4C1a1a)
Saturated Paste pH (4C1a1a2)
Air-Dry, <2 mm (4C1a1a2a1)

1. Introduction to Saturated Paste pH

A soil sample is saturated with water and allowed to stand overnight to prepare the saturated paste (method 4F2). The pH of the saturated paste is measure by immersing a calibrated, digital pH electrode into the paste and recording the value.

2. Scope and Field of Application

When interpretations are made about the soil, the saturated paste pH is usually compared to the 1:1 water pH and the 1:2 $CaCl_2$ pH. The usual pH sequence is as follows:

- 1:1 water pH > 1:2 $CaCl_2$ pH > saturated paste pH.
- If saturated paste pH > 1:2 $CaCl_2$ pH, the soil is not saline.
- If saturated paste pH ≥ 1:1 water pH, the soil may be Na saturated and does not have free carbonates.

Saturated paste pH may be used as a means of cross-checking salinity data for internal consistency and reliability between various soil chemical determinations (U.S. Salinity Laboratory Staff, 1954). Some rules of thumb that apply to the saturated paste are:

- Soluble carbonates are present only if the pH is >9.
- If the pH is ≤7, soluble bicarbonates are seldom >3 or 4 meq L^{-1}.
- If the pH is >9, soluble Ca^{2+} and Mg^{2+} are seldom >2 meq L^{-1}.
- Gypsiferous/gypseous soils seldom have a pH >8.2.

3. Principle

The saturated paste is prepared as described in method 4F2. Water is added to a soil sample while stirring the mixture until the soil paste meets the saturation criteria; i.e., the soil paste glistens as it reflects light, flows slightly when the container is tipped, and slides freely and cleanly from a spatula unless the soil has a high clay content. The pH of paste is measured with a calibrated combination electrode/digital pH meter.

3.1 Interferences

To maintain uniformity in pH determination, measure the pH just beneath the surface of saturated paste. The difference in the sediment and supernatant pH is called the suspension effect (McLean, 1982).

Wiping the electrode dry with a cloth, laboratory tissue, or similar material may cause electrode polarization. Clean the pH electrode by rinsing with reverse osmosis (RO) water.

4. Apparatus

4.1 Digital pH/ion meter

4.2 Electrode, standard glass body combination

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Buffers, pH 4.00, 7.00, and 9.18

6. Health and Safety

Personal Protective Equipment (PPE).—Use disposable gloves with appropriate polymer rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Follow standard laboratory safety practices.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Prepare a saturated paste (method 4F2).

8.2 Calibrate the pH meter with pH 4.00, 7.00, and 9.18 buffer solutions.

8.3 After calibration, gently rinse the electrode with RO water. Do not wipe the electrode with a tissue as this may cause a static charge on the electrode, scratch the electrode, or both.

8.4 Gently lower the electrode in the saturated paste until the KCl junction of the electrode is beneath the surface of saturated paste.

8.5 Allow the pH meter to stabilize before recording the pH. Record pH to the nearest 0.01 unit.

8.6 Gently raise the pH electrode from the paste and rinse with RO water until clean.

9. Calculations

9.1 Report saturated paste pH to the nearest 0.01 pH unit. No calculations are required for this procedure

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

McLean, E.O. 1982. Soil pH and lime requirement. p. 199–224. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

U.S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. L.A. Richards (ed.). USDA Agric. Handbook 60. U.S. Govt. Print. Office, Washington, DC.

Hydrogen-Ion Activity (4C)
Soil Suspensions (4C1)
Electrode (4C1a)
Standard Glass Body Combination (4C1a1)
Digital pH/Ion Meter (4C1a1a)
Oxidized pH (4C1a1a3)

1. Introduction to Oxidized pH

Sulfidic material is waterlogged mineral, organic, or mixed soil material with a pH of 3.5 or higher, often with a pH near neutrality. The horizon contains oxidizable sulfur compounds. If a sample is incubated as a 1-cm thick layer under moist, aerobic conditions (field capacity) at room temperature, it will show a drop in pH of 0.5 or more units to a pH value of 4.0 or less (1:1 by weight in water or in a minimum of water to permit measurement) within 8 weeks due to the formation of sulfuric acid (Van Breemen, 1982; Soil Survey Staff, 2014). This method determines if known or suspected sulfidic materials will oxidize to form a sulfuric horizon (Soil Survey Staff, 2014).

Sulfidic materials may be present in a soil as H_2S and identified by a "rotten-egg" smell or as FeS in a saturated soil and identified by its blue-black color. If such soils are drained and oxidized, the soil pH could drop to 3.5 or less, making the soil unsuitable for many uses.

2. Scope and Field of Application

Due to the potential for rapid changes in sample properties, a predictive method should be applied to determine if samples possess reactive sulfide. Field tests that can be used as predictive methods include hydrogen peroxide, 1 *N* hydrochloric acid, and lead acetate strips. A pH should be taken in the field at the time of sampling. That value should be included with samples submitted to the KSSL. The information is to establish a field state pH to compare to the initial oxidized pH reading. Samples must be packed in air-tight containers that are filled completely to exclude all air and should be shipped to the KSSL as soon as possible. Samples should be frozen if not shipped immediately or if the shipping will take several days.

3. Principle

In the laboratory, this procedure should be started immediately upon receipt of samples. Samples should be frozen if the procedure is not started immediately. Transfer enough soil to fill a plastic weigh boat with a layer that is 1 cm thick. Sample should be obtained from the bottom, saturated portion of the bulk sample. Run samples in duplicate for quality assurance. Initial pH is measured at 1:1 sample-to-water content. Samples are incubated under aerobic conditions

with weekly drying cycles. On a weekly basis, samples are rewet to 1:1 soil to water content, stirred, and equilibrated and pH is measured. Measurements are repeated until the pH reaches a nearly constant value. Measurements are repeated for a minimum of 16 weeks and for longer if the pH is still dropping after 16 weeks.

3.1 Interferences

Oxidation of sulfides and reduction in soil pH can potentially occur if samples are exposed to air before analysis begins in the laboratory. Samples must be shipped in air-tight containers. A pH reading must be recorded when samples are collected, and this value must be provided to the KSSL with the samples. This reading is necessary to ensure that pH has not significantly changed between sampling and the initial laboratory measurement of oxidized pH.

Minimize sample preparation time and stirring prior to the first recorded laboratory pH reading as these may result in the introduction of sufficient O_2 to change the pH reading.

Wiping the electrode dry with a cloth, laboratory tissue, or similar material may cause electrode polarization. Clean the pH electrode by rinsing with reverse osmosis (RO) water.

4. Apparatus

4.1 Plastic weighing boats or plastic condiment cups, 8 to 10 oz for representative sample

4.2 Digital pH/ion meter

4.3 Electrode, standard glass body combination

4.4 Optional for dryer atmospheric locations: Benchtop humidifier. Closed container with openings (inlet and outlet) providing for humidified airflow. A tube from the inlet of this closed container is connected to the outlet of a stoppered 2.5-L container full of RO water. Stoppered container can have air supplied by laboratory house air or small pump to supply air to a bubbling stone.

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 pH buffers, pH 4.00, 7.00, and 9.18 for pH meter calibration. Lower range pH buffer may be required if pH of samples falls below 4.0.

6. Health and Safety

Personal Protective Equipment (PPE).—Use disposable gloves with appropriate polymer rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Follow standard laboratory safety precautions.

7. Sample Preparation

For oxidized pH analysis, transfer enough saturated field-state soil to fill a plastic weighing boat two-thirds full. Sample should be obtained from the bottom, saturated portion of the bulk sample storage.

8. Procedure

8.1 Calibrate the pH meter with buffer solutions.

8.2 After equipment calibration, gently wash the electrode with RO water. Do not wipe the electrode with a tissue as this may cause a static charge on the electrode.

8.3 Transfer enough soil to fill a small plastic weigh boat with a layer that is approximately 1 cm thick. The pH should be measured at 1:1 sample-to-water ratio. Add RO water as necessary and stir sample to homogenize.

8.4 Stir the sample and then determine pH by carefully placing the electrode into the soil mixture. Ensure that the KCl junction and sensor membrane are in contact with the mixture. Allow the pH meter to stabilize before recording the pH. Record the pH to the nearest 0.01 pH unit. Compare the initial pH to the field pH (provided by the sample submitter) to ensure that no significant sulfide oxidation and pH decline occurred during sample transport.

8.5 After pH determination, place sample in a closed benchtop container (fig. 4C1a1a3–1). Keep at room temperature (20 to 25 °C). Maintain sufficient moisture so that samples are aerobic and moist during incubation. Allow sample to gradually dry so that it becomes near air-dry by the next weekly measurement. Maintain a lid on the sample container as necessary to prevent samples from drying too rapidly. If samples dry out too quickly between weekly measurements, provide humidified air flow through the

Figure 4C1a1a3–1.—Samples in a humidifier used for measuring oxidized pH.

container (provide inlet and outlet in the container). Humidified air flow can be provided to the inlet from a tube connected to the outlet of a stoppered container that has pressurized air bubbling through RO water. Soil taxonomy indicates that samples are to be incubated under "moist, aerobic conditions and repeatedly dried and remoistened on a weekly basis."

8.6 At weekly intervals, moisten the samples with RO water to 1:1 water-to-sample ratio, stir to homogenize (stirring also introduces air), and allow to equilibrate for 30 minutes. Record the pH, date, and time until the pH reaches a nearly constant value. Record for a minimum of 16 weeks. Record for longer if the pH is still dropping after 16 weeks.

9. Calculations

9.1 No calculations are required for this procedure. Report the initial pH and weekly recorded oxidized pH values to the nearest 0.1 pH unit.

9.2 Report the field pH for verification of sample quality.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Soil Survey Staff. 2014. Keys to soil taxonomy. 12th ed. USDA–NRCS.

Van Breemen, N. 1982. Genesis, morphology, and classification of acid sulfate soils in coastal plains. p. 95–108. *In* J.A. Kittrick, D.S. Fanning, and L.R. Hossner (eds.) Acid sulfate weathering. Soil Soc. Am. Spec. Publ. No.10. ASA and SSSA, Madison, WI.

Hydrogen-Ion Activity (4C)
Soil Suspensions (4C1)
Electrode (4C1a)
Standard Glass Body Combination (4C1a1)
Digital pH/Ion Meter (4C1a1a)
Organic Materials $CaCl_2$ pH, Final Solution ≈0.01 *M* $CaCl_2$ (4C1a1a4)

1. Introduction to Organic pH

This analysis of pH in organic material is intended for the measuring the pH of field-state Histosols and uses a calcium chloride solution.

2. Scope and Field of Application

This method for determining pH is used in soil taxonomy to distinguish reaction classes for Histosols and Histels (Soil Survey Staff, 2014).

- Dysic families have a pH <4.5 in 0.01 *M* $CaCl_2$ in all parts of the organic materials in the control section.
- Euic families have a pH >4.5 in 0.01 *M* $CaCl_2$ in some part of the control section.

This test of organic soil material can be used in field offices using field-moist soil.

3. Principle

Place 2.5 mL (2.5 cm^3) of prepared sample into a 30-mL plastic container and add 4 mL of 0.015 *M* $CaCl_2$. Mix the soil and $CaCl_2$ solution, cover, and allow to equilibrate for at least 1 hour. Uncover and measure pH using pH paper or pH meter.

3.1 Interferences

The specific volume of moist material depends on how the sample is packed. Packing of the material, therefore, must be standardized so comparable results can be obtained by different soil scientists (Soil Survey Staff, 2014).

Clean the electrode by rinsing with reverse osmosis (RO) water. Do not wipe the electrode dry with a cloth, laboratory tissue, or similar material as this may cause electrode polarization.

4. Apparatus

4.1 Polycons, 30-mL

4.2 Digital pH/ion meter

4.3 Electrode, standard glass body combination

4.4 Half-syringe, 6-mL. Cut plastic syringe barrel longitudinally to form a half-cylinder measuring device.

4.5 Metal spatula

4.6 Scissors

4.7 Paper towels

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Calcium chloride solution ($CaCl_2$), 0.015 *M*

Components: Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) (CAS# 10035-04-8), RO water

- In a 500-mL polyethylene bottle, add the following in order:
  - 300 mL of RO water
  - 1.10 g of $CaCl_2 \cdot 2H_2O$
  - Fill to volume with RO water.
- Invert to mix.

5.3 Buffers, pH 4.00 and 7.00

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

7. Sample Preparation

Field-state Histosol sample is cut into 0.5- to 1.0-cm long segments. It is important to obtain a sample that is representative for material size and type.

8. Procedure

8.1 If the Histosol sample is dry, add water and let stand to saturate.

8.2 Place approximately 20 cc of representative sample on a paper towel in a linear mound. Use the paper towel to absorb excess water from the sample if necessary. See figure 4C1a1a4–1.

8.3 Remove the sample and place on a fresh paper towel. The sample should be firm but still saturated with water.

8.4 Use scissors to cut sample into 0.5- to 1.0-cm long segments.

8.5 Using a metal spatula, take a representative sample and fill the half-syringe barrel (apparatus 4.4.) to the 5-mL mark (or 2.5-mL [2.5-cm^3] volume). See figure 4C1a1a4–2.

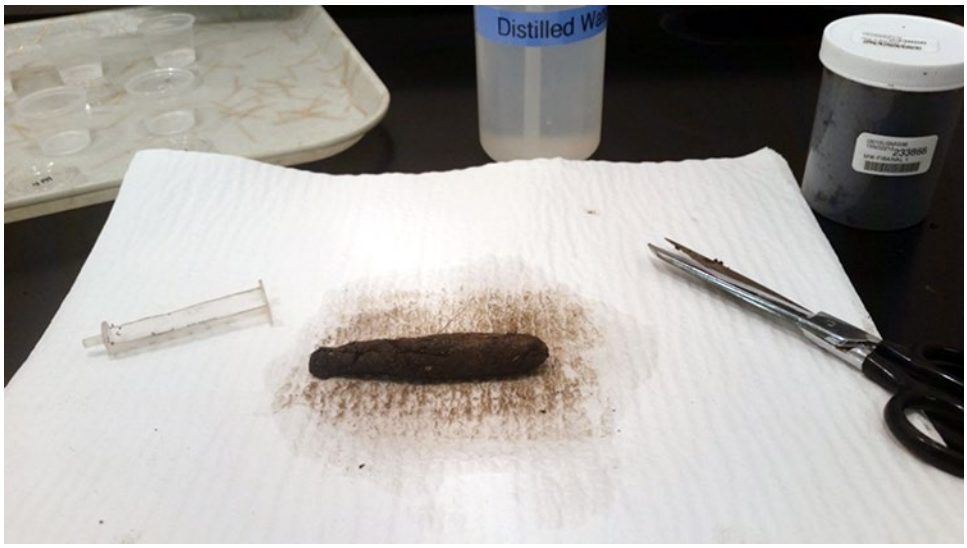

Figure 4C1a1a4–1.—Sample preparation. Sample ibers are cut into 0.5- to 1.0-cm long segments.

Figure 4C1a1a4–2.—Sample preparation. Sample segments are packed in syringe.

8.6 Place the prepared, measured sample in a 30-mL polycon and add 4 mL of 0.015 *M* $CaCl_2$.

8.7 Mix sample and $CaCl_2$ solution, cover, and allow to equilibrate at least 1 hour.

8.8 Stir sample, immerse electrode, and measure pH. Rinse electrode with RO water.

- If a pH meter is not available, place pH strip across the surface of sample. Close cover and allow to react approximately 5 minutes.

Remove pH strip with tweezers. Use a wash bottle to gently wash soil from bottom of strip. Compare color of active segment (center) with reference segments and with pH scale on box to determine pH.

9. Calculations

9.1 Report the 0.01 *M* $CaCl_2$ pH to the nearest 0.1 pH unit. No calculations are required for this procedure.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Soil Survey Staff. 2014. Keys to soil taxonomy. 12th ed. USDA–NRCS.

Hydrogen-Ion Activity (4C)
Soil Suspensions (4C1)
Electrode (4C1a)
Standard Glass Body Combination (4C1a1)
Digital pH/Ion Meter (4C1a1a)
Subaqueous Soil pH (4C1a1a5)

1. Introduction to Subaqueous Soil pH

Subaqueous soils and permanently saturated soils can contain reduced sulfur compounds. These compounds can oxidize upon exposure to air and cause significant declines in pH. The oxidation of sulfur compounds also changes the composition of ionic chemical species, including the creation of sulfate anions. This method can be performed in conjunction with Electrical Conductivity, Subaqueous Soils 1:5 (method 4F1c1a1b2).

2. Scope and Field of Application

The pH determined by this method can be compared to pH measured in the field at the time of sampling to determine if significant oxidation of the sample has occurred. Method 4F1c1a1b2 is used to determine the electrical conductivity of subaqueous and permanently saturated soils. If oxidation of sulfides has occurred, the measured EC may not accurately represent the in-situ pH of the sample.

3. Principle

A sample of subaqueous soil and in-situ water is placed in a sealed container that is completely filled with soil and ambient water to exclude any air. Samples are refrigerated or frozen until analysis. A sample that is 10 mL by volume is extracted from the bulk sample. RO water is added to the subsample, stirred for 10 seconds, and allowed to settle for no less than 10 minutes. A pH reading is recorded from the slurry. An electrical conductivity measurement is then obtained using method 4F1c1a1b2.

3.1 Interferences

Soil samples from brackish or saltwater sites may contain sulfides. These sulfides can oxidize and form sulfates if they are exposed to air, if testing is not performed for several days, or if the sample is not kept moist, refrigerated, or frozen.

Wiping the electrode dry with a cloth, laboratory tissue, or similar material can cause electrode polarization. Clean the electrode by rinsing with RODI water and patting it dry with tissue.

4. Apparatus

4.1 A device for extracting a 10-mL sample with minimum distortion. Examples include a coring drill bit that has a serrated-edge or an equivalent device, such as an open-ended syringe. The sample extracted for method 4F1c1a1b2 ($EC_{1:5}$) is also used for pH measurement. The device should be able to extract a 10-mL sample without compressing or distorting the sample. The device should be marked at the 10-mL volume.

4.2 100-mL beaker

4.3 100-mL graduated cylinder

4.4 Wooden stirring sticks

4.5 Digital pH/ion meter

4.6 Electrode, standard glass body combination

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.2 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.3 pH buffers, pH 4.00, 7.00, and 9.18 for pH meter calibration

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

7. Sample Preparation

Sealed, field-moist, whole-soil samples are required. Cores extracted for subaqueous soil investigations can be subsampled for this test. All air is excluded from the subsamples, which are kept sealed and frozen or in a refrigerator at 4°C to keep biological activity low. A 10-ml sample is taken for method 4F1c1a1b2 ($EC_{1:5}$) and is also used for this method.

8. Procedure

These steps are also outlined in method 4F1c1a1b2, Electrical Conductivity, Subaqueous Soils 1:5.

8.1 Samples should be analyzed immediately when received. Samples should be frozen if not immediately analyzed.

8.2 Calibrate pH meter prior to sample extraction to minimize exposure of sample to air.

8.3 Using the coring bit or other appropriate device, extract a 10-mL subsample of moist, whole soil and place it into a 100-mL beaker.

8.4 Measure 50 mL of RO water into a graduated cylinder and pour water over the 10-mL soil sample. Stir for 10 seconds. Allow to stand for 10 minutes.

8.5 Record pH of slurry once the meter reading has stabilized.

8.6 The sample is then used for the continuation of method 4F1c1a1b2.

9. Calculations

9.1 No calculations are needed.

9.2 Report pH to the nearest 0.1 pH unit.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

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U.S. Department of Agriculture, Natural Resources Conservation Service (USDA–NRCS). 2021. National soil survey handbook, title 430–VI. http://soils.usda.gov/technical/handbook/ (accessed 5 November 2021).

Hydrogen-Ion Activity (4C)

Soil Suspensions (4C1)

Electrode (4C1a)

Combination pH-Reference Electrode (4C1a2)

Automatic Titrator (4C1a2a)

1:1 Water pH (4C1a2a1)

Air-Dry or Field-Moist, <2 mm (4C1a2a1a-b1)

1:2 0.01 *M* $CaCl_2$ pH (4C1a2a2)

Air-Dry or Field-Moist, <2 mm (4C1a2a2a-b1)

1. Introduction to Calcium Chloride pH

The 1:1 water pH and 1:2 0.01 *M* $CaCl_2$ pH determinations are common. These measurements have taxonomic application and can be used to determine soil reaction class.

2. Scope and Field of Application

The combination of exchange and hydrolysis in salt solutions (0.1 *M* to 1.0 *M*) can lower the measured pH by 0.5 to 1.5 units compared to the pH measured in RO water (Foth and Ellis, 1988). These pH values are used as criteria for reaction classes (acid and nonacid) in some taxonomic families (Soil Survey Staff, 2014).

Typically, $CaCl_2$ pH is lower than the 1:1 water pH.

3. Principle

A 20-g soil sample is mixed with 20 mL of reverse osmosis (RO) water (1:1 w:v) with occasional stirring and allowed to stand 1 hour. The sample is then stirred for 30 s, and the 1:1 water pH is measured. The 0.02 *M* $CaCl_2$ is added to soil suspension, the sample is stirred, and the 1:2 0.01 *M* $CaCl_2$ pH is measured.

3.1 Interferences

Atmospheric CO_2 affects the pH of the soil-water mixture. Closed containers and nonporous materials prevent equilibration with CO_2. If especially precise work is being done, the partial pressure of CO_2 and the equilibrium point must be considered at the time of pH determination.

Clays may clog the KCl junction and slow the electrode response. Wiping the electrode dry with cloth, laboratory tissue, or similar material may cause electrode polarization. Rinse the electrode with distilled water.

4. Apparatus

4.1 Measuring scoop, handmade, ≈20-g capability

4.2 Paper or plastic cup, 120-mL (4 fl. oz.), disposable

4.3 Dispenser, 30-mL

4.4 Beverage stirring sticks, wood

4.5 Automatic titrator

4.6 Combination pH-reference electrode

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 pH buffers, pH 4.00, 7.00, and 9.18

5.3 Calcium chloride solution ($CaCl_2$), 0.02 *M*

Components: Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) (CAS# 10035-04-8), RO water

- In a 10-L polyethylene carboy, add the following in order:
  - 6 L of RO water
  - 23.52 g of $CaCl_2 \cdot 2H_2O$
  - Fill to 8 L with RO water.
- Swirl to mix.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Use a calibrated scoop to measure ≈20 g of <2-mm or fine-grind, air-dry soil. If sample is moist, use calibrated scoop to achieve ≈20 g of air-dry soil.

8.2 Place the sample in a 120-mL (4-oz) disposable cup.

8.3 Dispense 20 mL of RO water into sample and stir with wooden beverage stirrer.

8.4 Allow to stand 1 h, stirring occasionally.

8.5 Calibrate the pH meter using the pH 9.18, 7.00, and 4.00 buffer solutions.

9. Calculations

9.1 Report the 1:1 water pH and the 1:2 0.01 *M* $CaCl_2$ pH to the nearest 0.1 pH unit. No calculations are required for this procedure.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

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Hydrogen-Ion Activity (4C)
Soil Suspensions (4C1)
Electrode (4C1a)
Combination pH-Reference Electrode (4C1a2)
Automatic Titrator (4C1a2a)
1 *N* KCl pH (4C1a2a3)
Air-Dry or Field-Moist, <2 mm (4C1a2a3a-b1)

1. Introduction to Potassium Chloride pH

The primary use of the pH in 1:1 1 *N* KCl solution is to test for the presence of exchangeable aluminum. The absolute value of KCl pH bears a strong correlation with aluminum saturation (USDA–NRCS, 2005).

2. Scope and Field of Application

Potassium chloride pH (KCl) is used to measure soil acidity through aluminum hydrolysis. A 1 *N* KCl salt solution added to the sample will displace hydronium and aluminum ions completely. Aluminum, displaced by K^+ on the exchange complex, consumes OH^- ions and increases $[H^+]$; as a result, the solution pH is lowered. Generally, exchangeable aluminum is present if the 1 *N* KCl pH is <5.2. If the 1 *N* KCl pH is >5.2, aluminum is non-exchangeable due to hydrolysis, polymerization, and precipitation. Therefore, in highly weathered, low fertility Oxisols, the criterion "1 *N* KCl pH >5.0" indicates that aluminum toxicity is not a concern.

1 *N* KCl pH can be used directly as a criterion for the Acric ("acr") great groups of Oxisols. It is also used in a simple calculation with the 1:1 water pH. The "delta pH" (a term for 1 *N* KCl pH minus 1:1 water pH) is used as a criterion for the Anionic subgroups of Oxisols.

Readings in 1 *N* KCl also tend to be uniform and are more popular in regions with soils that are more acidic. If KCl is used to extract exchangeable aluminum, the pH reading (in KCl) shows the pH at which the aluminum was extracted (Keys to Soil Taxonomy, 12th edition, 2014).

3. Principle

A 20-g soil sample is mixed with 20 mL of 1 *N* KCl. The sample is allowed to stand for 1 h with occasional stirring. The sample is stirred for 30 s, and after waiting 1 min, the KCl pH is read.

3.1 Interferences

Wiping the electrode dry with a cloth, laboratory tissue, or similar material may cause electrode polarization. Rinse electrode with reverse osmosis (RO) water.

4. Apparatus

4.1 Measuring scoop, custom machined, ≈20 g

4.2 Plastic cup, 120-mL (4 fl. oz.), disposable

4.3 Dispenser, 0 to 20 mL

4.4 Beverage stirring sticks, wood

4.5 Automatic titrator, with control unit, sample changer, dispenser, and software

4.6 Combination pH-reference electrode

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 pH buffers, pH 4.00, 7.00, and 9.18

5.3 Potassium chloride solution, 1.0 *N*

Components: Potassium chloride (KCl) (CAS# 7447-40-7), RO water

- In a 1-L volumetric flask, add the following in order:
  - 700 mL of RO water
  - 74.56 g of KCl
  - Fill to volume with RO water.
- Invert to mix.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

7. Sample Preparation

For 1 *N* KCl pH, the field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Use a calibrated scoop to measure ≈20 g of <2-mm or fine-grind, air-dry soil. If sample is moist, use calibrated scoop to achieve ≈20 g of air-dry soil.

8.2 Place the sample in a 120-mL (4-oz) disposable cup.

8.3 Dispense 20 mL of 1 *N* KCl into sample and stir with wooden beverage stirrer.

8.4 Allow to stand 1 h, stirring occasionally.

8.5 Calibrate the pH meter using the pH 4.00, 7.00, and 9.18 buffer solutions.

8.6 Sample stirring, intervals for readings, pH reading, and rinsing of electrode are controlled by preset analysis parameters in the computer software.

9. Calculations

No calculations are required for this procedure. Report KCl pH to the nearest 0.1 pH unit.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

McLean, E.O. 1982. Soil pH and lime requirement. p. 199–224. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

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Hydrogen-Ion Activity (4C)
Soil Extracts (4C2)
Electrode (4C2a)
Standard Glass Body Combination (4C2a1)
Digital pH/Ion Meter (4C2a1a)
Aqueous Extraction (4C2a1a1)
Single-Point Extraction (4C2a1a1a)
1:5, 23-h, 1-h (4C2a1a1a1)
Air-Dry or Field-Moist, <2 mm (4C2a1a1a1a-b1)

1. Introduction to Aqueous Extraction pH

An aliquot of water is added to a soil sample and allowed to equilibrate for 24 hours. The soil solution is extracted to measure such aspects as pH, EC, and elements in suspension. Studies at the KSSL reported a correlation between water-extractable elements for soils and their concentration in runoff from agricultural watersheds (Elrashidi et al., 2005a, 2005b).

2. Scope and Field of Application

Applied nutrients, such as phosphorus and nitrogen, in runoff from agricultural fields are leading causes of poor water quality in the United States (USEPA, 1996). When environmental impacts of conventional agricultural practices on natural water resources are evaluated, the water-soluble elements and their associated properties (e.g., pH, electrical conductivity) should be measured in soil under conditions similar to those present during runoff events.

3. Principle

A 7.0-g sample of soil is added to 35 mL of water in a 50-mL disposable centrifuge tube. The suspension is maintained at room temperature for 23 h and then shaken on a reciprocating shaker for 1 hour. The supernatant is filtered, and the pH is measured.

3.1 Interferences

Clays may clog the KCl junction and slow the electrode response. Clean the electrode by rinsing with RO water and patting it dry with tissue. Wiping the electrode dry with a cloth, laboratory tissue, or similar material can cause electrode polarization.

4. Apparatus

4.1 Digital pH/ion meter

4.2 Electrode, standard glass body combination

4.3 Centrifuge tubes, 50-mL, disposable, polyethylene, with caps

4.4 Centrifuge, capable of 4,000 rpm

4.5 Mechanical reciprocating shaker, 200 oscillations min^{-1}, 1½-in strokes

4.6 Vortex, mini

4.7 Syringe, 20 cc plastic

4.8 Syringe filters, 25-mm, 0.45-µm pore size

4.9 1 oz plastic cup with hinged lids

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 pH Buffers, pH 4.00, 7.00, and 9.18

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. Subsamples are further processed via planetary ball mill to 80 mesh; either size fraction is appropriate for this test. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 The soil extract is prepared in accordance with method 4D2a2.

8.2 Calibrate the pH meter with pH 4.00, 7.00, and 9.18 buffer solutions.

8.3 After equipment calibration, gently wash the electrode with RO water. Do not wipe the electrode with a tissue as this may cause a static charge on the electrode.

8.4 Gently lower the electrode into extract until the KCl junction of the electrode is beneath the surface.

8.5 Allow the pH meter to stabilize before recording the pH. Record pH to the nearest 0.01 unit.

8.6 Gently raise the pH electrode and rinse with RO water until clean.

9. Calculations

9.1 Report pH to the nearest 0.1 pH unit. No calculations are required for this procedure.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

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Soil Test Analyses (4D)

Soil testing has been widely used as a basis for determining lime and fertilizer needs (Soil and Plant Analysis Council, 1999). In more recent years, some of these tests have been employed in more diverse agronomic and environmental uses (SERA–IEG 17, 2000). The KSSL has therefore expanded its suite of soil analyses to more completely characterize the inorganic and organic nitrogen fractions and to provide phosphorus (P) analyses for a broad spectrum of soil applications.

Methods development for characterization of soil P (Bray and Kurtz, 1945; Olsen et al., 1954; Chang and Jackson, 1957) has been instrumental in understanding the principles, nature, and behavior of P in soils (Olsen and Sommers, 1982). Amounts, forms, and distribution of soil P vary with soil-forming factors (Walker, 1974; Stewart and Tiessen, 1987); level and kind of added P (Barrow, 1974; Tisdale et al., 1985; Sharpley, 1996); other soil and land management factors (Haynes, 1982; Sharpley, 1985); and soil P-sorption characteristics (Goldberg and Sposito, 1984; Van Riemsdijk et al., 1984; Polyzopoulos et al., 1985; Frossard et al., 1993). Knowledge of these factors and their impact on the fate and transport of soil P has been used in developing soil P interpretations for such broad and diverse applications as fertility, taxonomic classification, genesis and geomorphology models, and environmental studies (Burt et al., 2002).

To characterize the P in a soil system requires the selection of an appropriate method of determination as influenced by such factors as study objectives, soil properties, sample condition, sample environment, accuracy, and reproducibility (Olsen and Sommers, 1982). Most soil P determinations have two phases; i.e., preparation of a solution that contains the soil P or fraction thereof and the quantitative determination of P in the solution. Most P analyses of soil solutions have been colorimetric procedures because such procedures are sensitive, reproducible, and lend themselves to automated analysis, accommodating water samples, digest solutions, and extracts (SERA–IEG 17, 2000). Inductively coupled plasma (ICP) spectrophotometry can also be used for P determination. The popularity of the ICP procedure has increased due to the use of multi-element soil extractants (SERA–IEG 17, 2000). Results from colorimetric analyses and those from ICP are not always comparable. ICP estimates the total amount of P in solution while the colorimetric procedures measure P that can react with the color-developing reagent (SERA–IEG 17, 2000).

The selected colorimetric method for P determination depends on the concentration of solution P, the concentration of interfering substances in the solution to be analyzed, and the particular acid system involved in the analytical procedure (Olsen and Sommers, 1982). The KSSL performs a number of P analyses. These analyses include, but are not limited to, anion-resin extractable (4D1a1a1a1-2); water soluble (4D2a1a1); Bray P-1 (4D3a1); Olsen sodium-

bicarbonate (4D5a1); Mehlich No. 3 (4D6a1); citric acid soluble (4D7a1); and New Zealand P Retention (4D8a1). The methods for total P analysis (4H1a1b1-21 and 4H1b1a1a1-12) are described in the section of this manual titled "Total Analysis."

Nitrogen is ubiquitous in the environment because it is continually cycled among plants, soil organisms, soil organic matter, water, and the atmosphere (National Research Council, 1993). Nitrogen is one of the most important plant nutrients and forms some of the most mobile compounds in the soil-crop system. As such, it is commonly related to water-quality problems. Total nitrogen includes both organic and inorganic forms. The KSSL method for total nitrogen (4H2a2) is described in the section of this manual titled "Total Analysis."

Inorganic nitrogen in soils is predominately NO_3 and NH_4. Nitrite is seldom found in detectable amounts, except in neutral to alkaline soils that received certain fertilizers (Maynard and Kalra, 1993; Mulvaney, 1996). There is considerable diversity among laboratories regarding the extraction and determination of NO_3 and NH_4 (Maynard and Kalra, 1993). Nitrate is water soluble, and the most common extractant is a water-based KCl solution. Refer to Maynard and Kalra (1993) and Mulvaney (1996) for a review of extractants.

The concept of an organic nitrogen fraction that is readily mineralized has been used to assess soil nitrogen availability in cropland, forests, and waste-disposal sites (Campbell et al., 1993). Incubation-leaching techniques have been used to quantify the mineralizable pool of soil organic nitrogen.

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Soil Test Analyses (4D)
Anion Resin Exchange Extraction (4D1)
Double-Point Extraction (4D1a)
1-h, 24-h, 1 *M* NaCl (4D1a1a1)
UV-Visible Spectrophotometer, Dual-Beam (4D1a1a1a)
Phosphorus, Two Points (4D1a1a1a1-2)
Air-dry or Field-Moist, <2 mm (4D1a1a1a1-2a-b1)

1. Introduction to Double-Point Phosphorus Extraction

The double-point anion exchange resin (DP-AER) extraction method is used to investigate phosphorus (P) availability, capacity, and release characteristics in soils (Elrashidi et al., 2012). The amount of P released from soil and adsorbed by a resin can be used to measure available P, assess available residual phosphates, estimate P release characteristics and potential runoff for agricultural land, and measure the buffer capacity of soils.

This method describes a two-point measurement (1 and 24 h extraction) sufficient to develop linear equations that predict P release characteristics (PRC), describing the whole relationship between the extraction time (1 min to 48 h) and amount of P released (mg kg^{-1}) for soils (Elrashidi et al., 2003).

2. Scope and Field of Application

Anion resins remove P from extracting solutions without chemical alterations and with only minor pH changes. Plotting log of extraction periods (0.25, 0.50, 1, 2, 4, 8, 24, 48 h) against amounts of P released (mg kg^{-1}) shows a linear relationship in 24 U.S. benchmark soils (Elrashidi et al., 2003). This method is not appropriate for analyzing O horizons.

3. Principle

A 2-mm or fine-grind soil sample undergoes two intervals of agitation with a resin bag in reverse osmosis deionized (RODI) water for 1 hour. Phosphorus released from soil during shaking is adsorbed onto the resin. Concentrated HCl is added to sample extracts along with ascorbic acid-molybdate solution. The "Mo blue" methods are based on the following principle: In an acid molybdate solution containing orthophosphate ions, a phosphomolybdate complex forms that can be reduced by ascorbic acid to a Mo blue color. Absorbance of the solution is read using a spectrophotometer at 882 nm. Data are reported as mg P kg^{-1} soil.

The resin is reusable after being shaken for 1 h in 1 *M* NaCl solution and then rinsed with RODI water.

3.1 Interferences

The intensity of blue varies with the P concentration but is also affected by other factors, such as acidity, arsenates, silicates, and substances that influence the oxidation-reduction conditions of the system (Olsen and Sommers, 1982).

4. Apparatus

4.1 Electronic balance, ±1.0-mg sensitivity

4.2 Mechanical reciprocating shaker, 100 oscillations min^{-1}, 1½-in strokes

4.3 Bottles, polyethylene, 250-, 125-, and 60-mL

4.4 Funnel, 60° angle, long stem, 50-mm diameter

4.5 Filter paper, Whatman 42 or equivalent, 150-mm

4.6 Cups, plastic

4.7 Dispenser, 50-mL

4.8 Pipettes, electronic digital, 2,500-µL and 10-mL, with tips, 2,500-µL and 10-mL

4.9 Cuvettes, plastic, 4.5-mL, 1-cm light path

4.10 Spectrophotometer

4.11 Hot plate and magnetic stir bar

4.12 Nitex nylon fabric for resin bags, 300-µm pores, and nylon thread

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.2 Sodium bicarbonate ($NaHCO_3$) (CAS# 144-55-8)

5.3 Anion exchange resin (AER), 510–610 µm spherical beads. (The KSSL can be contacted for more information.)

Preparation: Convert to bicarbonate form by soaking bags overnight in 1.0 *M* $NaHCO_3$ solution and washing out excess salt with RODI water. Store in RODI water in refrigerator. Replace resin when electrical conductivity is >5.0 µS/cm.

5.4 Concentrated hydrochloric acid (HCl) (CAS# 7647-01-0), 12 *N,* trace pure grade

5.5 Concentrated sulfuric acid (H_2SO_4) (CAS# 7664-93-9), 36 *N,* trace pure grade

5.6 Ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}•4H_2O$] (CAS# 12054-85-2)

5.7 Potassium antimonyl tartrate trihydrate [$C_8H_4K_2O_{12}Sb•3H_2O$] (CAS# 28300-74-5)

5.8 Phosphorus standard, commercially prepared, 100 mg/L^{-1} P

5.9 Sodium chloride (NaCl) (CAS# 7647-14-5)

5.10 Ascorbic acid ($C_6H_8O_6$) (CAS# 50-81-7)

5.11 Sodium chloride solution, 1 *M*

Components: Sodium chloride (NaCl), RODI water

- In a 1-L glass volumetric flask, add the following in order:
  - 800 mL of RODI water.
  - 58.4 g NaCl
  - Fill to 1 L with RODI water.
- Invert to mix.

5.12 Sulfuric-tartrate-molybdate solution (Reagent A)

Components: Ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}•4H_2O$], potassium antimonyl tartrate trihydrate [$C_8H_4K_2O_{12}Sb•3H_2O$], concentrated sulfuric acid (H_2SO_4), RODI water

- In a 1-L glass volumetric flask, add the following in order:
  - 200 mL of RODI water.
- Bring to a boil
  - 60 g of ammonium molybdate tetrahydrate
- Let solution cool to room temperature.
  - 1.455 g of potassium antimony tartrate
  - 700 mL of sulfuric acid
  - Fill to 1 L with RODI water.
- Invert to mix.
- Store in a dark bottle in the refrigerator.

5.13 Ascorbic acid solution, 0.75 *N*

Components: Ascorbic acid ($C_6H_8O_6$), RODI water

- In a 100-mL polyethylene flask, add the following in order:
  - 75 mL of RODI water.
  - 13.2 g of ascorbic acid
  - Fill to volume with RODI water.
- Invert to mix.
- Make fresh daily.

5.14 Working ascorbic acid molybdate solution (Reagent B)

Components: Reagent A, ascorbic acid solution, RODI water

- In a 1-L polyethylene volumetric flask, add the following in order:
  - 800 mL of RODI water.
  - Mix 25 mL of Reagent A
  - 10 mL of ascorbic acid solution
  - Fill to volume with RODI water.
- Allow to stand at least 1 h before using.
- Prepare fresh daily.

5.15 Standard P calibration and verification standard solutions (Standards S1–S6)

Components: Concentrated hydrochloric acid (HCl); 1 *M* NaCl solution; Phosphorus Standard, commercially prepared, 100 mg/L P

- Refer to table 4D1a–1 for dilutions and concentrations.
- Allow to equilibrate to room temperature before use.
- Make fresh weekly.
- Store in the refrigerator.
- Table 4D1a–2 lists solution concentrations.

5.15.1 Blank

- In a 100-mL glass volumetric flask, add the following in order:
  - 70 mL of NaCl solution
  - 4 mL of HCl
  - Fill to volume with NaCl solution.
- Invert to mix thoroughly.

5.15.2 Standard S1

- In a 100-mL glass volumetric flask, add the following in order:
  - 70 mL of NaCl solution
  - 0.25 mL of Phosphorus Standard, 100 mg/L P
  - 4 mL of HCl
  - Fill to volume with NaCl solution.
- Invert to mix thoroughly.

5.15.3 Standard S2

- In a 100-mL glass volumetric flask, add the following in order:
  - 70 mL of NaCl solution
  - 0.50 mL of Phosphorus Standard, 100 mg/L P
  - 4 mL of HCl
  - Fill to volume with NaCl solution.
- Invert to mix thoroughly.

5.15.4 Standard S3

- In a 100-mL glass volumetric flask, add the following in order:
  - 70 mL of NaCl solution
  - 1.0 mL of Phosphorus Standard, 100 mg/L P
  - 4 mL of HCl
  - Fill to volume with NaCl solution.
- Invert to mix thoroughly.

5.15.5 Standard S4

- In a 100-mL glass volumetric flask, add the following in order:
  - 70 mL of NaCl solution
  - 2.0 mL of Phosphorus Standard, 100 mg/L P
  - 4 mL of HCl
  - Fill to volume with NaCl solution.
- Invert to mix thoroughly.

5.15.6 Standard S5

- In a 100-mL glass volumetric flask, add the following in order:
  - 70 mL of NaCl solution
  - 3.0 mL of Phosphorus Standard, 100 mg/L P
  - 4 mL of HCl
  - Fill to volume with NaCl solution.
- Invert to mix thoroughly.

5.15.7 Standard S6

- In a 100-mL glass volumetric flask, add the following in order:
  - 70 mL of NaCl solution
  - 4.0 mL of Phosphorus Standard, 100 mg/L P
  - 4 mL of HCl
  - Fill to volume with NaCl solution.
- Invert to mix thoroughly.

Table 4D1a–1—Preparation of Phosphorus Calibration and Calibration Verification Solutions, Standards S1–S6. (Prepare in 100-mL volumetrics.)

Standard	1,000 mg/L P	1.0 *M* NaCl	HCl
	(mL)	*(mL)*	*(mL)*
Blank	0	70 mL initially. Bring to volume.	4.0
S1	0.25		
S2	0.5		
S3	1.0		
S4	2.0		
S5	3.0		
S6	4.0		

Table 4D1a–2.—Concentrations of Phosphorus Calibration and Calibration Verification Solutions, Standards S1–S6.

Standard	Reagent Concentration
	(mg P L^{-1})
Blank	0
S1	0.25
S2	0.5
S3	1.0
S4	2.0
S5	3.0
S6	4.0

5.16 Quality Control: A KSSL soil standard and a blank are routinely included in every batch of 24 samples.

6. Health and Safety

Warning.—Many metal salts are extremely toxic and may be fatal if ingested.

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids. Dispense concentrated acids and bases in fume hood.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

Note: Samples are analyzed in duplicate; prepare two bottles of each soil sample to be analyzed. Prepare one standard and one blank for each batch of samples.

8.1 Weigh 2 g of <2-mm, air-dry soil and place in a 250-mL polyethylene bottle. Add 100 mL of RODI water to bottle.

8.2 Place 4-g resin bag in each sample bottle and control sample. Transfer sample to shaker. Shake for 1 h at 100 oscillations min^{-1} at room temperature (20 ±2 °C).

8.2.1 After 1 h, remove resin bag from soil suspension.

8.2.2 Rinse bag with ≈5 mL of RODI water into a condiment cup, catching any soil particles that may have adhered to resin bag.

8.2.3 Add the 5 mL of rinse into sample bottle. Use a new cup for each sample.

8.2.4 Set aside (save) this 1-h resin bag.

8.3 To each 250-mL sample and control bottle, place a new 4-g resin bag. Shake for 23 h at 100 oscillations min^{-1} at room temperature (20 ±2 °C).

8.3.1 After 23 h shaking, remove resin bag from soil suspension.

8.3.2 Rinse bag with 5 mL of RODI water. Pour 5 mL of rinse water into the soil suspension.

8.3.3 Set aside (save) this 23-h resin bag.

8.4 Cleaning 1-h and 23-h resin bags: Place each resin bag in its own 125-mL polyethylene bottle containing 50 mL of 1.0 *M* NaCl solution. Transfer the bottles to shaker and shake for 1 h at 100 oscillations min^{-1} at room temperature (20 ±2 °C).

8.5 For all 1-h, 23-h, and control samples, decant samples into 60-mL polyethylene bottles. Filter if soil particles are observed in the extract.

8.6 Add 2 mL of concentrated hydrochloric acid to each bottle. If extracts are not to be analyzed immediately after collection, store samples at 4 °C. Analyze samples within 72 h.

8.7 Use a pipette to transfer a 1-mL aliquot of the sample to a plastic cup. Use a clean pipette tip for each sample.

8.8 Use a pipette to transfer a 1-mL aliquot of each calibration standard S1–S6 to a plastic cup. Use a clean pipette tip for each standard.

8.9 Dispense 4 mL of Reagent B to each sample aliquot and standard. Swirl to mix. The color reaction requires a minimum of 20 min before the analyst records readings. Samples must be analyzed within 2 hours.

8.10 Transfer sample extract and standards to cuvettes.

8.11 Set the spectrophotometer to read at 882 nm. Autozero with calibration blank.

- Calibrate the instrument using standards S1–S6 and blank.
- If the calibration curve has <0.99 linearity, recalibration is required.

8.12 Run samples using calibration curve. If samples are outside the calibration range, dilute sample extracts with extracting solution and re-analyze.

8.13 Record results to the nearest 0.01 unit for the sample extract and each S1–S6 standard.

9. Calculations

9.1 For a 1-hour phosphorus extraction, convert extract P (mg L^{-1}) to soil P (mg kg^{-1}) as follows:

$$\text{Soil } P^{1hr} \text{ (mg kg}^{-1}) = (A \times B \times C \times R \times 1{,}000) / E$$

A = Sample extract reading (mg L^{-1})

B = Extract volume (L)

C = Dilution, if performed

R = Air-dry/oven-dry ratio (method 3D1) or field-moist/oven-dry ratio (method 3D2)

1,000 = Conversion factor to kg-basis

E = Sample weight (g)

9.2 For a 23-hour phosphorus extraction, convert extract P (mg L^{-1}) to soil P (mg kg^{-1}) as follows:

$$\text{Soil } P^{23hr} \text{ (mg kg}^{-1}) = (A \times B \times C \times R \times 1{,}000) / E$$

A = Sample extract reading (mg L^{-1})

B = Extract volume (L)

C = Dilution, if performed

R = Air-dry/oven-dry ratio (method 3D1) or field-moist/oven-dry ratio (method 3D2)

1,000 = Conversion factor to kg-basis

E = Sample weight (g)

9.3 To plot the phosphorus release from soil for any time less than 1 hour:

$$P \text{ mg/kg} = I + S_1 \times (\text{Log time})$$

Time = Any time less than 1 hour

I = Intercept (P^{1hr})

S1 = Slope between 1 minute and 1 hour

$$\frac{P^{1hr}}{\text{Log } (1/60)} + \frac{P^{1hr}}{(-1.78)}$$

Where:

$$(P^{1hr}) - \frac{(P^{1hr})}{(1.78)} \times \text{Log Time}$$

9.4 To plot the phosphorus release from soil for any time more than 1 hour:

$$P \text{ mg/kg} = I + S_2 \times (\text{Log time})$$

Time = Any time more than 1 hour

I = Intercept (P^{1hr})

S2 = Slope between 1 hour and 24 hours

$$\frac{(P^{23hr}) - (P^{1hr})}{\log (24)} = \frac{(P^{23hr}) - (P^{1hr})}{(1.38)}$$

Where:

$$P\ \frac{mg}{kg} = (P^{1hr}) + \frac{(P^{23hr}) - (P^{1hr})}{1.38} \times (\text{Log Time})$$

9.5 Report data to the nearest 0.1 mg P kg^{-1} soil.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

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Soil Test Analyses (4D)
Aqueous Extraction (4D2)
Single-Point Extraction (4D2a)
1:10, 30-min (4D2a1)
UV-Visible Spectrophotometer, Dual-Beam (4D2a1a)
Phosphorus (4D2a1a1)
Air-Dry or Field-Moist, <2 mm (4D2a1a1a-b1)

1. Introduction to Single Point Phosphorus Extraction

Phosphorus (P) occurs in soil in both solution and solid phases. These forms influence P availability in relation to root absorption and plant growth, runoff and water quality problems, and P loadings. This method determines the P concentration levels in a soil extract and allows the chemical environment of plant roots to be defined in quantitative terms (Adams, 1974).

2. Scope and Field of Application

The water or dilute salt extracts represent an attempt to approximate the concentration of P in the soil solution. Water soluble P has been defined as P measured in water, dilute salt extracts (e.g., 0.01 *M* $CaCl_2$), displaced soil solutions, or saturation paste extracts (Olsen and Sommers, 1982). Even though the water-soluble fraction principally consists of inorganic orthophosphate ions, evidence indicates that some organic P is also included (Rigler, 1968). The sum of water-soluble P and pH-3-extractable P has also been defined as the available P in runoff (Jackson, 1958). This method is not appropriate for analyzing O horizons.

3. Principle

A 2.5-g sample of <2-mm, air-dry soil is mechanically shaken for 30 min in 25 mL of reverse osmosis deionized water. The sample is centrifuged, the extract is filtered, and absorbance is read using a spectrophotometer at 882 nm. Data are reported as mg P kg^{-1} soil.

3.1 Interferences

The “Mo blue methods” are very sensitive for P. They are based on the following principle: In an acid molybdate solution containing orthophosphate ions, a phosphomolybdate complex forms that can be reduced by ascorbic acid, $SnCl_2$, and other reducing agents to a molybdate-blue color.

The intensity of blue varies with the P concentration but is also affected by other factors, such as acidity, arsenates, silicates, and substances that influence the oxidation-reduction conditions of the system (Olsen and Sommers, 1982).

The commercially prepared phosphorus standard must be prepared in a water matrix; phosphorus is pH dependent, and an acid matrix will change the pH.

4. Apparatus

4.1 Electronic balance, ±1.0-mg sensitivity

4.2 Mechanical reciprocating shaker, 200 oscillations min^{-1}, 1½-in strokes

4.3 Centrifuge tubes, 50-mL, disposable, polyethylene

4.4 Filter paper, Whatman 42 or equivalent, 150-mm

4.5 Funnel, 60° angle, long stem, 50-mm diameter

4.6 Centrifuge, capable of 3,000 rpm

4.7 Volumetric flasks, 2-L, 100-mL, and 25-mL

4.8 2-L Bottles, plastic, dark

4.9 Pipettes, electronic digital, 2,500-µL and 10-mL, with tips, 2,500-µL and 10-mL

4.10 Cups, plastic

4.11 Cuvettes, plastic, 4.5-mL, 1-cm light path

4.12 Dispenser, 30-mL or 10-mL

4.13 Spectrophotometer

4.14 Hot plate with magnetic stir bar

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.2 Concentrated sulfuric acid (H_2SO_4) (CAS# 7664-93-9), 36 *N,* trace pure grade

5.3 Ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}•4H_2O$] (CAS# 12054-85-2)

5.4 Potassium antimony–(III) oxide tartrate [$C_8H_4K_2O_{12}Sb•3H_2O$] (CAS# 28300-74-5)

5.5 Phosphorus Standard, commercially prepared, 100 mg/L P

5.6 Ascorbic acid ($C_6H_8O_6$) (CAS# 50-81-7)

5.7 Molybdate solution

Components: Ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}•4H_2O$], potassium antimony–(III) oxide tartrate [$C_8H_4K_2O_{12}Sb•3H_2O$], concentrated sulfuric acid (H_2SO_4), RODI water

Note: Three solutions are prepared separately and then combined in a 2-L flask to create the molybdate solution:

- In a 2-L glass volumetric flask, add the following in order:

- 1 L of RODI water.
- 141 mL of concentrated sulfuric acid

- The result is a 5 *N* sulfuric acid solution.
- In a 500-mL glass volumetric flask, add the following in order:
  - 250 mL of RODI water.
    - Bring to boil.
  - 12.0 g ammonium molybdate tetrahydrate
- Allow solution to cool to room temperature before continuing.
- In a 200-mL glass volumetric flask, add the following in order:
  - 100 mL of RODI water.
  - 0.2908 g of potassium antimony tartrate
- Add the ammonium molybdate and potassium antimony solutions to the 5 *N* sulfuric acid solution.
- Mix thoroughly and dilute with RODI to 2 L.
- Store in dark bottle and refrigerate.

5.8 Ascorbic acid solution

Components: Ascorbic acid ($C_6H_8O_6$), molybdate solution, RODI water

- In a 500-mL glass volumetric flask, add the following in order:
  - 400 mL of molybdate solution
  - 2.112 g of ascorbic acid
- Mix thoroughly.
- Prepare fresh daily.

5.9 Working stock standard P solution, 10.0 mg P L^{-1} (Reagent A)

Components: Phosphorus Standard, commercially prepared, 100 mg/L P; RODI water

- In a 1-L polyethylene volumetric flask, add the following in order:
  - 800 mL of RODI water.
  - 100 mL of Phosphorus Standard, 10.0 mg/L
- Fill to volume with RODI water.
- Invert to thoroughly mix.
- Make fresh daily.

5.10 Standards S1–S4: Standard P calibration and verification solutions

Components: Reagent A, Ascorbic acid solution, RODI water

- Refer to table 4D2a1–1 for dilutions and concentrations.
- Allow to equilibrate to room temperature before use.

- Make fresh daily.
- Table 4D2a1–2 lists solution concentrations.

5.10.1 Standard blank

- In a 25-mL polyethylene volumetric flask, add the following in order:
  - 4 mL of Ascorbic acid solution
  - Fill to volume with RODI water.
- Invert to mix thoroughly.

5.10.2 Standard S1

- In a 25-mL polyethylene volumetric flask, add the following in order:
  - 0.5 mL of Reagent A
  - 4 mL of Ascorbic acid solution
  - Fill to volume with RODI water.
- Invert to mix thoroughly.

5.10.3 Standard S2

- In a 25-mL polyethylene volumetric flask, add the following in order:
  - 1.0 mL of Reagent A
  - 4 mL of Ascorbic acid solution
  - Fill to volume with RODI water.
- Invert to mix thoroughly.

5.10.4 Standard S3

- In a 25-mL polyethylene volumetric flask, add the following in order:
  - 1.5 mL of Reagent A
  - 4 mL of Ascorbic acid solution
  - Fill to volume with RODI water.
- Invert to mix thoroughly.

5.10.5 Standard S4

- In a 25-mL polyethylene volumetric flask, add the following in order:
  - 2.0 mL of Reagent A
  - 4 mL of Ascorbic acid solution
  - Fill to volume with RODI water.
- Invert to mix thoroughly.

Table 4D2a1–1.—Preparation of Phosphorous Calibration and Verification Solutions, Standards S1–S4. (Prepare in 25-mL volumetrics.)

Reagents	Reagent A	Ascorbic Acid Solution	RODI Water
	(mL)	*(mL)*	
Blank	0	4	Bring to volume with RODI water
S1	0.5	4	
S2	1.0	4	
S3	1.5	4	
S4	2.0	4	

Table 4D2a1–2.—Concentrations of Phosphorous Calibration and Verification Solutions, Standards S1–S4.

Standards	Standard Concentrations
	(mg P L^{-1})
Blank	0
S1	0.2
S2	0.4
S3	0.6
S4	0.8

5.11 Quality Control: A KSSL soil standard and a blank are routinely included in every batch of 24 samples.

6. Health and Safety

Warning.—Many metal salts are extremely toxic and may be fatal if ingested.

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids. Dispense concentrated acids and bases in fume hood.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. Subsamples are further processed via planetary ball mill to 80 mesh; either size fraction is appropriate for this test. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Weigh 2.5 g of <2-mm or fine-grind, air-dry soil and place into a 50-mL centrifuge tube. If sample is moist, weigh enough soil to achieve ≈2.5 g of air-dry soil.

8.2 Add 25.0 mL of RODI water to sample. Place the sample in shaker and shake for 30 min at 200 oscillations min^{-1} at room temperature (20 ±2 °C).

8.3 Remove the sample from the shaker. Centrifuge at 3,000 rpm for 20 min, decant, filter, and collect extract in receiving cup. If extracts are not to be analyzed immediately after collection, store samples at 4 °C. Analyze samples within 24 h.

8.4 Pipette 2 mL of sample extract into plastic cup. Add 4 mL of ascorbic acid solution and 19 mL of RODI water.

8.5 Allow a minimum of 10 min for color development before analysis. Color remains stable for 24 h.

8.6 Transfer sample extracts and standard solutions S1–S4 into 4.5 mL cuvettes.

8.7 Set spectrophotometer to 882 nm. Autozero with calibration blank.

- Calibrate the instrument using standards S1–S4 and blank.
- If the calibration curve has <0.99 linearity, recalibration is required.

8.8 Run samples using calibration curve.

8.9 Record results to the nearest 0.01 unit for each sample extract and standard.

8.10 If samples are outside the calibration range, dilute samples with extracting solution and re-analyze.

9. Calculations

9.1 Convert extract P (mg L^{-1}) to soil P (mg kg^{-1}) as follows:

$$\text{Soil P (mg kg}^{-1}\text{)} = (A \times B \times C1 \times C2 \times R \times 1{,}000) / E$$

A = Sample extract reading (mg kg^{-1})

B = Extract volume (L)

C1 = Dilution, required

C2 = Dilution, if performed

R = Air-dry/oven-dry ratio (method 3D1) or field-moist/oven-dry ratio (method 3D2)

1,000 = Conversion factor to kg-basis

E = Sample weight (g)

9.2 Report data to the nearest 0.1 mg P kg^{-1} soil.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

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Soil Tests (4D)
Aqueous Extraction (4D2)
Single-Point Extraction (4D2a)
1:5, 23-h, 1-h (4D2a2)
Air-Dry or Field-Moist, <2 mm (4D2a2a-b1)

1. Introduction to Aqueous Extraction

An aliquot of water is added to a soil sample and allowed to equilibrate for 24 hours. The soil solution is extracted to measure such aspects as pH, EC, and elements in suspension. Studies at the KSSL reported a correlation between water-extractable elements for soils and their concentration in runoff from agricultural watersheds (Elrashidi et al., 2005a, 2005b).

2. Scope and Field of Application

In the laboratory, the soil-and-water system is allowed to equilibrate before extracting the soil solution. The pH, EC, and elements are then measured in the water extract. Studies at the KSSL reported a correlation between water-extractable elements for soils and their concentration in runoff from agricultural watersheds (Elrashidi et al., 2005a, 2005b).

3. Principle

A 7.0-g sample of soil is added to 35 mL of water in a 50-mL disposable centrifuge tube. The soil-and-water suspension is maintained at room temperature for 23 h and then shaken on a reciprocating shaker for 1 hour. The supernatant is filtered prior to analysis. The extract obtained is analyzed for the following:

- Ion chromatography (method 4D2a2a1a1-7), measuring Br^-, Cl^-, F^-, NO_3^-, NO_2^-, PO_4^{3-}, and SO_4^{2-}
- Acid titration (method 4D2a2b1a1-2), measuring CO_3^{2-} and HCO_3^-
- Inductively coupled plasma atomic emission spectrophotometer (ICP–MS) (method 4D2a2d1-22), measuring concentration of all or selected elements (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Se, Si, Sr, V, and Zn)
- Electrical conductivity (method 4F1b1a1)
- pH (method 4C2a1a1a1)

3.1 Interferences

No interferences are known for this method.

4. Apparatus

4.1 Electronic balance, ±1.0-mg sensitivity

4.2 Centrifuge tubes, 50-mL, disposable, polyethylene
4.3 Centrifuge capable of 4,000 rpm
4.4 Vortexer, mini
4.5 Mechanical reciprocating shaker, 100 oscillations min^{-1}, 1½-in strokes
4.6 Syringe, 20 cc, plastic
4.7 Syringe filters, 25-mm, 0.45-µm pore size
4.8 1-oz plastic cup with hinged lids
4.9 1-oz condiment cup

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. Subsamples are further processed via planetary ball mill to 80 mesh; either size fraction is appropriate for this test. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedures

8.1 Weigh 7.0 g of <2-mm or fine-grind, air-dry soil to the nearest mg, place into a 50-mL tube, and add 35 mL of RODI water. If sample was moist, weigh enough soil to achieve ≈7.0 g of air-dry soil.
8.2 Vortex sample to integrate soil sample into the water column.
8.3 Allow the soil-and-water suspension to equilibrate at room temperature for 23 h.
8.4 Vortex samples to integrate hydrated clays and aggregates into water column.
8.5 Transfer the sample to a shaker. Shake for 1 h at 100 oscillations min^{-1} at room temperature (20 ±2 °C).
8.6 Centrifuge tube at 4,000 rpm for 30 minutes.
8.7 Using 20 cc syringe, draw up 20 mL of sample extract.

8.8 Attach Whatman 0.45-µm filter to syringe and expel first 3 mL as waste.

8.9 Filter and reserve a 10-mL aliquot to read EC and pH. The remaining sample is used for the IC, ICP, titrator, and automated ion analyzer. If extracts are not to be analyzed immediately after collection, then store samples at 4 °C. Analyze samples within 72 h.

8.10 Data are reported by methods and best practice as determined for the specific analysis and instrumentation listed in section 9.

9. Calculations

9.1 Calculations are reported in individual methods for:

- Ion chromatography (4D2a2a1a1)
- Acid titration (4D2a2b1a1-2)
- Inductively coupled plasma atomic emission spectrophotometer (ICP–MS) (4D2a2d1-22)
- Automated ion analyzer (4D2a2c1a1)
- pH (4C2a1a1a1)
- Electrical conductivity (4F1b1a1)

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Elrashidi, M.A., J.D. Harder, D. Schroeder, P. Brakhage, C.A. Seybold, and C. Schaecher. 2005a. Loss of phosphorus by runoff for agricultural watersheds. Soil Sci. 170:543–558.

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Soil Tests (4D)
Aqueous Extraction (4D2)
Single-Point Extraction (4D2a)
1:5, 23-h, 1-h (4D2a2)
Ion Chromatograph (4D2a2a)
Conductivity Detector (4D2a2a1)
Self-Generation Suppressor (4D2a2a1a)
Acetate, Bromide, Chloride, Fluoride, Nitrate, Nitrite, Phosphate, Sulfate (4D2a2a1a1-7)
Air-Dry or Field-Moist, <2 mm (4D2a2a1a1-7a-b1)

1. Introduction to Ion Chromatography Aqueous Extraction Analysis

Nutrients, particularly phosphorus and nitrogen, in runoff from agricultural land are leading causes of poor water quality in the United States (USEPA, 1996). When the environmental impact of agricultural land on natural water resources is evaluated, the amount of water-soluble elements and associated properties (e.g., pH, EC) should be measured in soil under conditions similar to those present during runoff events.

2. Scope and Field of Application

This method determines water-soluble Br^-, Cl^-, F^-, NO_3^-, NO_2^-, PO_4^{3-}, and SO_4^{2-} under equilibrium conditions. This method is an important tool to evaluate availability of essential plant nutrients in agricultural land for studies regarding soil health and crop production. Further, the method can be implemented in water quality studies to determine the amount of soil elements that can be transported by runoff water from agriculture land to surface and ground waters (streams, rivers, lakes).

3. Principle

A soil-and-water suspension is maintained at room temperature for 23 hours and then shaken on a reciprocating shaker for 1 hour. The supernatant is filtered and diluted according to its electrical conductivity. Anions (Br^-, Cl^-, F^-, NO_3^-, NO_2^-, PO_4^{3-}, and SO_4^{2-}) are determined using ion chromatography and reported in units of mmol (−)/L.

3.1 Interferences

Some soil extracts contain suspended solids. Filtering after dilution removes the particles.

Analyst should account for co-elution of organic anions with parameter adjustment.

4. Apparatus

4.1 Ion chromatograph

4.2 Digital diluter/dispenser, with 10,000-µL and 1,000-µL syringes, gas tight

4.3 1.5-mL polypropylene vial kits with caps and septa

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.2 Helium gas

5.3 **Primary stock high purity standard solutions,** 1,000 mg/L, commercially prepared:

1,000 mg/L CH_3COO^-; Acetate Standard

1,000 mg/L Br^-; Bromide Standard

1,000 mg/L Cl^-; Chloride Standard

1,000 mg/L F^-; Fluoride Standard

1,000 mg/L NO_3^-; Nitrate Standard

1,000 mg/L NO_2^-; Nitrite Standard

1,000 mg/L SO_4^{2-}; Sulfate Standard

1,000 mg/L PO_4^{3-}; Phosphate Standard

5.4 **Reagents A1–A4: Calibration verification and calibration standard preparations**

Components: 1,000 mg L^{-1} High Purity Standards, RODI water

- Refer to table 4D2a2a–1 for mixing instructions.
- Standard concentrations are mixed by serial dilution.
- The Blank standard for this test is RODI water.
- Invert to thoroughly mix.
- Store in a polyethylene container in a refrigerator.
- Make fresh weekly.
- Refer to table 4D2a2a–2 for final elemental concentrations of solutions.

Table 4D2a2a–1.—Preparation of Anion Calibration Standards Anion 1–Anion 4 and Calibration Verification Standard. (Prepare in 500-mL volumetric flasks.)

Calibration Std.	Fluoride	Acetate	Chloride	Nitrite	Nitrate	Sulfate	Phos-phate	RODI Water
	(mL)	*(mL)*	*(mL)*	*(mL)*	*(mL)*	*(mL)*	*(mL)*	
Anion 4 (High)	0.5	5	20	5	20	20	20	Fill to 500 mL with RODI water
Anion 3 (Mid)	0.25	2.5	10	2.5	10	10	10	
Anion 2 (Low)	Add 50 mL of Anion 4 standard to 500-mL flask							
Anion 1 (Low Low)	Add 25 mL of Anion 4 standard to 500-mL flask							
Anion CVS	0.1	1	4	1	4	4	4	

Table 4D2a2a–2.—Concentrations of Anion Calibration Standards and Calibration Verification Standard.

Calibration Std.	Fluoride	Acetate	Chloride	Nitrite	Nitrate	Sulfate	Phos-phate
	(ppm)	*(ppm)*	*(ppm)*	*(ppm)*	*(ppm)*	*(ppm)*	*(ppm)*
Anion 4 (High)	1	10	40	10	40	40	40
Anion 3 (Mid)	0.5	5	20	5	20	20	20
Anion 2 (Low)	0.1	1	4	1	4	4	4
Anion 1 (Low Low)	0.05	0.5	2	0.5	2	2	2
Anion CVS	0.2	2	8	2	8	8	8

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or

apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids.

Follow the manufacturer's safety precautions when using the chromatograph.

7. Sample Preparation

A filtered and diluted supernatant is acquired from <2-mm air-dried soil. The supernatant is stored at 4 °C. Biological activity is low.

8. Procedure

8.1 Prior to analysis, examine results from carbonate and bicarbonate testing to determine if sample dilutions are necessary. If bicarbonate is present, a lesser dilution concentration may be required. Estimate the total soluble anion concentration (meq L^{-1}).

8.1.1 Anion concentration (meq L^{-1}) = $EC_S \times 10 - (HCO_3^- + CO_3^{2-})$

EC_S = Electrical Conductivity of Saturated Extract (EC_S); reported to the nearest 0.01 mmhos cm^{-1} (dS m^{-1}) by conductivity bridge in method 4F2b1

8.1.2 Determine carbonate:

CO_3^{2-} (mmol (−) L^{-1}) = $[2 \times T_{8.25} \times N] / V$

8.1.3 Determine bicarbonate:

HCO_3^- (mmol (−) L^{-1}) = $[(T_{4.60} - T_{8.25} - B) \times N] / V$

$T_{8.25}$ = Titer for $CO_3^{2-} \rightarrow HCO_3^-$ (mL)

$T_{4.60}$ = Titer for $HCO_3^- \rightarrow H_2CO_3$ (mL)

N = Normality of H_2SO_4 (mmol(+)/mL)

B = Average titer of blank solution (mL)

V = Volume of saturation extract titrated (L)

2 = Multiplier to calculate CO_3^{2-} (mmol (−) L^{-1}) from $T_{8.25}$

Carbonate and bicarbonate concentrations are determined in acid titration procedure (method 4F2c1c1a1-2).

8.1.4 Subtract the CO_3^{2-} and HCO_3^- concentrations from the total anion concentration.

8.1.5 The remainder is the estimated concentration (meq L^{-1}) of anions to be separated by ion chromatography.

Table 4D2a2a–3.—Dilution Factors for Extracts.

EC of Extract		Dilution Factor
From	To	
138.5	250.0	6,000
100.3	138.5	3,000
56.5	100.3	1,500
27.6	56.5	800
13.3	27.6	400
7.1	13.3	200
4.1	7.1	100
2.5	4.1	50
1.6	2.5	20
1.1	1.6	10
0.9	1.1	5
0	0.9	3

8.2 Place Anion 1–Anion 4 and diluted extract samples in the vials and cap with filter caps.

8.3 Set-up and operation of ion chromatograph (IC): Refer to the manufacturer's manual for the set-up and operation of the chromatograph. An example of instrument parameters, ranges, and typical settings follows:

Anion Parameters	Range and/or Typical Setting
Calibration model	Peak Area
Detector	Conductivity
Column type	Dionex Ionpac CS12A
Gradient program	Gradient
Column program	Hold 13 mmol KOH, 9 min/linear increase to 55 mmol KOH, 9–16 min/hold 55 mmol KOH, 16–20 min
Pump flow setting	0.9 mL/min
Pump pressure	≈2,700 psi
Injection volume	25 µL
Column temperature	30 ºC
Suppressor current	112 mA

9. Calculations

9.1 The instrument readings for analyte concentration are in mg L^{-1}. These analyte concentrations are converted to mmol (−) L^{-1} as follows:

Analyte Concentration in Soil (meq L^{-1}) = (A x B) / C

A = Analyte concentration in extract (mg L^{-1})

B = Dilution ratio, if needed

C = Equivalent weight (mg meq^{-1})

Cl^{-} = 35.45

SO_4^{2-} = 48.03

F^{-} = 19.00

NO_3^{-} = 62.00

NO^{2-} = 46.00

Br^{-} = 79.90

PO_4^{3-} = 31.66

9.2 Report ion concentrations in the 1:5 extracts to the nearest 0.1 mmol (−) L^{-1}.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist for final review.

10.6 Compare individual results to method detection limits (MDL) and practical quantitation limits (PQL) before reporting analysis results.

10.6.1 Report numerical values for results that are above the PQL.

10.6.2 Report “trace” for results that are between the MDL and PQL.

10.6.3 Report “non-detect” for results that are below the MDL.

MDL and PQL in Reporting Units

Analyte	MDL	PQL
	(mg kg^{-1} of oven-dried soil)	*(mg kg^{-1} of oven-dried soil)*

11. References

Elrashidi, M.A., J.D. Harder, D. Schroeder, P. Brakhage, C.A. Seybold, and C. Schaecher. 2005a. Loss of phosphorus by runoff for agricultural watersheds. Soil Sci. 170:543–558.

Elrashidi, M.A., M.D. Mays, A. Fares, C.A. Seybold, J.L. Harder, S.D. Peaslee, and P. Van Neste. 2005b. Loss of nitrate-nitrogen by runoff and leaching for agricultural watersheds. Soil Sci. 170:969–984.

Khym, J.X. 1974. Analytical ion-exchange procedures in chemistry and biology: Theory, equipment, techniques. Prentice-Hall, Inc., Englewood Cliffs, NJ.

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Soil Tests (4D)
Aqueous Extraction (4D2)
Single-Point Extraction (4D2a)
1:5, 23-h, 1-h (4D2a2)
Automatic Titrator (4D2a2b)
Combination pH-Reference Electrode (4D2a2b1)
Acid Titration, H_2SO_4 (4D2a2b1a)
Carbonate and Bicarbonate (4D2a2b1a1-2)
Air-Dry or Field-Moist, <2 mm (4D2a2b1a1-2a-b1)

1. Introduction to Carbonate/Bicarbonate Acid Titration

Carbonate and bicarbonate anions are among those most dependent upon soil moisture. The total amount of dissolved ions generally increases with increasing soil moisture content. While some ions increase others may decrease, thereby making interpretations about carbonate and bicarbonate in soil solution dependent upon soil solution conditions. When this principle is applied to evaluating the environmental impact of agricultural land on natural water resources, the amount of water-soluble elements and associated properties should be measured in soil under conditions similar to those present during runoff events.

2. Scope and Field of Application

In the laboratory, the soil-and-water system is allowed to equilibrate before extracting the soil solution. The pH, EC, and elements are then measured in the water extract. Studies at the KSSL reported a correlation between water-extractable elements for soils and their concentration in runoff from agricultural watersheds (Elrashidi et al., 2005a, 2005b).

3. Principle

A <2-mm or fine grind soil sample is treated with RODI water, shaken, and filtered. An aliquot of the soil extract is titrated on an automatic titrator to pH 8.25 (CO_3^{2-}) and 4.60 (HCO_3^-) end points. The carbonate and bicarbonate are calculated from the titers, aliquot volume, blank titer, and acid normality.

Carbonate and bicarbonate are reported in mmol (−) L^{-1} (meq L^{-1}). If the pH of the extract ≤4.60, then carbonate and bicarbonate are not determined.

3.1 Interferences

Clean the electrode by rinsing with distilled water. Wiping the electrode dry with a cloth, laboratory tissue, or similar material may cause electrode polarization. Cleaning the electrode with detergent may decrease the response time.

Slow electrode response time may cause the end point to be overshot; address this issue by slowing the burette speed and increasing the delay time. If troubleshooting efforts fail, replace electrode.

Blanks may not titrate properly because some sources of reverse osmosis (RO) water have a low pH.

4. Apparatus

4.1 Automatic titrator, with control unit, sample changer, dispenser, and software

4.2 Combination pH-reference electrode

4.3 Pipettes, electronic digital, 2,500-µL and 10-mL, with tips, 2,500-µL and 10-mL

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.3 Compressed helium (minimum purity 99.999%)

5.4 Sulfuric acid (H_2SO_4) (CAS# 7664-93-9), concentrated 36 *N,* trace pure grade

5.5 H_2SO_4, 0.0240 *N,* standardized

Components: Sulfuric acid (H_2SO_4); RODI water, degassed

- To a 5-L polyethylene carboy, add the following in order:
  - 4 L of RODI water, degassed for ≈15 min
  - 2.67 mL of concentrated H_2SO_4
- Standardize acid solution using method 4A.
- Re-standardize the acid at regular intervals.

5.6 pH buffers, pH 4.00, 7.00, and 9.18

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids. Dispense concentrated acids and bases in fume hood.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. Subsamples are further processed via planetary ball mill to 80 mesh; either size fraction is appropriate for this test. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Weigh 7.0 g of <2-mm or fine-grind, air-dry soil to the nearest mg, place into a 50-mL tube, and add 35 mL of RODI water. If sample was moist, weigh enough soil to achieve ≈7.0 g of air-dry soil.

8.2 Vortex sample to integrate soil sample into the water column.

8.3 Allow the soil-and-water suspension to equilibrate at room temperature for 23 h.

8.4 Vortex samples to integrate hydrated clays and aggregates into water column.

8.5 Transfer the sample to a shaker. Shake for 1 h at 100 oscillations min^{-1} at room temperature (20 ±2 °C).

8.6 Centrifuge tube at 4,000 rpm for 30 minutes.

8.7 Using 20 cc syringe, draw up 20 mL of sample extract.

8.8 Attach Whatman 0.45 µm filter to syringe and expel first 3 mL as waste.

8.9 Filter and reserve a 10-mL aliquot to read EC and pH. The remaining sample is used for the IC, ICP, titrator, and automated ion analyzer. If extracts are not to be analyzed immediately after collection, then store samples at 4 °C. Analyze samples within 72 h.

8.10 Pipette 3 mL of the sample extract into a 250-mL titration beaker. Add 72 mL of RO water to the sample extract for a final volume of 75 mL.

8.11 Create 8 to 12 blanks by adding 75 mL of RO water into 250-mL titration beakers.

8.12 Refer to manufacturer's manual for operation of the automatic titrator.

8.13 Calibrate automatic titrator with 9.18, 7.00, and 4.00 pH buffers.

8.14 Place the 250-mL titration beakers in the sample changer and begin titration.

- Carbonate titration end point is pH 8.25.
- Bicarbonate titration end point is pH 4.60.

8.15 Record titer and other titration parameters.

9. Calculations

9.1 Determine carbonate:

$$CO_3^{2-}\ (\text{mmol(-)}\ L^{-1}) = [2 \times T_{8.25} \times N] / V$$

9.2 Determine bicarbonate:

$$HCO_3^{-}(\text{mmol}\ (-)\ L^{-1}) = [(T_{4.60} - T_{8.25} - B) \times N] / V$$

$T_{8.25}$ = Titer for $CO_3^{2-} \rightarrow HCO_3^{-}$ (mL)
$T_{4.60}$ = Titer for $HCO_3^{-} \rightarrow H_2CO_3$ (mL)
N = Normality of H_2SO_4 (mmol(+)/mL)
B = Average titer of blank solution (mL)

V = Volume of saturation extract titrated (L)

2 = Multiplier to calculate CO_3^{2-} (mmol (−) L^{-1}) from $T_{8.25}$

9.3 Report saturation extract CO_3^{2-} and HCO_3^- concentrations to the nearest 0.1 mmol (−) L^{-1}

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Elrashidi, M.A., J.D. Harder, D. Schroeder, P. Brakhage, C.A. Seybold, and C. Schaecher. 2005a. Loss of phosphorus by runoff for agricultural watersheds. Soil Sci. 170:543–558.

Elrashidi, M.A., M.D. Mays, A. Fares, C.A. Seybold, J.L. Harder, S.D. Peaslee, and P. Van Neste. 2005b. Loss of nitrate-nitrogen by runoff and leaching for agricultural watersheds. Soil Sci. 170:969–984.

U.S. Environmental Protection Agency (USEPA). 1996. Environmental indicators of water quality in the United States. United States Environmental Protection Agency, U.S. Gov. Print. Office, Washington, DC.

Soil Test Analyses (4D)
Aqueous Extraction (4D2)
Single-Point Extraction (4D2a)
1:5, 23-h, 1-h (4D2a2)
Inductively Coupled Plasma Mass Spectrophotometer (4D2a2d)
Aluminum, Arsenic, Barium, Boron, Cadmium, Calcium, Chromium, Cobalt, Copper, Iron, Lead, Magnesium, Manganese, Molybdenum, Nickel, Phosphorus, Potassium, Selenium, Silicon, Sodium, Strontium, Vanadium, and Zinc (4D2a2d1-23)
Air-Dry or Field-Moist, <2-mm (4D2a2d1-23a-b1)

1. Introduction to ICP–MS Aqueous Extraction Analysis

Inductively Coupled Plasma Mass Spectrophotometry (ICP–MS) is a multi-element technique with a large analytical range and low detection limit. Plasma is used to ionize a sample and detect atomic ions. This information is helpful in determining amounts of lead or arsenic in soil for public health or phosphorus and sodium for agricultural purposes.

2. Scope and Field of Application

This method determines water-dissolved elements under equilibrium conditions in soil. Elements extracted from soil include:

- Available forms of essential plant macro- and micro-nutrients (N, P, C, S, K, Ca, Mg, Fe, Mn, Cu, Zn, B, and Mo), and
- Water-soluble forms of trace elements and toxic heavy metals (Al, As, Se, Ba, Cd, Co, Cr, Ni, Pb, Sr, and Si).

This method is an important tool to evaluate availability of essential plant nutrients in agricultural land for studies regarding soil health and crop production. It can also be implemented in water quality studies to determine the amount of soil elements that can be transported by runoff water from agriculture land to surface and ground waters (streams, rivers, lakes).

3. Principle

The extract is prepared in method 4D2a2. A 7.0-g sample of soil is added to 35 mL of water in a 50-mL disposable centrifuge tube. The soil-and-water suspension is maintained at room temperature for 23 hours and then shaken on a reciprocating shaker for 1 hour. The supernatant is filtered into a new disposable centrifuge tube.

Calibration standards plus a blank are prepared for elemental analysis. The concentration of all or selected elements (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Se, Sr, Si, V, and Zn) are determined by inductively

coupled plasma mass spectrophotometer (ICP–MS). Data from this procedure are reported as mg kg^{-1} soil.

3.1 Interferences

Interferences are corrected or minimized by using an internal standard, collision/reaction cell technology, and careful selection of specific masses for data reporting. Interference corrections are made by ICP–MS software.

4. Apparatus

4.1 Pipettes, electronic digital, 250-µL and 10-mL

4.2 ICP–MS, with associated autosampler, heat exchanger, computer, and software

4.3 Compressed gasses, argon (minimum purity 99.99%), hydrogen (minimum purity 99.999%), and helium (minimum purity 99.999%)

4.4 Quartz torch, for use with high matrix introduction (HMI)

4.5 Peristaltic pump (for automatic injection of internal standard)

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.2 Concentrated hydrochloric acid (HCl) (CAS# 7647-01-0), 12 *N,* trace pure grade

5.3 Concentrated nitric acid (HNO_3) (CAS# 7697-37-2), 16 *N,* trace pure grade

5.4 **Water extractable elements**; commercially prepared solution containing:

1,000 µg/mL Ca, K, Mg
150 µg/mL P, Sr
100 µg/mL Al, Ba, Fe, Mn
50 µg/mL Cu, V, Zn
10 µg/mL Co, Cr, Ni, Pb
5 µg/mL As, Cd
1 µg/mL Mo

5.5 **High purity concentrated elements;** commercially prepared, individual high purity elemental standards. Individual solutions containing:

1,000 mg/L Au, Gold Standard
1,000 mg/L B, Boron Standard
1,000 mg/L Bi, Bismuth Standard
1,000 mg/L Ge, germanium standard
1,000 mg/L In, Indium Standard
1,000 mg/L Li^6; $Lithium^6$ Standard

1,000 mg/L P, Phosphorus Standard
1,000 mg/L Sc, Scandium Standard
1,000 mg/L Se, Selenium Standard
1,000 mg/L Si, Silicon Standard
1,000 mg/L Tb, Terbium standard
1,000 mg/L Y, Yttrium Standard

5.6 Agilent Stock Tuning Solution; commercially prepared

5.7 Agilent 7500 Series PA Tuning 1 Solution; commercially prepared

5.8 Selenium stock solution, 10 µg/mL

Components: Selenium Standard, 1,000 mg/mL; nitric acid (HNO_3); RODI water

- To a 500-mL glass volumetric flask, add the following in order:
  - 5 mL of 1,000 µg/mL Se; Selenium standard
  - 9 mL of nitric acid
  - Fill to volume with RODI water.
- Invert to mix thoroughly.

5.9 Reagents A1-A4: Water extractable elemental calibration and verification standards: Stock, high, medium, and low

Components: 10 µg/mL Selenium Stock solution, nitric acid (HNO_3), Water Extractable Elements solution, RODI water

- Refer to table 4D2a2d–1 below mixing instructions.
- Standards are mixed in serial dilution.
- Refer to table 4D2a2d–3 for concentrations.

5.9.1 Standard A4 (Stock)

- To a 500-mL glass volumetric flask, add the following in order:
  - 300 mL of RODI water
  - 5 mL of Water Extractable Elements solution
  - 5 mL of Selenium Stock solution
  - 9 mL of nitric acid
  - Fill to volume with RODI water.
- Invert to mix.

5.9.2 Standard A3 (High)

- To a 500-mL glass volumetric flask, add the following in order:
  - 300 mL of RODI water
  - 50 mL of Standard A4
  - Fill to volume with RODI water.
- Invert to mix.

5.9.3 Standard A2 (Medium)

- To a 500-mL glass volumetric flask, add the following in order:
  - 300 mL of RODI water
  - 50 mL of Standard A3
  - Fill to volume with RODI water.
- Invert to mix.

5.9.4 Standard A1 (Low)

- To a 500-mL glass volumetric flask, add the following in order:
  - 300 mL of RODI water
  - 50 mL of Standard A2
  - Fill to volume with RODI water.
- Invert to mix.

Table 4D2a2d–1.—Preparation of Water Extractable Elements, ICP–MS Mixed Elements Solutions. (Prepare in 500-mL volumetric flasks.)

Element or Component	A4: Stock	A3: High	A2: Medium	A1: Low
	(mL)	*(mL)*	*(mL)*	*(mL)*
Water extractable elements	5	300 mL of RODI water initially	300 mL of RODI water initially	300 mL of RODI water initially
Nitric acid (HNO_3)	9			
10 µg/mL Se stock	5	50 mL of A4	50 mL of A3	50 mL of A2
RODI water	300 mL initially, fill to volume	Fill to volume with RODI water	Fill to volume with RODI water	Fill to volume with RODI water

5.10 Elemental calibration and verification standards

5.10.1 P-1000

Components: High purity phosphorus standard, 1,000 mg/mL P; RODI water

- To a 1-L glass volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 1 mL of 1,000 mg/L P; Phosphorus Standard
  - Fill to volume with RODI water.

- Invert to mix.
- Refer to table 4D2a2d–3 for concentrations.

5.10.2 P-100

Components: Calibration standard P-1000 solution, RODI water

- To a 1-L glass volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 100 mL of P-1000 solution
  - Fill to volume with RODI water.
- Invert to mix.
- Refer to table 4D2a2d–3 for concentrations.

5.10.3 B-1000

Components: High purity boron standard, 1,000 mg/mL B; RODI water

- To a 1-L polypropylene volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 1 mL of 1,000 mg/mL B; Boron Standard
  - Fill to volume with RODI water.
- Invert to mix.
- Transfer to 1-L polypropylene bottle.
- Refer to table 4D2a2d–3 for concentrations.

5.10.4 B-100

Components: Calibration standard B-1000 solution, RODI water

- To a 1-L polypropylene volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 100 mL of B-1000 solution
  - Fill to volume with RODI water.
- Invert to mix.
- Transfer to 1-L polypropylene bottle.
- Refer to table 4D2a2d–3 for concentrations.

5.10.5 Si-1000

Components: High purity silicon standard, 1,000 mg/mL Si; RODI water

- To a 1-L polypropylene volumetric flask, add the following in order:
  - 500 mL of RODI water

- 1 mL of 1,000 mg/mL Si, Silicon Standard
- Fill to volume with RODI water.

- Invert to mix.
- Refer to table 4D2a2d–3 for concentrations.

5.10.6 Si-100

Components: Calibration standard Si-1000 solution, RODI water

- To a 1-L polypropylene volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 100 mL of Si-1000 solution
  - Fill to volume with RODI water.
- Invert to mix.
- Refer to table 4D2a2d–3 for concentrations.

5.11 Internal standards solution (1 µg/mL Li^6, Sc, Ge, Y, In, Tb, Bi)

Components: Nitric acid (HNO_3), hydrochloric acid (HCl), RODI water, high purity elemental standards:

1,000 mg/L Au, Gold Standard
1,000 mg/L Bi, Bismuth Standard
1,000 mg/L Ge, Germanium Standard
1,000 mg/L In, Indium Standard
1,000 mg/L Li^6, Lithium6 Standard
1,000 mg/L Sc, Scandium Standard
1,000 mg/L Tb, Terbium Standard
1,000 mg/L Y, Yttrium Standard

- To a 1-L polypropylene flask, add the following in order:
  - 300 mL of RODI water
  - 18 mL of nitric acid
  - 6 mL of hydrochloric acid
  - 0.250 mL of 1,000 µg/mL Au, Gold Standard
  - 1 mL of 1,000 mg/L Bi, Bismuth Standard
  - 1 mL of 1,000 mg/L Ge, Germanium Standard
  - 1 mL of 1,000 mg/L In, Indium Standard
  - 1 mL of 1,000 mg/L Li^6, Lithium^6 Standard
  - 1 mL of 1,000 mg/L Sc, Scandium Standard
  - 1 mL of 1,000 mg/L Tb, Terbium Standard
  - 1 mL of 1,000 mg/L Y, Yttrium Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.12 Tuning solution

Components: Agilent Stock Tuning Solution, nitric acid (HNO_3), RODI water

- To a 1-L polypropylene volumetric flask, add the following in order:
  - 300 mL of RODI water
  - 1 mL of Agilent Stock Tuning Solution
  - 18 mL of nitric acid
  - Fill to volume with RODI water.
- Invert to mix.

5.13 PA tuning solution

Components: Agilent 7500 Series PA Tuning 1 Solution, nitric acid (HNO_3), RODI water

- To a 1-L polypropylene volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 18 mL of nitric acid
  - 100 mL of commercially prepared Agilent 7500 Series PA Tuning 1 solution
  - Fill to volume with RODI water.
- Invert to mix.

5.14 Reagent B1–B4: ICP–MS rinse solutions

Components: Nitric acid (HNO_3); hydrochloric acid (HCl); high purity gold standard, 1,000 mg/mL Au; RODI water

- Refer to table 4D2a2d–2 for mixing instructions.
- The Initial Rinse solution is prepared in a 2-L flask. All other solutions are prepared in 1-L flasks.
- All rinses are brought to volume with RODI water.

5.14.1 Reagent B1: Initial rinse

- To a 2-L polypropylene volumetric, add the following in order:
  - 300 mL of RODI water
  - 58 mL of nitric acid
  - Fill to volume with RODI water.
- Invert to mix.

5.14.2 Reagent B2: Rinse #1

- To a 1-L polypropylene volumetric, add the following in order:
  - 300 mL of RODI water
  - 29 mL of nitric acid
  - 1 mL of 1,000 µg/mL Au, Gold Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.14.3 Reagent B3: Rinse #2

- To a 1-L polypropylene volumetric, add the following in order:
  - 300 mL of RODI water
  - 15 mL of nitric acid
  - 45 mL of hydrochloric acid
  - 1 mL of 1,000 µg/mL Au, Gold Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.14.4 Reagent B4: Rinse #3

- Fill a 1-L polypropylene volumetric to volume with RODI water.

Table 4D2a2d–2.—ICP–MS Rinse Solutions.

Component	B1 Initial Rinse	B2 Rinse #1	B3 Rinse #2	B4 Rinse #3
	(mL)	*(mL)*	*(mL)*	
	2-L flask	*1-L flasks*		
Nitric acid (HNO_3)	58	29	15	RODI water only
Hydrochloric acid (HCl)	---	---	45	
1,000 µg/mL Au	---	1	1	
RODI water	300 mL initially, fill to volume			

Table 4D2a2d–3.—Standard Concentrations in µg/mL for Each Element.

Element	Blank	A4 (Low)	A3 (Mid)	A2 (High)	P-100	P-1000	B-100	B-1000	Si-100
Al	0	1	10	100	---	---	---	---	---
As	0	0.05	0.5	5	---	---	---	---	---
Ba	0	1	10	100	---	---	---	---	---
B	0	---	---	---	---	---	100	1,000	
Cd	0	0.05	0.5	5	---	---	---	---	---
Ca	0	10	100	1,000	---	---	---	---	---
Cr	0	0.1	1	10	---	---	---	---	---
Co	0	0.1	1	10	---	---	---	---	---
Cu	0	0.5	5	50	---	---	---	---	---
Fe	0	1	10	100	---	---	---	---	---

Table 4D2a2d–3.—Standard Concentrations in µg/mL for Each Element—Continued

Element	Blank	A4 (Low)	A3 (Mid)	A2 (High)	P-100	P-1000	B-100	B-1000	Si-100
Pb	0	0.1	1	10	---	---	---	---	---
Mg	0	10	100	1,000	---	---	---	---	---
Mn	0	1	10	100	---	---	---	---	---
Mo	0	0.01	0.1	1	---	---	---	---	---
Ni	0	0.1	1	10	---	---	---	---	---
P	0	---	---	---	100	1,000	---	---	---
K	0	10	100	1,000	---	---	---	---	---
Se	0	0.1	1	10	---	---	---	---	---
Si	0	---	---	---	---	---	---	---	100
Na	0	10	100	1,000	---	---	---	---	---
Sr	0	1.5	15	150	---	---	---	---	---

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids.

Dispense concentrated acids and bases in fume hood.

Follow the manufacturer's safety precautions when using the ICP–MS.

7. Sample Preparation

A sample supernatant is created from RODI water and <2-mm air-dried soil. Biological activity is low.

8. Procedure

8.1 Reporting m/z and tune step for each element analyzed.

Element	m/z	Tune 1 (H2)	Tune 2 (He)	Tune 3 (No gas)
Al	27	--	X	--
As	75	--	X	--
Ba	137	--	--	X

Element	m/z	Tune 1 (H2)	Tune 2 (He)	Tune 3 (No gas)
B	11	--	X	--
Cd	111	--	X	--
Ca	44	X	--	--
Cr	52	--	X	--
Co	59	--	X	--
Cu	63	--	X	--
Fe	57	--	X	--
Pb	208	--	--	X
Mg	24	--	X	--
Mn	55	--	X	--
Mo	98	--	--	X
Ni	60	--	X	--
P	31	--	X	--
K	39	--	X	--
Se	78	X	--	--
Si	28	X	--	--
Na	23	--	X	--
Sr	88	--	--	X
V	51	--	X	--
Zn	66	--	X	--

8.2 Establish detection limits using the blank standard solution. The instrumental detection limits are calculated using 3 times the standard deviation of 10 readings of the blank. These values establish the lower detection limits for each element. Analyzed values that are lower than the detection limits are reported as “ND”, or non-detected.

9. Calculations

9.1 Calculate the mg kg^{-1} of an element in the soil from µg L^{-1} in solution as follows:

$$\text{Analyte concentration in soil (mg kg}^{-1}\text{)} = [(A \times B \times C \times R \times 1{,}000)/E] \times 1{,}000$$

A = Sample extract reading (µg L^{-1})

B = Extract volume (L)

C = Dilution, if performed

R = Air-dry/oven-dry or field-moist/oven-dry ratio (methods 3D1 and 3D2)

1,000 = Conversion factor in numerator to kg-basis

E = Sample weight (g)

1,000 = Factor in denominator (µg mg^{-1})

9.2 Analysis is generally done on one mass per element. If more than one mass is analyzed, only the reporting mass is used for data reporting purposes. The particle-size fraction digested needs to be identified with each sample.

9.3 Data are reported to the nearest 0.01 mg kg^{-1}.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist for final review.

10.6 Compare individual results to method detection limits (MDL) and practical quantitation limits (PQL) before reporting analysis results.

10.6.1 Report numerical values for results that are above the PQL.

10.6.2 Report “trace” for results that are between the MDL and PQL.

10.6.3 Report “non-detect” for results that are below the MDL.

MDL and PQL in Reporting Units

Analyte	MDL	PQL
	(mg kg^{-1} of oven-dried soil)	*(mg kg^{-1} of oven-dried soil)*

11. References

Elrashidi, M.A., J.D. Harder, D. Schroeder, P. Brakhage, C.A. Seybold, and C. Schaecher. 2005a. Loss of phosphorus by runoff for agricultural watersheds. Soil Sci. 170:543–558.

Elrashidi, M.A., M.D. Mays, A. Fares, C.A. Seybold, J.L. Harder, S.D. Peaslee, and P. Van Neste. 2005b. Loss of nitrate-nitrogen by runoff and leaching for agricultural watersheds. Soil Sci. 170:969–984.

U.S. Environmental Protection Agency (USEPA). 1996. Environmental indicators of water quality in the United States. United States Environmental Protection Agency, U.S. Govt. Print. Office, Washington, DC.

Soil Tests (4D)
Aqueous Extraction (4D2)
Single-Point Extraction (4D2a)
1:500, 12-h (4D2a3)
Ion Chromatograph (4D2a3a)
Conductivity Detector (4D2a3a1)
Self-Generation Suppressor (4D2a3a1a)
Sulfate (4D2a3a1a1)
Air-Dry or Field-Moist, <2 mm (4D2a3a1a1a-b1)

1. Introduction to Ion Chromatography and Sulfate Analysis

The content of water-soluble sulfate is used in soil taxonomy as a required characteristic for the sulfuric horizon (Soil Survey Staff, 2014). The sulfuric horizon connotes the presence of active acid sulfate soils and has pH values of 3.5 or less (determined by 1:1 by weight in water).

2. Scope and Field of Application

The presence of 0.05 percent or more water-soluble sulfate is used as an additional criterion for evidence of a sulfuric horizon when pH ≤3.5 is caused by active acid sulfate effects and minerals such as jarosite are not present (Soil Survey Staff, 2014). The sulfuric horizon is commonly accompanied by concentrations of iron- and sulfur-bearing minerals, such as jarosite $KFe_3(SO_4)_2(OH)_6$. These minerals are pyrite-alteration products that have been exposed to an oxidizing environment. Such minerals may be absent from some sulfuric horizons.

3. Principle

The 1:500 soil extract is diluted according to its electrical conductivity. The diluted sample is injected into the ion chromatograph, the anions are separated, and a conductivity detector is used to measure the sulfate content. Data are reported as percent water soluble SO_4^{2-}.

3.1 Interferences

Some soil extracts contain suspended solids. Filtering after dilution removes the particles.

Organic anions that have low molecular weight will co-elute with inorganic anions from the column.

4. Apparatus

4.1 Bottles with caps, 500-mL, HDPE

4.2 Syringe filters, 0.45-µm

4.3 Mechanical reciprocating shaker, 200 oscillations min^{-1}, 1½-in strokes

4.4 Ion chromatograph

4.5 Digital diluter/dispenser, with syringes 10,000-µL and 1,000-µL, gas tight

4.6 1.5-mL plastic vials with septa cap

4.7 Centrifuge tubes, 15-mL

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.2 Helium gas. De-gas the RODI water used in eluent generation for at least 15 minutes.

5.3 **Primary stock standards;** commercially made, high purity:

1,000 mg/L Br^-, Bromide Standard
1,000 mg/L Cl^-, Chloride Standard
1,000 mg/L F^-, Fluoride Standard
1,000 mg/L NO_3^-, Nitrate Standard
1,000 mg/L NO_2^-, Nitrite Standard
1,000 mg/L SO_4^{2-}, Sulfate Standard
1,000 mg/L PO_4^{3-}, Phosphate Standard
1,000 mg/L CH_3COO^-, Acetate Standard
1,000 mg/L Na^+, Sodium Standard
1,000 mg/L NH_4^+, Ammonium Standard
1,000 mg/L K^+, Potassium Standard
1,000 mg/L Mg_2^+, Magnesium Standard
1,000 mg/L Ca_2^+, Calcium Standard

5.4 **Anion and cation calibration standards**

Components: Primary Stock Standards, 1,000 mg L^{-1}; RODI water

- Refer to table 4D2a3a–1 for anion mixing instructions.
- Refer to table 4D2a3a–2 for anion concentrations.
- Refer to table 4D2a3a–3 for cation mixing instructions.
- Refer to table 4D2a3a–4 for cation concentrations.
- Make fresh weekly.
- Cation calibration standards are used as a quality control for anion balances and results. Cations are tested in addition to the anions to verify charge balance as a means of quality control even though only percent sulfate is reported.

5.4.1 Anion 4

- To a 500-mL glass volumetric flask, add the following in order:
  - 200 mL of RODI water

- 0.5 mL of Fluoride Standard
- 5.0 mL of Acetate Standard
- 20.0 mL of Chloride Standard
- 5.0 mL of Nitrite Standard
- 20.0 mL of Nitrate Standard
- 20 mL of Sulfate Standard
- 20 mL of Phosphate Standard
- Fill to volume with RODI water.

- Invert to mix.

5.4.2 Anion 3

- To a 500-mL glass volumetric flask, add the following in order:
  - 200 mL of RODI water
  - 0.25 mL of Fluoride Standard
  - 2.5 mL of Acetate Standard
  - 10.0 mL of Chloride Standard
  - 2.5 mL of Nitrite Standard
  - 10.0 mL of Nitrate Standard
  - 10 mL of Sulfate Standard
  - 10 mL of Phosphate Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.4.3 Anion 2

- To a 500-mL glass volumetric flask, add the following in order:
  - 200 mL of RODI water
  - 50 mL of Anion 4 Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.4.4 Anion 1

- To a 500-mL glass volumetric flask, add the following in order:
  - 200 mL of RODI water
  - 25 mL of Anion 4 Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.4.5 Anion calibration verification standard (CVS)

- To a 500-mL glass volumetric flask, add the following in order:
  - 200 mL of RODI water
  - 0.1 mL of Fluoride Standard

- 1.0 mL of Acetate Standard
- 4.0 mL of Chloride Standard
- 1.0 mL of Nitrite Standard
- 4.0 mL of Nitrate Standard
- 4.0 mL of Sulfate Standard
- 4.0 mL of Phosphate Standard
- Fill to volume with RODI water.

- Invert to mix.

Table 4D2a3a–1.—Preparation of Anion Calibration Standards Anion 1–Anion 4 and Calibration Verification Standard.

Calibration Std.	Fluoride	Acetate	Chloride	Nitrite	Nitrate	Sulfate	Phos-phate	RODI Water
	(mL)	*(mL)*	*(mL)*	*(mL)*	*(mL)*	*(mL)*	*(mL)*	
Anion 4 (High)	0.5	5	20	5	20	20	20	Fill to 500 mL with RODI water
Anion 3 (Mid)	0.25	2.5	10	2.5	10	10	10	
Anion 2 (Low)	Add 50 mL of Anion 4 standard to 500-mL flask							
Anion 1 (Low Low)	Add 25 mL of Anion 4 standard to 500-mL flask							
Anion CVS	0.1	1	4	1	4	4	4	

Table 4D2a3a–2.—Concentrations of Anion Calibration Standards Anion 1–Anion 4 and Calibration Verification Standard.

Calibration Std.	Fluoride	Acetate	Chloride	Nitrite	Nitrate	Sulfate	Phos-phate
	(ppm)	*(ppm)*	*(ppm)*	*(ppm)*	*(ppm)*	*(ppm)*	*(ppm)*
Anion 4 (High)	1	10	40	10	40	40	40
Anion 3 (Mid)	0.5	5	20	5	20	20	20
Anion 2 (Low)	0.1	1	4	1	4	4	4
Anion 1 (Low Low)	0.05	0.5	2	0.5	2	2	2
Anion CVS	0.2	2	8	2	8	8	8

5.4.6 Cation 4

- To a 500-mL glass volumetric flask, add the following in order:
  - 200 mL of RODI water
  - 15 mL of Sodium Standard
  - 5.0 mL of Ammonium Standard
  - 2.5 mL of Potassium Standard
  - 5.0 mL of Magnesium Standard
  - 15.0 mL of Calcium Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.4.7 Cation 3

- To a 500-mL glass volumetric flask, add the following in order:
  - 200 mL of RODI water
  - 7.5 mL of Sodium Standard
  - 2.5 mL of Ammonium Standard
  - 1.25 mL of Potassium Standard
  - 2.5 mL of Magnesium Standard
  - 7.5 mL of Calcium Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.4.8 Cation 2

- To a 500-mL glass volumetric flask, add the following in order:
  - 200 mL of RODI water
  - 50 mL of Cation 4 Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.4.9 Cation 1

- To a 500-mL glass volumetric flask, add the following in order:
  - 200 mL of RODI water
  - 25 mL of Cation 4 Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.4.10 Cation CVS

- To a 500-mL glass volumetric flask, add the following in order:
  - 200 mL of RODI water
  - 3.0 mL of Sodium Standard
  - 1.0 mL of Ammonium Standard

- 0.5 mL of Potassium Standard
- 1.0 mL of Magnesium Standard
- 3.0 mL of Calcium Standard
- Fill to volume with RODI water.

- Invert to mix.

Table 4D2a3a–3.—Preparation of Cation Calibration Standards Cation 1–Cation 4 and Calibration Verification Standard. (Prepare in 500-mL volumetric flasks.)

Calibration Std.	Sodium	Ammonium	Potassium	Magnesium	Calcium	RODI Water
	(mL)	*(mL)*	*(mL)*	*(mL)*	*(mL)*	
Cation 4 (High)	15	5	2.5	5	15	Fill to 500 mL with RODI water
Cation 3 (Mid)	7.5	2.5	1.25	2.5	7.5	
Cation 2 (Low)	Add 50 mL of Cation 4 standard to 500-mL flask					
Cation 1 (Low Low)	Add 25 mL of Cation 4 standard to 500-mL flask					
Cation CVS	3	1	0.5	1	3	

Table 4D2a3a–4.—Concentrations of Cation Calibration Standards Cation 1–Cation 4 and Calibration Verification Standard.

Calibration Std.	Sodium	Ammonium	Potassium	Magnesium	Calcium
	(ppm)	*(ppm)*	*(ppm)*	*(ppm)*	*(ppm)*
Cation 4 (High)	30	10	5	10	30
Cation 3 (Mid)	15	5	2.5	5	15
Cation 2 (Low)	3	1	0.5	1	3
Cation 1 (Low Low)	1.5	0.5	0.25	0.5	1.5
Cation CVS	6	2	1	2	6

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Follow the manufacturer's safety precautions when using the chromatograph.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Weigh 1.0 g of <2-mm or fine-grind, air-dry soil to the nearest mg, place into a 500-mL bottle, and add 500 mL of RODI water. If sample is moist, weigh enough to achieve ≈1.0 g of air-dry soil.

8.2 Transfer the sample to a shaker. Shake for 12 h at 100 oscillations min^{-1} at room temperature (20 ±2 °C).

8.3 Add 50 mL of filtered sample extract to 50-mL disposable centrifuge tube.

8.4 Measure and record EC of sample extract.

8.5 Dilute the soil extract with the RODI water as indicated in table 4D2a3a–5.

Table 4D2a3a–5.—Dilution Factors for Extracts.

EC of Extract		Dilution Factor
From	To	
138.5	250.0	6,000
100.3	138.5	3,000
56.5	100.3	1,500
27.6	56.5	800
13.3	27.6	400
7.1	13.3	200
4.1	7.1	100
2.5	4.1	50
1.6	2.5	20
1.1	1.6	10
0.9	1.1	5
0	0.9	3

8.6 Place Anion 1–Anion 4 and diluted extract samples in the vials and cap with filter caps.

8.7 Set-up and operation of ion chromatograph (IC): Refer to the manufacturer's manual for the set-up and operation of the chromatograph. Examples of instrument parameters, ranges, and typical settings follow.

Table 4D2a3a–6.—Example of Instrument Anion Parameters.

Anion Parameters	Range and/or Typical Setting
Calibration model	Peak Area
Detector	Conductivity
Column type	Ionpac CS12A
Gradient program	Gradient
Column program	Hold 13 mmol KOH, 9 min/linear increase to 55 mmol KOH, 9-16 min/hold 55 mmol KOH, 16-20 min
Pump flow setting	0.9 mL/min
Pump pressure	≈2,700 psi
Injection volume	25 µL
Column temperature	30 ºC
Suppressor current	112 mA

Table 4D2a3a–7.—Example of Instrument Cation Parameters.

Cation Parameters	Range and/or Typical Setting
Calibration model	Peak Area
Detector	Conductivity
Column type	Ionpac CS12A
Gradient program	Isocratic
Column program	20 mmol Methane Sulfonic Acid
Pump flow setting	0.9 mL/min
Pump pressure	≈2,700 psi
Injection volume	25 µL
Column temperature	30 ºC
Suppressor current	53 mA

8.8 IC Calibration and Analysis

8.8.1 Calibrate the chromatograph and analyze samples according to the instrument method. Analyze a CVS for both anions and cations every 12 samples. If the CVS is outside the accepted range (+/- 10%), recalibrate and re-analyze from the last CVS that passed.

8.8.2 If samples are outside the calibration range for one or more analytes, further dilution of the sample extract is required. Dilute sample extracts with RODI water and re-analyze.

8.8.3 Perform one quality control using Anion CVS and Cation CVS for every 12 samples. If reading is not within the accepted range (+/- 10%), recalibrate and re-analyze from the last CVS that is within range.

8.8.4 Record analyte readings to 0.01 mg L^{-1}.

9. Calculations

9.1 The instrument readings for analyte concentration are in mg L^{-1} and are converted to percent sulfate in the soil as follows:

$$\text{Sulfate Concentration in Soil (\%)} = \{[(A \times B \times C)/1{,}000]/E\} \times 100$$

A = Analyte (SO_4^{2-}) concentration in extract (mg L^{-1})

B = Sample extract volume (0.5 L)

C = Dilution ratio, if needed

1,000 = Conversion factor to change units from mg to g

E = Sample weight (1 g)

100 = Conversion to percent

9.2 Report the water soluble SO_4^{2-} to the nearest hundredths of a percent.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist for final review.

10.6 Compare individual results to method detection limits (MDL) and practical quantitation limits (PQL) before reporting analysis results.

10.6.1 Report numerical values for results that are above the PQL.

10.6.2 Report “trace” for results that are between the MDL and PQL.

10.6.3 Report “non-detect” for results that are below the MDL.

MDL and PQL in Reporting Units

Analyte	MDL	PQL
	(mg kg^{-1} of oven-dried soil)	*(mg kg^{-1} of oven-dried soil)*

11. References

Soil Survey Staff. 2014. Keys to soil taxonomy. 12th ed. USDA–NRCS.

Soil Test Analyses (4D)
Bray P-1 Extraction (4D3)
UV-Visible Spectrophotometer, Dual-Beam (4D3a)
Phosphorus (4D3a1)
Air-Dry or Field-Moist, <2 mm (4D3a1a-b1)

1. Introduction to Bray 1 Phosphorus

The Bray P-1 procedure is used as an index of available phosphorus in the soil. Bray P-1 extractant selectively removes a portion of the adsorbed forms of phosphorus with a weak, acidified ammonium fluoride solution. This solution solubilizes calcium and aluminum phosphates and partially extracts iron phosphates compounds.

2. Scope and Field of Application

Bray P-1 has limited ability to extract phosphorus in calcareous soils due to neutralization of the weak acid extractant by carbonates. This method has been most successful on acid soils (Olsen and Sommers, 1982) and is not appropriate for analyzing O horizons.

3. Principle

A 2.5-g soil sample is shaken with 25 mL of Bray P-1 extracting solution. The mixture is centrifuged, and a sample aliquot is treated with a color reagent. The color is allowed to develop, and absorbance of the solution is read at 882 nm. Data are reported as mg P kg^{-1} soil.

3.1 Interferences

The Bray P-1 procedure is sensitive to the soil/extractant ratio, shaking rate, and time. Studies have shown that incomplete or excessive extraction of phosphorus to be the most significant contributor to interlaboratory variation.

The commercially prepared phosphorus standard must be prepared in a water matrix. Phosphorus is pH dependent, and an acid matrix changes the pH.

4. Apparatus

4.1 Electronic balance, ±0.10-mg sensitivity

4.2 Mechanical reciprocating shaker, 200 oscillations min^{-1}, 1½-in strokes

4.3 Centrifuge tubes, 50-mL, disposable, polyethylene

4.4 Funnel, 60° angle, long stem, 50-mm diameter

4.5 Filter paper, Whatman 42 or equivalent, ashless, 9-cm diameter

4.6 Centrifuge, capable of 2,000 rpm

4.7 Pipettes, electronic digital, 2,500-µL and 10-mL, with tips, 2,500-µL and 10-mL

4.8 Cups, plastic

4.9 Cuvettes, plastic, 4.5-mL, 1-cm light path

4.10 Dispenser, 30-mL or 10-mL

4.11 Spectrophotometer

4.12 Hot plate with magnetic stir bar

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.2 Concentrated hydrochloric acid (HCl) (CAS# 7647-01-0), 12 *N,* trace pure grade

5.3 Concentrated sulfuric acid (H_2SO_4) (CAS# 7664-93-9), 36 *N,* technical grade

5.4 Ammonium fluoride (NH_4F) (CAS# 12125-01-8)

5.5 Ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}•4H_2O$] (CAS# 12054-85-2)

5.6 Potassium antimony–(III) oxide tartrate [$C_8H_4K_2O_{12}Sb•3H_2O$] (CAS# 28300-74-5)

5.7 Ascorbic acid ($C_6H_8O_6$) (CAS# 50-81-7)

5.8 Phosphorus Standard, commercially prepared, 100 mg/L P

5.9 Hydrochloric acid solution, 1 *N*

Components: Concentrated hydrochloric acid (HCl), RODI water

- In a 1-L glass volumetric flask, add the following in order:
  - 500 ml of RODI water.
  - 83.33 mL of concentrated HCl
  - Fill to volume with RODI water.
- Invert to mix thoroughly.

5.10 Bray no. 1 extracting solution (Reagent A)

Components: 1 *N* hydrochloric acid solution, ammonium fluoride (NH_4F), RODI water

- In a 10-L polyethylene carboy, add the following in order:
  - 4 L of RODI water.
  - 8.88 g of NH_4F
  - 200 mL of 1.0 *N* HCl
  - Fill to 8 L with RODI water.
- Solution will have a concentration of 0.03 *N* NH_4F and a pH of 2.6 ±0.5

5.11 Sulfuric-tartrate-molybdate solution (Reagent B)

Components: Ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}•4H_2O$],

potassium antimony–(III) oxide tartrate [$C_8H_4K_2O_{12}Sb•3H_2O$], concentrated sulfuric acid (H_2SO_4), RODI water

- To a 1-L glass volumetric flask, add 200 ml of RODI.
- Bring to boil, add the following in order:
  - 60 g of ammonium molybdate tetrahydrate
  - 1.455 g of antimony potassium tartrate
- Let solution cool to room temperature, add the following in order:
  - 700 mL of concentrated sulfuric acid (slowly)
  - Fill to 1-L with RODI water.
- Store in the dark in the refrigerator.

5.12 Ascorbic acid solution, 0.7 *N*

Components: Ascorbic acid ($C_6H_8O_6$), RODI water

- In a 50-mL glass volumetric flask, add the following in order:
  - 25 mL of RODI water.
  - 6.6 g of ascorbic acid
  - Fill to 50 mL with RODI water.
- Invert to mix thoroughly.
- Make fresh daily.

5.13 Working ascorbic acid molybdate solution (Reagent C)

Components: Reagent B, 0.7 *N* ascorbic acid solution, RODI water

- In a 1-L glass volumetric flask, add the following in order:
  - 800 mL of RODI water.
  - 25 mL of Reagent B
  - 10 mL of ascorbic acid solution
  - Fill to volume with RODI water.
- Allow to stand at least 1 h before using.
- Prepare fresh daily.

5.14 Standard P calibration solutions

Components: Commercially prepared Phosphorus Standard, 100 mg/L P in water; Reagent A

Preparation: Refer to table 4D3a–1 for mixing instructions

- Allow to equilibrate to room temperature before using.
- Make fresh weekly.
- Store in the refrigerator.
- Table 4D3a–2 lists solution concentrations.

5.14.1 Bray blank

- In a 250-mL glass volumetric flask, add 100 mL of Reagent A.

5.14.2 Standard BR-1

- In a 250-mL glass volumetric flask, add the following in order:
  - 1 mL of 100 mg/L P, Phosphorus Standard
  - Fill to volume with Reagent A.
- Invert to mix thoroughly.

5.14.3 Standard BR-2

- In a 250-mL glass volumetric flask, add the following in order:
  - 2 mL of 100 mg/L P, Phosphorus Standard
  - Fill to volume with Reagent A.
- Invert to mix thoroughly.

5.14.4 Standard BR-3

- In a 250-mL glass volumetric flask, add the following in order:
  - 5 mL of 100 mg/L P, Phosphorus Standard
  - Fill to volume with Reagent A.
- Invert to mix thoroughly.

5.14.5 Standard BR-4

- In a 250-mL glass volumetric flask, add the following in order:
  - 10 mL of 100 mg/L P, Phosphorus Standard
  - Fill to volume with Reagent A.
- Invert to mix thoroughly.

5.14.6 Standard BR-5

- In a 250-mL glass volumetric flask, add the following in order:
  - 12.5 mL of 100 mg/L P, Phosphorus Standard
  - Fill to volume with Reagent A.
- Invert to mix thoroughly.

Table 4D3a–1.—Preparation of Phosphorus Calibration Standards BR1–BR5. (Prepare in 250-mL glass volumetrics.)

Standard	100 mg/L P	Reagent A
	(mL)	
Bray blank	0	Bring to volume with Reagent A
BR-1	1	
BR-2	2	
BR-3	5	
BR-4	10	
BR-5	12.5	

Table 4D3a–2.—Concentrations of Phosphorus Calibration Standards BR1–BR5.

Standard	Phosphorus Concentration
	(mg/L^{-1})
Blank	---
BR-1	0.4
BR-2	0.8
BR-3	2.0
BR-4	4.0
BR-5	5.0

5.15 Quality Control: A KSSL soil standard and a blank are routinely included in every batch of 24 samples.

6. Health and Safety

Warning.—Many metal salts are extremely toxic and may be fatal if ingested.

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids. Dispense concentrated acids and bases in fume hood.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage. Upon request, the analysis can be performed using <2 mm field-moist samples.

8. Procedure

8.1 Weigh 2.5 g of <2-mm, air-dry soil to nearest mg on an electronic balance and place into a 50-mL centrifuge tube. If sample is field-moist, weigh out enough soil to achieve ≈2.5 g of air-dry soil.

8.2 Dispense 25.0 mL of extracting solution to sample tube.

8.3 Shake samples for 15 min at 200 oscillations min^{-1} at room temperature (20 °C).

8.4 Centrifuge at 2,000 rpm for 10 min, decant, filter, and collect extract in receiving cup. Analyze samples within 72 h.

8.4.1 If extracts are not to be analyzed immediately after collection, store samples at 4 °C.

8.5 Create a 1:5 dilution of samples and calibration standards.

8.6 Allow a minimum of 20 min for color to develop before analysis.

8.7 Transfer sample extracts and standard solutions to cuvettes.

8.8 Set the spectrophotometer to read at 882 nm. Autozero with calibration blank.

- Calibrate the instrument using Standards BR1–BR5 and a blank.
- If the calibration curve has <0.99 linearity, recalibration is required.

8.9 Run samples using calibration curve. .

8.10 Record results to the nearest 0.01 unit for the sample extract and each standard.

8.11 If samples are outside the calibration range, dilute sample extracts with extracting solution and re-analyze.

9. Calculations

9.1 Determine soil phosphorus concentration (mg/kg^{-1})

$$\text{Soil P } (mg/kg^{-1}) = (A \times B \times C \times R \times 1{,}000)/E$$

A = Sample extract reading ($mg\ L^{-1}$)

B = Extract volume (L)

C = Dilution, if performed

R = Air-dry/oven-dry ratio (method 3D1) or field-moist/oven-dry ratio (method 3D2)

1,000 = Conversion factor to kg-basis

E = Sample weight (g)

9.2 Report Bray1 phosphorus to the nearest 0.1 mg/kg^{-1}

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

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Soil Test Analyses (4D)
Olsen Sodium-Bicarbonate Extraction (4D5)
UV-Visible Spectrophotometer, Dual-Beam (4D5a)
Phosphorus (4D5a1)
Air-Dry or Field-Moist, <2 mm (4D5a1a-b1)

1. Introduction to Olsen Phosphorus

The Olsen procedure is used as an index of available phosphorus in the soil. Olsen extractant is applicable for use on neutral to calcareous soils (Buurman et al., 1996) and correlates well with Mehlich-3 P (R^2=0.918).

2. Scope and Field of Application

The Olsen procedure uses a 0.5 *M* sodium bicarbonate ($NaHCO_3$) solution at a pH of 8.5 to extract P from calcareous, alkaline, and neutral soils. Olsen extractant precipitates calcium carbonates in solution, which enhances the dissolution of Ca-phosphates. Moreover, this extracting solution removes dissolved and adsorbed P on calcium carbonate and iron oxide surfaces. (Elrashidi, 2001). This method is not appropriate for analyzing O horizons.

3. Principle

A 1.0-g soil sample is shaken with 20 mL of Olsen sodium-bicarbonate extracting solution for 30 minutes. The sample is centrifuged, filtered, and diluted with color reagent. Olsen extractant is 0.5 *M* sodium bicarbonate solution at pH 8.5. The absorbance of the solution is read using a spectrophotometer at 882 nm. Data are reported as mg/kg^{-1} P soil.

3.1 Interferences

The intensity of blue increases with the P concentration and is affected by other factors, such as acidity, arsenates, silicates, and substances that influence the oxidation-reduction conditions of the system (Olsen and Sommers, 1982). The commercially prepared phosphorus standard must be prepared in a water matrix; phosphorus is pH dependent, and an acid matrix changes the pH.

4. Apparatus

4.1 Electronic balance, ±1.0-mg sensitivity

4.2 Mechanical reciprocating shaker, 200 oscillations min^{-1}, 1½-in strokes

4.3 Centrifuge tubes, 50-mL, disposable, polyethylene

4.4 Funnel, 60° angle, long stem, 50-mm diameter

4.5 Filter paper, Whatman 42 or equivalent, 150 mm

4.6 Centrifuge, capable of 2,000 rpm

4.7 Pipettes, electronic digital, 1,000-µL and 10-mL, with tips, 1,000-µL and 10-mL

4.8 Cups, plastic

4.9 Dispenser, 30-mL or 10-mL

4.10 Cuvettes, plastic, 4.5-mL, 1-cm light path

4.11 Spectrophotometer

4.12 Hot plate with magnetic stir bar

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.2 Concentrated sulfuric acid (H_2SO_4) (CAS# 7664-93-9), 36 *N,* trace pure grade

5.3 Ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}•4H_2O$) (CAS# 12054-85-2)

5.4 Potassium antimonyl tartrate trihydrate [$C_8H_4K_2O_{12}Sb•3H_2O$] (CAS# 28300-74-5)

5.5 Anhydrous potassium dihydrogen phosphate, monobasic (KH_2PO_4) (CAS# 7778-77-0)

5.6 Ascorbic acid ($C_6H_8O_6$) (CAS# 50-81-7)

5.7 Sodium hydroxide (NaOH) (CAS# 1310-73-2)

5.8 Phosphorus Standard, commercially prepared, 100 mg/L P in water

5.9 Sulfuric acid solution,

Components: Concentrated sulfuric acid, RODI water

- To a 250-mL glass volumetric, add the following in order:
  - 150 mL of RODI water.
  - 56 mL of concentrated H_2SO_4
  - Fill to volume with RODI water.
- Invert to thoroughly mix.

5.10 Sodium hydroxide solution, 1 *M*

Components: Sodium hydroxide (NaOH), RODI water

- To a 100-mL glass volumetric flask, add the following in order:
  - 4 g NaOH
  - 100 mL of RODI water.
- Invert to thoroughly mix.

5.11 Olsen sodium bicarbonate extracting solution 0.5 *M* (Reagent A)

Components: Sodium bicarbonate ($NaHCO_3$), sodium hydroxide solution, RODI water

- To an 8-L polyethylene carboy, add the following in order:
  - 5 L of RODI water.
  - 252 g $NaHCO_3$
- Adjust the pH to 8.5 with 1 *M* NaOH
  - Fill to 6 L with RODI water.
- Mix thoroughly.
- Check pH daily.

5.12 Ammonium molybdate solution, 4%

Components: Potassium antimonyl tartrate trihydrate ($(NH_4)_6Mo_7O_{24}•4H_2O$), RODI water

- To a 100-mL glass volumetric, add the following in order:
  - 80 mL of RODI water.
    - Heat RODI water to 50 °C.
  - 4 g of ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}•4H_2O$]
  - Fill to volume with RODI water.
- Invert to mix.
- Store in the dark in the refrigerator.

5.13 Potassium antimonyl tartrate trihydrate, 0.275% solution (Reagent B)

Components: Potassium antimony–(III) oxide tartrate [$C_8H_4K_2O_{12}Sb•3H_2O$], RODI water

- To a 100-mL glass volumetric, add the following in order:
  - 80 mL of RODI water.
  - 0.275 g of potassium antimonyl tartrate trihydrate
  - Fill to volume with RODI water.
- Invert to mix.

5.14 Ascorbic acid solution, 1.75%

Components: Ascorbic acid ($C_6H_8O_6$), RODI water

- To a 100-mL glass volumetric flask, add the following in order:
  - 80 mL of RODI water.
  - 1.75 g of ascorbic acid
  - Fill to volume with RODI water.
- Prepare fresh daily.

5.15 Color developing reagent

Components: Sulfuric acid solution, ammonium molybdate solution, Reagent B, ascorbic acid solution, RODI water

- To a 500-mL glass volumetric, add the following in order:
  - 50 mL of H_2SO_4 solution

  - 15 mL of ammonium molybdate solution
  - 30 mL of ascorbic acid solution
  - 5 mL of Reagent B
  - 200 mL of RODI water
- Mix well after each addition.
- Prepare fresh daily.

5.16 Working stock standard P solution, 4.0 mg L^{-1} P (Reagent C)

Components: Phosphorus Standard, commercially prepared, 100 mg/L P; Reagent A

- To a 250-mL glass volumetric flask, add the following in order:
  - Pipette 10.0 mL of Phosphorus Standard
  - Fill to volume with Reagent A.
- Invert to thoroughly mix.
- Make fresh weekly.
- Store in the refrigerator.

5.17 Standards OL1–OL5; Standard P calibration solutions

Components: Reagent C, Reagent A

Preparation: Refer to table 4D5a–1 for dilutions and concentrations

- Dilute to volume with Reagent A.
- Invert to mix thoroughly.
- Allow to equilibrate to room temperature before use.
- Make fresh weekly.
- Store in the refrigerator.
- Table 4D5a–2 lists solution concentrations.

Table 4D5a–1.—Preparation of Phosphorous Calibration and Calibration Verification Solutions. (Prepare in 50-mL volumetrics.)

Standard	Reagent C	Reagent A
	(mL)	
Blank	0	Bring to volume with Reagent A
OL1	5	
OL2	10	
OL3	15	
OL4	20	
OL5	25	

Table 4D5a–2.—Concentrations of Standard Phosphorous Calibration Solutions.

Reagent	Reagent Concentration
	(mg P L^{-1})
Blank	---
OL1	0.4
OL2	0.8
OL3	1.2
OL4	1.6
OL5	2.0

5.18 Quality Control Samples

- 0.1 mg P L^{-1} solution made from commercial Phosphorus Standard
- Selected standards OL1–5
- KSSL soil standard
- Blanks

6. Health and Safety

Warning.—Many metal salts are extremely toxic and may be fatal if ingested.

Personal Protective Equipment (PPE).—When preparing reagents, especially concentrated acids and bases, use disposable gloves with appropriate polymer rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids. Dispense concentrated acids and bases in fume hood.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. Subsamples are further processed via planetary ball mill to 80 mesh. The <2-mm size fraction is the standard preparation for this test; 80-mesh sample may be used when samples have a high content of organic matter. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Weigh 1.0 g of <2-mm or fine-grind, air-dry soil to the nearest mg into a 50-mL centrifuge tube. If sample is moist, weigh enough soil to achieve ≈1.0 g of air-dry soil.

8.2 Dispense 20.0 mL of sodium bicarbonate extracting solution to tube.

8.3 Transfer the sample to the shaker. Shake for 30 min at 200 oscillations min^{-1} at room temperature (20 ±2 °C).

8.4 Remove the sample from the shaker. Centrifuge at 2,000 rpm for 10 min, decant, filter, and collect extract in receiving cup. If extracts are not to be analyzed immediately after collection, then store samples at 4 °C. Analyze samples within 72 h.

8.5 Use a pipette to transfer a 5-mL aliquot of the sample to a plastic cup. Use a clean pipette tip for each sample.

8.6 Use a pipette to transfer a 5-mL aliquot of standards OL1–OL5 and blank to a plastic cup. Use a clean pipette tip for each OL1–OL5 standard.

8.7 Dispense 5 mL of color developing reagent to sample aliquot and to each standard OL1–OL5 and blank. Swirl to mix. Allow 1 h for color development. Color will remain stable for 24 h.

Note: Do not place sample cups close together as carbon dioxide is released and solution will bubble.

8.8 Transfer sample extract and standards to cuvettes.

8.9 Set the spectrophotometer to read at 882 nm. Autozero with calibration blank.

8.10 Calibrate the instrument using standards OL1–OL5 and a blank. The data system then associates the concentrations with the instrument responses for each standard.

8.11 Run samples using calibration curve.

8.12 Record results to the nearest 0.01 unit for the sample extract and standard.

8.13 If samples are outside calibration range, dilute sample extracts with extracting solution and re-analyze.

9. Calculations

9.1 Convert the extract P (mg L^{-1}) to soil P (mg kg^{-1}):

$$\text{Soil P (mg kg}^{-1}) = (A \times B \times C \times R \times 1{,}000) / E$$

A = Sample extract reading (mg L^{-1})

B = Extract volume (L)

C = Dilution, if performed

R = Air-dry/oven-dry ratio (method 3D1) or field-moist/oven-dry ratio (method 3D2)

1,000 = Conversion factor to kg-basis

E = Sample weight (g)

9.2 Report data to the nearest 0.1 mg P kg^{-1} soil.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

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Soil Test Analyses (4D)
Mehlich No. 3 Extraction (4D6)
UV-Visible Spectrophotometer, Dual-Beam (4D6a)
Phosphorus (4D6a1)
Air-Dry or Field-Moist, <2 mm (4D6a1a-b1)

1. Introduction to Mehlich 3 Phosphorus

Mehlich-3 extraction is used as an index of available phosphorous in the soil and is designed to be applicable across a wide range of soil conditions and pH. Mehlich-3 uses acetic acid and ammonium fluoride (NH_4F) compounds to extract phosphorus from the soil.

2. Scope and Field of Application

Mehlich-3 was developed as a multi-element soil extraction for Ca, Mg, K, Na, and P appropriate for a wide range of soils correlating well with Mehlich-1, Mehlich-2, and ammonium acetate extractions (Soil and Plant Analysis Council, 1999).

For acid to neutral pH soils, Mehlich-3 correlates well with Bray P-1 (R^2=0.966). For calcareous soils, Mehlich-3 correlates with Olsen extractant (R^2=0.918).

This method is not appropriate for analyzing O horizons.

3. Principle

A 2.5-g soil sample is shaken with 25 mL of Mehlich-3 extracting solution. The mixture is centrifuged, and a sample aliquot is treated with Mehlich-3 color reagent. The color is allowed to develop, and absorbance of the solution is read at 882 nm. Data are reported as mg/kg^{-1} soil.

3.1 Interferences

The “Mo blue methods” are very sensitive for phosphorous. They are based on the following principle: In an acid molybdate solution containing orthophosphate ions, a phosphomolybdate complex forms that can be reduced by ascorbic acid, $SnCl_2$, and other reducing agents to a molybdate-blue color.

The intensity of blue is affected by acidity, arsenates, silicates, and substances that influence the oxidation-reduction conditions of the system (Olsen and Sommers, 1982).

The commercially prepared phosphorus standard must be prepared in a water matrix; phosphorus is pH dependent, and an acid matrix will change the pH.

4. Apparatus

4.1 Electronic balance, ±1.0-mg sensitivity

4.2 Mechanical reciprocating shaker, 200 oscillations min^{-1}, 1½-in strokes

4.3 Centrifuge tubes, 50-mL, disposable, polyethylene

4.4 Funnel, 60° angle, long stem, 50-mm diameter

4.5 Filter paper, Whatman 42 or equivalent, 150-mm

4.6 Centrifuge, capable of 2,000 rpm

4.7 Pipettes, electronic digital, 1,000-µL and 10-mL, with tips, 1,000-µL and 10-mL

4.8 Dispenser, 30-mL or 10-mL

4.9 Cups, plastic

4.10 Cuvettes, plastic, 4.5-mL, 1-cm light path

4.11 Spectrophotometer

4.12 Hot plate and magnetic stir bar

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.2 Concentrated sulfuric acid (H_2SO_4) (CAS# 7664-93-9), 36 *N,* trace pure grade

5.3 Concentrated nitric acid (HNO_3) (CAS # 7697-37-2), 16 *N,* trace pure grade

5.4 Ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}•4H_2O$] (CAS# 12054-85-2)

5.5 Potassium antimony–(III) oxide tartrate [$C_8H_4K_2O_{12}Sb•3H_2O$] (CAS# 28300-74-5)

5.6 Phosphorus Standard, commercially prepared, 100 mg/L P.

5.7 EDTA $(HO_2CCH_2)_2NCH_2CH_2N(CH_2CO_2H)_2$ (CAS# 60-00-4)

5.8 Ascorbic acid ($C_6H_8O_6$) (CAS# 50-81-7)

5.9 Ammonium fluoride (NH_4F) (CAS# 12125-01-8)

5.10 Ammonium nitrate (NH_4NO_3) (CAS# 6484-52-2)

5.11 Acetic acid (CH_3COOH) (CAS# 64-19-7)

5.12 Mehlich No. 3 stock solution (Reagent A)

Components: Ammonium fluoride (NH_4F), EDTA, RODI water

- In a 1-L polyethylene flask, add the following in order:
  - 600 mL of RODI water.
  - 55.56 g of NH_4F
  - 29.23 g of EDTA (FW 292.24)
  - Fill to 1-L volume with RODI water.
- Invert to mix thoroughly.

5.13 Mehlich No. 3 working solution (Reagent A1)

Components: Concentrated nitric acid (HNO_3), ammonium nitrate (NH_4NO_3), acetic acid (CH_3COOH), Reagent A, RODI water

- In a 100-mL glass volumetric flask, separately prepare a 10% v/v nitric acid solution:
  - 100 mL of RODI water.
  - 10 mL of concentrated (70%) nitric acid
- In a 10-L polyethylene carboy, add the following in order:
  - 200.1 g of ammonium nitrate
  - 100 mL of Reagent A
  - 115 mL of acetic acid
  - 82 mL of nitric acid solution
  - Fill to 10 L volume with RODI water.
- Invert to mix thoroughly.

5.14 Sulfuric-tartrate-molybdate solution (Reagent B)

Components: Ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}•4H_2O$]; potassium antimony–(III) oxide tartrate [$C_8H_4K_2O_{12}Sb•3H_2O$]; concentrated sulfuric acid (H_2SO_4); RODI water

- In a 2-L glass volumetric, add the following in order:
  - 500 mL of RODI water.
    - Bring to boil.
  - 100 g of ammonium molybdate tetrahydrate
  - 2.425 g of potassium antimony tartrate
    - Let solution cool to room temperature.
  - 1,400 mL of sulfuric acid
  - Fill to volume with RODI water.
- Invert to mix thoroughly
- Store refrigerated in the dark.

5.15 Ascorbic acid solution, 0.47 *N*

Components: Ascorbic acid ($C_6H_8O_6$), RODI water

- In a 100-mL polyethylene flask, add the following in order:
  - 80 mL of RODI water.
  - 8.8 g of ascorbic acid
  - Fill to volume with RODI water.
- Invert to mix thoroughly.
- Make fresh daily.

5.16 Working ascorbic acid molybdate solution (Reagent C)

Components: Reagent B, ascorbic acid solution, RODI water

- In a 1-L glass volumetric flask, add the following in order:
  - 10 mL of ascorbic acid solution
  - 20 mL of Reagent B
  - Fill to volume with RODI water.
- Allow solution to come to room temperature before using.
- Prepare fresh daily.

5.17 Standard P calibration and verification solutions (Standards M1-M8)

Components: Phosphorus Standard, commercially prepared, 100 mg/L P; Reagent A1

- Refer to table 4D6a–1 for mixing instructions:
- Invert to thoroughly mix.
- Store in a polyethylene container in a refrigerator.
- Make fresh weekly.
- Table 4D6a–2 lists solution concentrations.

5.17.1 Mehlich blank

- To a 250-mL glass volumetric flask, add 250 mL of Reagent A1.

5.17.2 Standard M1

- To a 250-mL glass volumetric flask, add the following in order:
  - 1 mL of 100 mg/L P, Phosphorus Standard
  - Fill to volume with Reagent A1.
- Invert to mix thoroughly.

5.17.3 Standard M2

- To a 250-mL glass volumetric flask, add the following in order:
  - 2 mL of 100 mg/L P, Phosphorus Standard
  - Fill to volume with Reagent A1.
- Invert to mix thoroughly.

5.17.4 Standard M3

- To a 250-mL glass volumetric flask, add the following in order:
  - 2.5 mL of 100 mg/L P, Phosphorus Standard
  - Fill to volume with Reagent A1.
- Invert to mix thoroughly.

5.17.5 Standard M4

- In a 250-mL glass volumetric flask, add the following in order:
  - 5 mL of 100 mg/L P, Phosphorus Standard
  - Fill to volume with Reagent A1.
- Invert to mix thoroughly.

5.17.6 Standard M5

- In a 250-mL glass volumetric flask, add the following in order:
  - 10 mL of 100 mg/L P, Phosphorus Standard
  - Fill to volume with Reagent A1.
- Invert to mix thoroughly.

5.17.7 Standard M6

- In a 250-mL glass volumetric flask, add the following in order:
  - 20 mL of 100 mg/L P, Phosphorus Standard
  - Fill to volume with Reagent A1.
- Invert to mix thoroughly.

5.17.8 Standard M7

- In a 250-mL glass volumetric flask, add the following in order:
  - 25 mL of 100 mg/L P, Phosphorus Standard
  - Fill to volume with Reagent A1.
- Invert to mix thoroughly.

5.17.9 Standard M8

- In a 250-mL glass volumetric flask, add the following in order:
  - 30 mL of 100 mg/L P, Phosphorus Standard
  - Fill to volume with Reagent A1.
- Invert to mix thoroughly.

Table 4D6a–1.—Preparation of Phosphorous Calibration and Verification Standards M1–M8. (Prepare in 250-mL volumetrics.)

Standard	100 mg/L P	Reagent A1
	(mL)	
Mehlich blank	0	Bring to volume with Reagent A1
M1	1	
M2	2	
M3	2.5	
M4	5	
M5	10	
M6	20	
M7	25	
M8	30	

Table 4D6a–2.—Concentrations of Phosphorous Calibration Standards M1–M8.

Standard	Reagent Concentrations
	(mg P L^{-1})
Mehlich blank	---
M1	0.4
M2	0.8
M3	1.0
M4	2.0
M5	4.0
M6	8.0
M7	10.0
M8	12.0

5.18 Quality Control: A KSSL soil standard and a blank are routinely included in every batch of 24 samples.

6. Health and Safety

Warning.—Many metal salts are extremely toxic and may be fatal if ingested.

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids. Dispense concentrated acids and bases in fume hood.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. Subsamples are further processed via planetary ball mill to 80 mesh. The <2-mm size fraction is the standard preparation for this test; 80-mesh sample may be used when samples have a high content of organic matter. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Weigh 2.5 g of <2-mm or fine-grind, air-dry soil to the nearest mg into a 50-mL centrifuge tube. If sample is moist, weigh enough soil to achieve ≈2.5 g of air-dry soil.

8.2 Dispense 25.0 mL of extracting solution to the tube.

8.3 Transfer the sample to the shaker. Shake for 5 min at 200 oscillations min^{-1} at room temperature (20 ±2 °C).

8.4 Remove the sample from the shaker. Centrifuge at 2,000 rpm for 10 min, decant, filter, and collect extract in receiving cups. Store samples at 4 °C. Analyze samples within 72 h.

8.5 Use the pipette to transfer a 0.5-mL aliquot of the sample to a plastic cup. Transfer a 0.5-mL aliquot of each standard M1–M8 and a blank to a plastic cup. Use a clean pipette tip for each sample and each standard.

8.6 Dispense 13.5 mL of the Reagent C to each sample and standard. Swirl to mix.

8.7 Allow a minimum of 20 min for color development. Color will remain stable for 6 h.

8.8 Transfer sample extracts and standard solutions to cuvettes.

8.9 Set the spectrophotometer to read at 882 nm. Autozero with calibration blank

- Calibrate the instrument by using standards M1–M8 and a blank.
- If the calibration curve has <0.99 linearity, recalibration is required.

8.10 Run samples using calibration curve. .

8.11 If samples are outside calibration range, dilute sample extracts with extracting solution and re-analyze.

8.12 Record results to the nearest 0.01 unit for the sample extract and each standard.

9. Calculations

9.1 Convert extract P (mg L^{-1}) to soil P (mg kg^{-1}) as follows:

$$\text{Soil P (mg kg}^{-1}) = (A \times B \times C \times R \times 1{,}000) / E$$

A = Sample extract reading (mg L^{-1})

B = Extract volume (L)

C = Dilution, if performed

R = Air-dry/oven-dry ratio (method 3D1) or field-moist/oven-dry ratio (method 3D2)

1,000 = Conversion factor to kg-basis

E = Sample weight (g)

9.2 Report data to the nearest 0.1 mg P kg^{-1} soil.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Mehlich, A. 1984. Mehlich 3 soil text extractant: A modification of Mehlich 2 extractant. Commun. Soil Sci. Plant Anal. 15:1409–1416.

Murphy, J., and J.R. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chem. Acta. 27:31–36.

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Soil Test Analyses (4D)

Mehlich No. 3 Extraction (4D6)

Inductively Coupled Plasma Atomic Emission Spectrophotometer (4D6b)

Axial Mode (4D6b1)

Cross-Flow Nebulizer (4D6b1b)

Aluminum, Arsenic, Barium, Calcium, Cadmium, Cobalt, Chromium, Copper, Iron, Potassium, Magnesium, Manganese, Molybdenum, Sodium, Nickel, Phosphorus, Lead, Selenium, Silicon, Strontium, and Zinc (4D6b1b1-21)

Air-Dry or Field-Moist, >2 mm (4D6b1b1-18a-b1)

1. Introduction to Mehlich No. 3 ICP–AES Analysis

Mehlich No. 3 is used as an index of available phosphorous in the soil. It was developed by Mehlich (1984) as a multielement soil extraction (Ca, Mg, K, Na, P). Mehlich No. 3 uses acetic acid and ammonium fluoride (NH_4F) compounds to extract phosphorus and other elements from the soil.

2. Scope and Field of Application

Extraction of P by Mehlich No. 3 is designed to be applicable across a wide range of soil properties with reaction ranging from acid to basic (Mehlich, 1984).

- Mehlich No. 3 correlates well with Bray P-1 on acid to neutral (R^2=0.966) soils but not calcareous soils (Soil and Plant Analysis Council, 1999).
- Mehlich No. 3 correlates with Olsen extractant on calcareous soils (R^2=0.918), even though the quantity of Mehlich No. 3 Extractable P is considerably higher (Soil and Plant Analysis Council, 1992).
- The Mehlich No. 3 extractant is neutralized less by carbonate compounds in soil than the double acid (Mehlich No. 1) and Bray P-1 extractants. It is also less aggressive towards apatite or other Ca-phosphate than the double acid and Bray P-2 extractants (Tran and Simard, 1993).
- Mehlich No. 3 can also be used to extract Ca, Mg, K, and Na in a wide range of soils and correlates well with Mehlich No. 1, Mehlich No. 2, and NH_4OAc (Soil and Plant Analysis Council, 1999).
- Additionally, Mehlich No. 3 can be used to extract Al, Cd, Cu, Fe, Mn, Ni, Pb, and Zn (Elrashidi et al., 2003).

3. Principle

A 2.5-g soil sample is shaken with 25 mL of Mehlich No. 3 extracting solution. The sample is centrifuged, filtered, and the clear extracts are analyzed along with calibration standards and a blank of Mehlich No. 3 solution. An inductively coupled plasma atomic emission spectrophotometer (ICP–AES) is used for analysis. The concentration of Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo,

Na, Ni, P, Pb, Se, Si, Sr, and Zn are determined by an inductively coupled plasma atomic emission spectrophotometer (ICP–AES) in axial mode. Data are reported as mg kg^{-1} soil.

3.1 Interferences

Spectral and matrix interferences exist and are corrected or minimized by using both an internal standard and inter-elemental correction factors by ICP–AES software.

Sodium and silicon standards are mixed separately to avoid false calibration readings or concentrations. The standard used for silicon is sodium silicate. Isolating these standards ensures accurate calibration and detection.

Careful selection of specific wavelengths for data reporting is important.

Samples and standards are matrix-matched to reduce interferences.

4. Apparatus

4.1 Electronic balance, ±1.0-mg sensitivity

4.2 Mechanical reciprocating shaker, 200 oscillations min^{-1}, 1½-in strokes

4.3 Centrifuge tubes, 50-mL, disposable, polyethylene

4.4 Funnel, 60° angle, long stem, 50-mm diameter

4.5 Filter paper, Whatman 42 or equivalent, 150-mm

4.6 Centrifuge, capable of 2,000 rpm

4.7 Pipettes, electronic digital, 1,000-µL and 10-mL, with tips

4.8 Dispenser, 30-mL capability

4.9 Cups, plastic

4.10 Inductively coupled plasma atomic emission spectrophotometer (ICP–AES)

4.11 Recirculating chiller

4.12 Compressed gasses, argon (minimum purity 99.996%) and nitrogen (minimum purity 99.999%)

4.13 Quartz torch, alumina injector (2.0 mm id)

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.2 Concentrated nitric acid (HNO_3) (CAS # 7697-37-2), 16 *N,* trace pure grade

5.3 Acetic acid (CH_3COOH) (CAS# 64-19-7)

5.4 Ammonium fluoride (NH_4F) (CAS# 12125-01-8)

5.5 Ammonium nitrate (NH_4NO_3) (CAS# 6484-52-2)

5.6 EDTA $(HO_2CCH_2)_2NCH_2CH_2N(CH_2CO_2H)_2$ (CAS# 60-00-4)

5.7 High purity concentrated elements, individual high purity elemental standards, commercially prepared. Individual solutions containing:

1,000 mg/L Al, Aluminum Standard
1,000 mg/L As, Arsenic Standard
1,000 mg/L B, Boron Standard
1,000 mg/L Ba, Barium Standard
1,000 mg/L Bi, Bismuth Standard
1,000 mg/L Ca, Calcium standard
1,000 mg/L Cd, Cadmium Standard
1,000 mg/L Co, Cobalt Standard
1,000 mg/L Cr, Chromium Standard
1,000 mg/L Cu, Copper Standard
1,000 mg/L Fe, Iron Standard
1,000 mg/L K, Potassium Standard
1,000 mg/L Mg, Magnesium Standard
1,000 mg/L Mn, Manganese Standard
1,000 mg/L Mo, Molybdenum Standard
1,000 mg/L Na, Sodium Standard
1,000 mg/L Ni, Nickel Standard
1,000 mg/L P, Phosphorus Standard
1,000 mg/L Pb, Lead Standard
1,000 mg/L Se, Selenium Standard
1,000 mg/L Si, Silicon Standard
1,000 mg/L Sr, Strontium Standard
1,000 mg/L Zn, Zinc Standard

5.8 Mehlich No. 3 stock solution (Reagent A)

Components: Ammonium fluoride (NH_4F), EDTA $(HO_2CCH_2)_2NCH_2CH_2N(CH_2CO_2H)_2$, RODI water

- To a 1-L glass volumetric flask, add the following in order:
  - 600 mL of RODI water
  - 55.56 g of NH_4F
  - 29.23 g of EDTA (FW 292.24)
  - Fill to volume with RODI water.
- Invert to mix.

5.9 Mehlich No. 3 working solution (Reagent A1)

Components: Nitric acid (HNO_3), ammonium nitrate (NH_4NO_3), acetic acid (CH3COOH), Reagent A, RODI water

- Prepare solution in two parts.

- To a 100-mL glass volumetric flask, prepare a 10% v/v nitric acid solution:
  - 100 mL of RODI water
  - 10 mL of concentrated (70%) HNO_3
- Invert to mix.
- To a 10-L polypropylene carboy, add the following in order:
  - 5 L of RODI water
  - 200.1 g of ammonium nitrate
  - 100 mL of Reagent A
  - 115 mL of acetic acid
  - 82 mL of the 10% nitric acid solution
  - Fill to volume with RODI water.
- Swirl to mix thoroughly.

5.10 Elemental standards (Reagents B1-B4)

Components: High purity elements 1,000 mg/L: Al, Ca, Cr, Fe, K, and Mg; Reagent A1

- Preparation: Refer to table 4D6b–1 for mixing instructions.
- Standards are mixed in serial dilution.
- Lesser concentrations are mixed by serial dilution.
- Invert to thoroughly mix.
- Store in a polyethylene container in a refrigerator.
- Make fresh weekly.
- Refer to table 4D6b–2 for final elemental concentrations of solutions.

5.10.1 Reagent B4 (High)

- To a 250-mL glass volumetric, add the following in order:
  - 25 mL of 1,000 mg/L Ca, Calcium Standard
  - 25 mL of 1,000 mg/L Mg, Magnesium Standard
  - 25 mL of 1,000 mg/L Al, Aluminum Standard
  - 5 mL of 1,000 mg/L K, Potassium Standard
  - 10 mL of 1,000 mg/L Fe, Iron Standard
  - 5 mL of 1,000 mg/L Cr, Chromium Standard
  - Fill to volume with Reagent A1.
- Invert to mix.

5.10.2 Reagent B3 (Medium)

- To a 100-mL glass volumetric, add the following in order:
  - 50 mL of Reagent B4
  - Fill to volume with Reagent A1.
- Invert to mix.

5.10.3 Reagent B2 (Low)

- To a 100-mL glass volumetric, add the following in order:
  - 10 mL of Reagent B3
  - Fill to volume with Reagent A1.
- Invert to mix.

5.10.4 Reagent B1 (Very Low)

- To a 100-mL glass volumetric, add the following in order:
  - 10 mL of Reagent B2
  - Fill to volume with Reagent A1.
- Invert to mix.

Table 4D6b–1.—Preparation of Elemental Calibration and Verification Standard Solutions B1–B4.

Element or Reagent	B4 High	B3 Medium	B2 Low	B1 Very Low
	(mL)	*(mL)*	*(mL)*	*(mL)*
	250-mL volumetric	*100-mL volumetrics*		
Ca	25	50 mL of Reagent B4	10 mL of Reagent B3	10 mL of Reagent B2
Mg	25			
Al	25			
K	5			
Fe	10			
Cr	5			
Reagent A1	Bring to volume with Reagent A1			

Table 4D6b–2.—Concentrations of Standard Solutions B1–B4.

Element	B4 High	B3 Medium	B2 Low	B1 Very Low
	(mg L^{-1})	*(mg L^{-1})*	*(mg L^{-1})*	*(mg L^{-1})*
Ca	100	50	5	0.5
Mg	100	50	5	0.5
Al	100	50	5	0.5
K	20	10	1	0.1
Fe	40	20	2	0.2
Cr	10	5	0.5	0.5

5.11 Na single element standard solutions (Reagents C1 and C2)

Components: High purity elements, 1,000 mg/L, Na; Reagent A1

- Preparation: Refer to table 4D6b–3 for mixing instructions.
- Invert to thoroughly mix.
- Store in a polyethylene container in a refrigerator.
- Make fresh weekly.
- Refer to table 4D6b–5 for final elemental concentrations of solutions.

5.11.1 Reagent C2 (High)

- To a 250-mL glass volumetric, add the following in order:
  - 25 mL of 1,000 mg/L Na, Sodium Standard
  - Fill to volume with Reagent A1.
- Invert to mix.

5.11.2 Reagent C1 (Medium)

- To a 100-mL glass volumetric, add the following in order:
  - 50 mL of Reagent C2
  - Fill to volume with Reagent A1.
- Invert to mix.

Table 4D6b–3.—Preparation of Sodium Calibration and Verification Standard Solutions C1 and C2.

Element	C2 (High Na)	C1 (Medium Na)
Na	In a 250-mL volumetric: • 25 mL of high purity elemental standard • Bring to volume with Reagent A1	In a 100-mL volumetric: • 50 mL of Reagent C2 • Bring to volume with Reagent A1

5.12 Si single element standard solutions (Reagents D1 and D2)

Components: High purity elements, 1,000 mg/L, Si; Reagent A1

- Preparation: Refer to table 4D6b–4 for mixing instructions.
- Invert to thoroughly mix.
- Store in a polyethylene container in a refrigerator.
- Make fresh weekly.
- Refer to table 4D6b–5 for final elemental concentrations of solutions.

5.12.1 Reagent D2 (High)

- To a 250-mL glass volumetric, add the following in order:

- 25 mL of 1,000 mg/L Si, Silicon Standard
- Fill to volume with Reagent A1.

- Invert to mix.

5.12.2 Reagent D1 (Medium)

- To a 100-mL glass volumetric, add the following in order:
  - 50 mL of Reagent D2
  - Fill to volume with Reagent A1.
- Invert to mix.

Table 4D6b–4.—Preparation of Silicone Calibration and Verification Standard Solutions D1 and D2.

Element	D2 (High Si)	D1 (Medium Si)
Si	In a 250-mL volumetric: • 25 mL of high purity elemental standard • Bring to volume with Reagent A1	In a 100-mL volumetric: • 50 mL of Reagent D1 • Bring to volume with Reagent A1

Table 4D6b–5.—Concentrations of Sodium and Silicone Calibration and Verification Standard Solutions, C1 C2, D1, D2.

Element	C2 (High Na)	C1 (Medium Na)	D2 (High Si)	D1 (Medium Si)
	(mg L^{-1})	*(mg L^{-1})*	*(mg L^{-1})*	*(mg L^{-1})*
Na	100	50	---	---
Si	---	---	100	50

5.13 Elemental calibration and verification standards solutions (Reagents E1–E3)

Components: High purity elements, 1,000 mg/L: P, As, Ba, Cd, Co, Cu, Mn, Mo, Ni, Pb, Se, Sr, and Zn; Reagent A1

- Refer to table 4D6b–6 for mixing instructions.
- Lesser concentrations are mixed by serial dilution.
- Prepare in 100-mL volumetrics.
- Invert to thoroughly mix.
- Store in a polyethylene container in a refrigerator.

- Make fresh weekly.
- Refer to table 4D6b–7 for concentrations.

5.13.1 Reagent E3 (High)

- To a 100-mL glass volumetric, add the following in order:
  - 25 mL of 1,000 mg/L P, Phosphorus Standard
  - 1 mL of 1,000 mg/L As, Arsenic Standard
  - 1 mL of 1,000 mg/L Ba, Barium Standard
  - 1 mL of 1,000 mg/L Cd, Cadmium Standard
  - 1 mL of 1,000 mg/L Co, Cobalt Standard
  - 1 mL of 1,000 mg/L Cu, Copper Standard
  - 1 mL of 1,000 mg/L Mn, Manganese Standard
  - 1 mL of 1,000 mg/L Mo, Molybdenum Standard
  - 1 mL of 1,000 mg/L Ni, Nickel Standard
  - 1 mL of 1,000 mg/L Pb, Lead Standard
  - 1 mL of 1,000 mg/L Se, Selenium Standard
  - 1 mL of 1,000 mg/L Sr, Strontium Standard
  - 1 mL of 1,000 mg/L Zn, Zinc Standard
  - Fill to volume with Reagent A1.
- Invert to mix.

5.13.2 Reagent E2 (Medium)

- To a 100-mL glass volumetric, add the following in order:
  - 10 mL of Reagent E3
  - Fill to volume with Reagent A1.
- Invert to mix.

5.13.3 Reagent E1 (Low)

- To a 100-mL glass volumetric, add the following in order:
  - 10 mL of Reagent E2
  - Fill to volume with Reagent A1.
- Invert to mix.

Table 4D6b–6.—Preparation of Elemental Calibration and Verification Standards, Solutions E1–E3. (Prepare in 100-mL volumetrics.)

Element or Reagent	E3 High	E2 Medium	E1 Low
	(mL)	*(mL)*	*(mL)*
P	25	10 mL of E3	10 mL of E2
As	1		
Ba	1		
Cd	1		
Co	1		
Cu	1		
Mn	1		
Mo	1		
Ni	1		
Pb	1		
Se	1		
Sr	1		
Zn	1		
Reagent A1	Bring to volume with Reagent A1		

Table 4D6b–7.—Concentrations of Elemental Calibration and Verification Standards, Solutions E1–E3.

Reagents E1–E3: Elemental Concentrations			
Element	**E3 (High)**	**E2 (Medium)**	**E1 (Low)**
	(mg L^{-1})	*(mg L^{-1})*	*(mg L^{-1})*
P	250	25	2.5
As	10	1	0.1
Ba	10	1	0.1
Cd	10	1	0.1
Co	10	1	0.1
Cu	10	1	0.1
Mn	10	1	0.1

Table 4D6b–7.—Continued

Reagents E1–E3: Elemental Concentrations			
Element	**E3 (High)**	**E2 (Medium)**	**E1 (Low)**
Mo	10	1	0.1
Ni	10	1	0.1
Pb	10	1	0.1
Se	10	1	0.1
Sr	10	1	0.1
Zn	10	1	0.1

5.14 Blanks are composed of Reagent A1 in a 100-mL volumetric. Store in a polyethylene container in a refrigerator. Make fresh weekly.

5.15 Reagents B1–B4 and E1–E3 concentrations are referenced for Atomic Emission Spectrometry (AES) checks during analysis and data processing.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids. Dispense concentrated acids and bases in fume hood.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Weigh 2.5 g of <2-mm or fine-grind, air-dry soil to the nearest mg into a 50-mL centrifuge tube. If sample is moist, weigh enough soil to achieve ≈2.5 g of air-dry soil.

8.2 Dispense 25.0 mL of extracting solution to the tube.

8.3 Transfer the sample to the shaker. Shake for 5 min at 200 oscillations min^{-1} at room temperature (20 ±2 °C).

8.4 Remove the sample from the shaker. Centrifuge at 2,000 rpm for 10 min, decant, filter, and collect extract in receiving cups. If extracts are not to be

analyzed immediately after collection, then store samples at 4 °C. Analyze samples within 72 h.

8.5 ICP–AES Set-up and Operation

8.5.1 Use the ICP–AES in radial mode to analyze elements. Use ultrasonic nebulization of sample. No initial dilutions of samples are necessary prior to analysis. Perform instrument checks (Hg alignment; BEC and %RSD of 1 mg L^{-1} Mn solution) prior to analysis as discussed in operation manual of instrument. Check instrument alignment and gas pressures to obtain optimum readings with maximum signal to noise ratio. Analyses are generally performed at two or more wavelengths for each element. The selected wavelengths are as follows:

Table 4D6b–8.—Reporting and Reference Elemental Wavelengths.

Element	Wavelength	
	Reporting	Reference
	(nm)	*(nm)*
Al	308.215	396.153
Fe	259.939	238.204
Ca	315.887	317.932
Mg	280.271	279.075
Na	589.592	588.995
K	766.490	---
Mn	260.570	257.608
P	178.221	214.915
As	193.69	---
Ba	233.525	455.507
Cd	226.501	214.435
Co	228.614	---
Cr	267.710	205.558
Cu	324.753	327.396
Ni	232.003	231.604,
Mo	202.31	---
Pb	220.353	216.998
Se	196.026	---
Si	212.412	---
Sr	460.733	---
Zn	213.857	206.197

8.5.2 Use Reagent A1 to dilute those samples with concentrations greater than the high standard. Rerun all elements and use only the data needed from the diluted analysis. Analyzed values lower than the detection limits are reported as “ND” or non-detected.

8.5.3 Establish detection limits using Reagent A1. The instrumental detection limits are calculated by using 3 times the standard deviation of 10 readings of the blank. These values establish the lower detection limits for each element. The digested fraction needs to be identified with each sample.

9. Calculations

9.1 The calculation of mg kg^{-1} of an element in the soil from mg L^{-1} in solution is as follows:

$$\text{Analyte concentration in soil (mg kg}^{-1}\text{)} = (A \times B \times C \times R \times 1{,}000) / E$$

A = Sample extract reading (mg L^{-1})

B = Extract volume (L)

C = Dilution, if performed

R = Air-dry/oven-dry ratio (method 3D1) or field-moist/oven-dry ratio

1,000 = Conversion factor to kg-basis

E = Sample weight (g)

9.2 Data are reported to the nearest 0.1 mg kg^{-1}.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist for final review.

10.6 Compare individual results to method detection limits (MDL) and practical quantitation limits (PQL) before reporting analysis results.

10.6.1 Report numerical values for results that are above the PQL.

10.6.2 Report “trace” for results that are between the MDL and PQL.

10.6.3 Report “non-detect” for results that are below the MDL.

MDL and PQL in Reporting Units

Analyte	MDL	PQL
	(mg kg^{-1} of oven-dried soil)	*(mg kg^{-1} of oven-dried soil)*

11. References

Elrashidi, M.A., M.D. Mays, and C.W. Lee. 2003. Assessment of Mehlich3 and ammonium bicarbonate DTPA extraction for simultaneous measurement of fifteen elements in soils. Commun. Soil Sci. and Plant Anal. 34:2817–2838.

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Soil Test Analyses (4D)
Citric Acid Soluble (4D7)
UV-Visible Spectrophotometer, Dual-Beam (4D7a)
Phosphorus (4D7a1)
Air-Dry or Field-Moist, <2 mm (4D7a1a-b1)

1. Introduction to Citric Acid soluble Phosphorus

Citric acid soluble phosphoric anhydride (P_2O_5) is a helpful test in identifying anthropic epipedons and those with archeological significance. "Anthropic epipedons may have an elevated phosphorus content from human additions of food debris (e.g., bones), compost, or manure, although a precise value is not required" (Soil Taxonomy, 2014).

2. Scope and Field of Application

The procedure used by the KSSL is based on the method developed by Dyer (1894).

Phosphorus (citrate-soluble) and phosphorus (citrate-insoluble) are recognized methods in the Official Methods of Analysis by the Association of Analytical Communities International (960.01 and 963.03; AOAC, 2000). The AOAC citrate-soluble P method considers the recovery of phosphoric anhydride sources such as agricultural fertilizers as available phosphorus, even though the Association of American Plant Food Control Officials does not recognize such soil additives as a source of available phosphorus.

3. Principle

The calcium carbonate equivalent (CCE) must be determined prior to citric-acid-soluble phosphorus analysis. Sufficient citric acid is added to the sample to neutralize the $CaCO_3$ and bring the solution concentration of citric acid to 1%. A 1:10 ratio of soil to solution is maintained for all samples. The slurry is shaken, a colorimetric phosphorus indicator is added, and absorbance is read using a UV–VIS spectrophotometer at 660 nm. Data are reported as mg P_2O_5 kg^{-1} soil.

3.1 Interferences

Unreacted carbonates interfere with the extraction of citrate-soluble phosphorus.

A high citrate level in a sample may interfere with the molybdate blue test. If this occurs, the method can be modified by evaporating the extract and ashing in a muffle furnace to destroy the citric acid.

Common chemical interferences in the determination of P_2O_5 include:

- Arsenate, fluoride, thorium, bismuth, sulfide, thiosulfate, thiocyanate, or excess molybdate.

- Concentration of Fe >1,000 ppm
- Silica and arsenic if the sample is heated

Refer to Snell and Snell (1949) and Metson (1956) for additional information on interferences in the citric acid extraction of P_2O_5.

4. Apparatus

4.1 Electronic balance, ±0.10-mg sensitivity

4.2 Mechanical reciprocating shaker, 200 oscillations min^{-1}, 1½ inch strokes

4.3 Centrifuge tubes, 50-mL, disposable, polyethylene

4.4 Bottles, with gas release caps

4.5 Filter paper, Whatman 42 or equivalent, 150-mm

4.6 Funnel, 60° angle, long-stem, 50-mm diameter

4.7 Pipettes, electronic digital, 1,000-µL and 10-mL, with tips, 1,000-µL and 10-mL

4.8 Dispenser, 30-mL to 10-mL

4.9 Cuvettes, plastic, 4.5-mL, 1-cm light path

4.10 Spectrophotometer

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water

5.2 Concentrated hydrochloric acid (HCl) (CAS# 7647-01-0), 12 *N*

5.3 Citric acid, anhydrous ($C_6H_8O_7$), (CAS# 77-92-9)

5.4 Ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}•4H_2O$] (CAS# 13106-76-8)

5.5 Stannous chloride ($SnCl_2•2H_2O$) (CAS# 10025-69-1)

5.6 Anhydrous potassium dihydrogen phosphate, monobasic (KH_2PO_4) (CAS# 7778-77-0)

5.7 Hydrochloric acid solution, 2 *N*

Components: Concentrated hydrochloric acid (HCl), 12 *N;* RODI water

- To a 100-mL glass volumetric, add the following in order:
  - 50 mL of RODI water
  - 16.7 mL of concentrated HCl
  - Fill to volume with RODI water.
- Swirl to mix.

5.8 Citric acid solution, 10%

Components: Citric acid, anhydrous ($C_6H_8O_7$); RODI water

- To a 1-L volumetric, add the following in order:
  - 500 mL of RODI water

- 100 g of anhydrous citric acid
- Fill to volume with RODI water.

- Swirl to mix.

5.9 Citric acid solution, 1%

Components: 10% citric acid solution, RODI water

- To a 1-L volumetric, add the following in order:
  - 500 mL of RODI water
  - 100.0 mL of 10% citric acid solution
  - Fill to volume with RODI water.
- Swirl to mix.

5.10 Ammonium molybdate solution, 1.5%

Components: Ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}•4H_2O$]; concentrated hydrochloric acid (HCl), 12 *N;* RODI water

- To a 500-mL glass beaker, add the following in order:
  - 300 mL of RODI water
  - 15.0 g of ammonium molybdate tetrahydrate
- Transfer molybdate solution to a 1-L glass volumetric flask.
- To the 1-L glass volumetric flask, add the following in order:
  - 310 mL of concentrated HCl
    - Allow solution to cool.
  - Fill to volume with RODI water.
- Store in brown bottle in the dark in a refrigerator.
- Solution is stable for ≈3 months.

5.11 Stock stannous chloride solution, 0.44 *N* (Reagent A)

Components: Stannous chloride ($SnCl_2•2H_2O$), concentrated hydrochloric acid (HCl)

- To a 100-mL volumetric flask, add the following in order:
  - 80 mL of concentrated HCl, 12 *N*
  - 10 g of stannous chloride
  - Fill to volume with concentrated HCl.
- Invert to mix thoroughly.
- Make fresh weekly.
- Store in a refrigerator.

5.12 Working stannous chloride solution (Reagent A1)

Components: Reagent A, RODI water

- To a 100-mL flask, add the following in order:
  - 50 mL of RODI water
  - 2 mL of Reagent A

- Fill to volume with RODI water.
- Invert to mix.
- Use immediately; solution is only stable for ≈4 h.

5.13 Stock standard P_2O_5 solution, 250 mg L^{-1} P (Reagent B)

Components: Anhydrous potassium dihydrogen phosphate, monobasic (KH_2PO_4); hydrochloric acid solution, 2 *N* (HCl); RODI water

- To a 1-L volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 1.099 g of anhydrous potassium phosphate (dried for 2 h at 110 °C)
  - 5 mL of 2 *N* HCl solution
  - Fill to volume with RODI water.
- Invert to mix.
- Store in polyethylene bottles.
- Make fresh weekly.
- Store in a refrigerator.

5.14 Working stock standard P_2O_5 solution, 2.5 mg L^{-1} P (Reagent B1)

Components: Reagent B, RODI water

- To a 1-L volumetric flask, add the following in order:
  - Pipette 10.0 mL of Reagent B
  - Fill to volume with RODI water.
- Invert to mix thoroughly.
- Make fresh daily.

5.15 Standard P_2O_5 calibration solutions

Components: 1% citric acid solution, ammonium molybdate solution, Reagent A1, Reagent B1, RODI water

- Refer to table 4D7a–1 for dilutions and table 4D7a–2 for concentrations.
- Fill to 25-mL volume with RODI water.
- Invert to mix thoroughly.
- Allow to equilibrate to room temperature before use.
- Prepare fresh weekly.
- Store in the refrigerator.

5.15.1 P-1

- In a 50-mL disposable centrifuge tube, add the following in order:
  - 1 mL of 1% citric acid solution
  - 4 mL of ammonium molybdate solution

- 2 mL of Reagent A1
- 1 mL of Reagent B1
- Fill to 25-mL volume with RODI water.

- Invert to mix.

5.15.2 P-2

- In a 50-mL disposable centrifuge tube, add the following in order:
  - 1 mL of 1% citric acid solution
  - 4 mL of ammonium molybdate solution
  - 2 mL of Reagent A1
  - 2 mL of Reagent B1
  - Fill to 25-mL volume with RODI water.
- Invert to mix.

5.15.3 P-3

- In a 50-mL disposable centrifuge tube, add the following in order:
  - 1 mL of 1% citric acid solution
  - 4 mL of ammonium molybdate solution
  - 2 mL of Reagent A1
  - 3 mL of Reagent B1
  - Fill to 25-mL volume with RODI water.
- Invert to mix.

5.15.4 P-4

- In a 50-mL disposable centrifuge tube, add the following in order:
  - 1 mL of 1% citric acid solution
  - 4 mL of ammonium molybdate solution
  - 2 mL of Reagent A1
  - 4 mL of Reagent B1
  - Fill to 25-mL volume with RODI water.
- Invert to mix.

5.15.5 P-5

- In a 50-mL disposable centrifuge tube, add the following in order:
  - 1 mL of 1% citric acid solution
  - 4 mL of ammonium molybdate solution
  - 2 mL of Reagent A1
  - 5 mL of Reagent B1

- Fill to 25-mL volume with RODI water.
- Invert to mix.

5.15.6 Blank

- In a 50-mL disposable centrifuge tube, add the following in order:
  - 1 mL of 1% citric acid solution
  - 4 mL of ammonium molybdate solution
  - 2 mL of Reagent A1
  - Fill to 25-mL volume with RODI water.
- Invert to mix.

Table 4D7a–1.—Preparation of Standard P_2O_5 Solutions P-1–P-5. (Prepare in disposable 50-mL centrifuge tubes.)

Reagent	P-1	P-2	P-3	P-4	P-5	Blank
	(mL)	*(mL)*	*(mL)*	*(mL)*	*(mL)*	*(mL)*
1% citric acid solution	1.0	1.0	1.0	1.0	1.0	1.0
Ammonium molybdate solution	4.0	4.0	4.0	4.0	4.0	4.0
Reagent A1	2.0	2.0	2.0	2.0	2.0	2.0
Reagent B1	1.0	2.0	3.0	4.0	5.0	---
RODI water	Dilute with RODI water to 25-mL volume					

Table 4D7a–2.—Concentrations of Standard P2O5 Solutions P-1–P-5.

Reagent	P-1	P-2	P-3	P-4	P-5	Blank
	(mg/L)	*(mg/L)*	*(mg/L)*	*(mg/L)*	*(mg/L)*	*(mg/L)*
Phosphorus	0.10	0.20	0.30	0.40	0.50	---

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Weigh 3 g of <2-mm or fine-grind, air-dry soil to the nearest mg into a bottle with gas release tops. If sample is moist, weigh enough soil to achieve ≈3 g of air-dry soil.

8.2 If the soil contains free $CaCO_3$, refer to table 4D7a–3 to determine the amount of 10% citric acid solution required to neutralize the $CaCO_3$.

8.3 If the soil does not contain free carbonates, add required volume of 10% citric acid solution into a graduated cylinder and bring to a volume of 30 mL with RODI water. Add this solution to the soil sample.

8.4 Place the bottle in a mechanical shaker and shake for 6 h at 200 oscillations min^{-1} at room temperature (20 ±2 °C) to dissolve and neutralize the $CaCO_3$.

8.5 If the soil contains no free $CaCO_3$, add 30 mL of 1% citric acid solution to the sample.

8.6 Cap the bottles, place in a mechanical shaker, and shake for 16 h at 200 oscillations min^{-1} at room temperature (20 ±2 °C).

8.7 Remove the sample from shaker and filter. Collect extract. If extracts are not to be analyzed immediately after collection, store samples at 4 °C. Analyze samples within 72 h.

8.8 In condiment cups, add the following in order:

- 1 mL of sample extract
- 4 mL of ammonium molybdate solution
- 2 mL of Reagent A1
- Fill to 25-mL volume with RODI water.
    - Swirl to mix.
    - Allow to stand 20 minutes for color development.

8.9 Transfer sample extracts and standards to cuvettes.

8.10 Set the spectrophotometer to read at 660 nm. Autozero with calibration blank.

8.11 Calibrate the instrument using calibration standards from table 4D7a–1.

- Recalibrate every 24 samples.
- If the calibration curve has <0.99 linearity, recalibration is required.

8.12 If samples are outside calibration range, dilute sample extracts with 1% or 10% citric acid extracting solution and re-analyze.

8.13 Record results to the nearest 0.01 unit for the sample extract and standard solutions.

Table 4D7a–3.—Percent Calcium Carbonate in Sample and Volume of Citric Acid Required. (Prepare in flask. Final volume should be 30 mL.)

$CaCO_3$	10% Citric Acid Solution	RODI	$CaCO_3$	10% Citric Acid Solution	RODI
(%)	*(mL)*	*(mL)*	*(%)*	*(mL)*	*(mL)*
0	3.0	27.0	32	15.3	14.7
1	3.4	26.6	33	15.7	14.3
2	3.8	26.2	34	16.1	13.9
3	4.2	25.8	35	16.4	13.6
4	4.5	25.5	36	16.8	13.2
5	4.9	25.1	37	17.2	12.8
6	5.3	24.7	38	17.6	12.4
7	5.7	24.3	39	18.0	12.0
8	6.1	23.9	40	18.4	11.6
9	6.5	23.5	41	18.7	11.3
10	6.8	23.2	42	19.1	10.9
11	7.2	22.8	43	19.5	10.5
12	7.6	22.4	44	19.9	10.1
13	8.0	22.0	45	20.3	9.7
14	8.4	21.6	46	20.7	9.3
15	8.8	21.2	47	21.0	9.0
16	9.1	20.9	48	21.4	8.6
17	9.5	20.5	49	21.8	8.2
18	9.9	20.1	50	22.2	7.8
19	10.3	19.7	51	22.6	7.4
20	10.7	19.3	52	23.0	7.0
21	11.1	18.9	53	23.3	6.7
22	11.4	18.6	54	23.7	6.3
23	11.8	18.2	55	24.1	5.9
24	12.2	17.8	56	24.5	5.5
25	12.6	17.4	57	24.9	5.1
26	13.0	17.0	58	25.3	4.7
27	13.4	16.6	59	25.6	4.4
28	13.7	16.3	60	26.0	4.0
29	14.1	15.9	61	26.4	3.6
30	14.5	15.5	62	26.8	3.2
31	14.9	15.1	63	27.2	2.8

9. Calculations

9.1 Convert the extract P_2O_5 (mg L^{-1}) to soil P_2O_5 (mg kg^{-1}):

$$\text{Soil } P_2O_5 \text{ (mg kg}^{-1}) = (A \times B \times C1 \times C2 \times R \times 1{,}000 \times 2.29) / E$$

A = P_2O_5 in sample extract (mg L^{-1})

B = Extract volume (L)

C1 = Automatic dilution

C2 = Dilution, if necessary

R = Air-dry/oven-dry ratio (method 3D1) or field-moist/oven-dry ratio (method 3D2)

1,000 = Conversion factor to kg-basis

2.29 = Conversion factor P to P_2O_5

E = Sample weight (g)

9.2 Report the 1% citrate acid extractable P_2O_5 in mg kg^{-1} to nearest whole number.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

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Soil Test Analyses (4D)
New Zealand P Retention (4D8)
UV-Visible Spectrophotometer, Dual-Beam (4D8a)
Phosphorus (4D8a1)
Air-Dry or Field-Moist, <2 mm (4D8a1a-b1)

1. Introduction to New Zealand Phosphorus

New Zealand phosphorus retention is the gravimetric percent of phosphorus removed from a solution by equilibration with a sample. High phosphorus retention (>85 %) is a taxonomic criterion for andic soil properties (Soil Survey Staff, 2010).

2. Scope and Field of Application

New Zealand phosphorus retention, also referred to as P adsorption, sorption, or fixation, is a taxonomic criterion for andic soil properties (Soil Survey Staff, 2014) and for identification of active Al in amorphous clay minerals that synthesize in rapidly weathering volcanic glass (Van Wambeke, 1992). This method is not appropriate for analyzing O horizons.

3. Principle

A solution containing 1,000 mg/L $^{-1}$ phosphorus is added to a sample and shaken for 24 hours. The mixture is centrifuged, and a sample aliquot is treated with a color reagent. The color is allowed to develop, and absorbance of the solution is read at 466 nm. The absorbance of the sample correlates to concentration of non-adsorbed P remaining in solution. Results are reported as percent P retained.

3.1 Interferences

There are no significant interferences that affect the P retention measurement.

4. Apparatus

4.1 Electronic balance, ±1.0-mg sensitivity

4.2 Mechanical reciprocating shaker, 100 oscillations min^{-1}, 1½-in strokes

4.3 Centrifuge, capable of 2,000 rpm

4.4 Centrifuge tubes, 50-mL, disposable, polyethylene

4.5 Cups, plastic

4.6 Pipettes, electronic digital, 1,000-µL and 10-mL, with tips, 1,000-µL and 10-mL

4.7 Dispenser, 30 mL–10 mL capability

4.8 Filter paper, Whatman 42 or equivalent, 150-mm

4.9 Cuvettes, plastic, 4.5-mL, 1-cm path

4.10 Spectrophotometer

4.11 Hot plate with magnetic stir bar

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.2 Superfloc 16, 0.2%, 2 g L^{-1} in RODI water

5.3 Concentrated nitric acid (HNO_3), 16 *N,* trace pure grade (CAS # 7697-37-2)

5.4 Anhydrous potassium dihydrogen phosphate, monobasic (KH_2PO_4) (CAS# 7778-77-0)

5.5 Sodium acetate trihydrate ($CH_3COONa•3H_2O$) (CAS# 6131-90-4)

5.6 Glacial acetic acid ($C_2H_4O_2$) (CAS# 64-19-7)

5.7 Ammonium metavanadate (NH_4VO_3) (CAS# 7803-55-6)

5.8 Ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}•4H_2O$] (CAS# 13106-76-8)

5.9 P retention solution, 1,000 mg L^{-1} phosphorus (Reagent A)

Components: Anhydrous potassium dihydrogen phosphate, monobasic (KH_2PO_4); sodium acetate trihydrate ($CH_3COONa•3H_2O$); glacial acetic acid ($C_2H_4O_2$); RODI water

- In a 10-L polyethylene carboy, add the following in order:
  - 6 L of RODI water
  - 35.2 g of KH_2PO_4 (dried for 2 h at 110 °C)
  - 217.6 g of sodium acetate trihydrate ($CH_3COONa•3H_2O$)
  - 92 mL of glacial acetic acid
  - Fill to 8 L with RODI water.
- The solution pH should range between 4.55 and 4.65.

5.10 Nitric acid solution

Components: Concentrated nitric acid (HNO_3), RODI water

- In a 2-L glass volumetric flask, add the following in order:
  - 1,000 mL of RODI water.
  - 200 mL of concentrated HNO_3
  - Fill to volume with RODI water.

5.11 Ammonium metavanadate solution

Components: Ammonium metavanadate (NH_4VO_3), RODI water

- In a 2-L glass volumetric flask, add the following in order:
  - 500 mL of RODI water
    - Bring to boil.

  - 1.6 g of NH_4VO
  - Fill to volume with RODI water.
- Allow the solution to cool to room temperature.

5.12 Ammonium molybdate solution

Components: Ammonium molybdate tetrahydrate $(NH_4)_6Mo_7O_{24}•4H_2O$, RODI water

- In a 2-L glass volumetric flask, add the following in order:
  - 1,000 mL of RODI water
    - Heat RODI to 50 °C.
  - 32 g of $(NH_4)_6Mo_7O_{24}•4H_2O$
  - Fill to volume with RODI water.
- Allow the solution to cool to room temperature.

5.13 Diluent for standard P calibration solutions (Reagent B)

Components: Sodium acetate trihydrate $(CH_3COONa•3H_2O)$, glacial acetic acid $(C_2H_4O_2)$, RODI water

- In a 2-L glass volumetric flask, add the following in order:
  - 54.4 g of sodium acetate trihydrate
  - 23 mL of glacial acetic acid
  - Fill to volume with RODI water.
- Invert to mix thoroughly.

5.14 Nitric vanadomolybdate acid solution (Reagent C)

Components: Nitric acid solution, ammonium metavanadate solution, ammonium molybdate solution

Note: Do not skip or transpose steps when preparing Reagent C.

- In a 10-L glass carboy, add the following in order:
  - 2 L of nitric acid solution
  - 2 L of ammonium metavanadate solution
  - 2 L of ammonium molybdate solution
- Swirl carboy to mix.

5.15 Standard P calibration solutions

Components: Reagent A, Reagent B

- Refer to table 4D8a–1 for mixing instructions and concentrations.
- Invert to mix thoroughly.
- Allow to equilibrate to room temperature before use.
- Make fresh as needed.
- Store in the refrigerator.
- Table 4D8a–2 lists solution concentrations.

5.15.1 NZ-1

- In a 100-mL glass volumetric flask, add the following:
  - 100 mL of Reagent A

5.15.2 NZ-2

- In a 100-mL glass volumetric flask, add the following in order:
  - 80 mL of Reagent A
  - 20 mL of Reagent B
- Invert to mix thoroughly.

5.15.3 NZ-3

- In a 100-mL glass volumetric flask, add the following in order:
  - 60 mL of Reagent A
  - 40 mL of Reagent B
- Invert to mix thoroughly.

5.15.4 NZ-4

- In a 100-mL glass volumetric flask, add the following in order:
  - 40 mL of Reagent A
  - 60 mL of Reagent B
- Invert to mix thoroughly.

5.15.5 NZ-5

- In a 100-mL glass volumetric flask, add the following in order:
  - 20 mL of Reagent A
  - 80 mL of Reagent B
- Invert to mix thoroughly.

5.15.6 NZ-6

- In a 100-mL glass volumetric flask, add the following:
  - 100 mL of Reagent B

Table 4D8a–1.—Preparation of Phosphorus Calibration Standards NZ-1–NZ-6. (Prepare in 100-mL glass volumetric flasks.)

Standard	Reagent A	Reagent B
	(mL)	*(mL)*
NZ-1	100	0
NZ-2	80	20
NZ-3	60	40
NZ-4	40	60
NZ-5	20	80
NZ-6	0	100

Table 4D8a–2.—Concentrations of Phosphorus Calibration Standards NZ-1–NZ-6.

Reagents	Phosphorus Concentration	Phosphorus Retention
	(mg L^{-1})	*(%)*
NZ-1	1,000	0
NZ-2	800	20
NZ-3	600	40
NZ-4	400	60
NZ-5	200	80
NZ-6	0	100

5.16 Quality Control: A KSSL soil standard and a blank are routinely included in every batch of 24 samples.

6. Health and Safety

Warning.—Many metal salts are extremely toxic and may be fatal if ingested.

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids. Restrict the use of concentrated HNO_3 to a fume hood.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Weigh 5 g of <2-mm, air-dry soil to the nearest mg into a 50-mL centrifuge tube. If sample is moist, weigh enough soil to achieve ≈5 g of air-dry soil.

8.2 Add 25.0 mL of Reagent A to centrifuge tube.

8.3 Shake for 24 h at 100 oscillations min^{-1} at room temperature (20 ±2 °C).

8.4 After shaking, add ≈3 drops of Superfloc to each tube.

8.5 Centrifuge at 2,000 rpm for 15 min, decant, filter, and collect extract in receiving cup.

- If extracts are not to be analyzed immediately after collection, then store samples at 4 °C.
- Analyze samples within 72 h.

8.6 Dilute samples and calibration standards at 1:20 (0.5 mL of sample to 9.5 mL of Reagent C).

8.7 Allow color to develop for 30 minutes.

8.8 Set spectrophotometer to read at 466 nm.

8.9 Calibrate the instrument using calibration standards from table 4D8a–1.

- Recalibrate every 24 samples.
- If the calibration curve has <0.99 linearity, recalibration is required.

8.10 Record results to the nearest whole percent.

9. Calculations

9.1 Determine % P retention

$$\% \text{ P retention} = 100r - [(A/1{,}000)100]$$

100r = 0% retention by soil

1,000 = total P in retention solution

100 = conversion to %

A = phosphorus measured in the sample extract.

9.2 Record results to the nearest whole percent.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

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CALCIUM CARBONATE AND GYPSUM (4E)

Calcium Carbonate Equivalent (4E)

3 *N* HCl Treatment (4E1)

CO_2 Analysis (4E1a)

Manometer, Electronic (4E1a1)

Calcium Carbonate Equivalent (4E1a1a1)

Air-Dry, <2-mm or <20-mm (4E1a1a1a1-2)

1. Introduction to Calcium Carbonate Equivalent

The term “calcium carbonate equivalent” (CCE) is defined as the acid-neutralizing capacity of an agricultural liming material expressed as a weight percentage of calcium carbonate ($CaCO_3$).

To measure CCE, samples are weighed into glass jars and a gelatin capsule containing aqueous hydrochloric acid (HCl) is added to the jar. The jar is sealed by a lid fitted with a rubber septum. As the gelatin capsule dissolves, HCl (aq) is released and reacts with carbonate in the sample, evolving carbon dioxide (CO_2) gas. The pressure of CO_2 in the headspace of the jar is measured using a manometer. The pressure of CO_2 is directly related to the mass of $CaCO_3$. A calibration is used to calculate percent CCE on an oven-dry soil basis.

2. Scope and Field of Application

The quantity and distribution of calcium carbonate ($CaCO_3$) in the soil profile are important factors affecting soil fertility, chemistry, and physical properties. Calcium carbonate interacts with and can influence plant-available nutrients by providing a reactive surface for adsorption and precipitation reactions.

Calcium carbonate equivalent data are used in soil taxonomy as identifying criteria for mollic epipedon, calcic horizon, and Rendolls suborder. If free calcium carbonate is present, content and depth are criteria for differentiating soil series. Carbonate accumulation and translocation in the soil profile are used to identify and interpret pedogenic processes.

$CaCO_3$ equivalent is most commonly reported on the <2-mm base. However, in some soils that have hard carbonate concretions, carbonates are determined on both the <2-mm (4E1a1a1a1) and the 2 to 20-mm basis (4E1a1a1a2). The $CaCO_3$ equivalent is routinely determined by the KSSL if pH >6.95 by the $CaCl_2$ method (4C1a2a2) or if effervescence is observed after treatment with 1 *N* HCl.

3. Principle

Samples are weighed into 120-mL threaded glass jars, and a gelatin capsule containing HCl (aq) is added to the jar. The jar is sealed by a lid that is fitted with a rubber septum. The HCl (aq) reacts with carbonate in the sample, evolving carbon

dioxide (CO_2) gas. A manometer is used to measure the pressure of CO_2 in the headspace of the jar in units of millimeters mercury (mm Hg). A pre-determined calibration curve is used to relate pressure to a mass of $CaCO_3$ equivalent, which is then used to calculate percent $CaCO_3$ equivalent (CCE) on an oven-dry soil basis.

3.1 Interferences

Presence of carbonates other than calcium; e.g., magnesium, sodium, and potassium carbonates.

Septa and O-rings have a limited lifetime and eventually leak CO_2.

4. Apparatus

4.1 Electronic balance, ±1.0-mg sensitivity

4.2 Analytical balance, ±1.0-µg sensitivity

4.3 Threaded glass jars, 120-mL, 60-mm diameter, 68-mm high

4.4 Jar lids fitted with rubber septa. Note: KSSL uses custom-machined lids.

4.5 O-rings for jar lids, 3.2 x 50.8 x 57.2 mm

4.6 Flanged, rubber septa. Flange OD: 21-mm; septum top OD: 16-mm; septum bottom OD: 14-mm

4.7 Manometer, analytical grade

4.8 Hypodermic needle, 23-gauge

4.9 Mechanical oscillating shaker, 140 rpm

4.10 Desiccator

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.2 Gelatin capsule, 10-mL, size 11

5.3 Calcium carbonate ($CaCO_3$) (CAS# 471-34-1), ACS reagent grade

5.4 Glycerin (CAS# 56-81-5)

5.5 Hydrochloric acid (HCl (aq)) (CAS# 7647-01-0), concentrated, 12 *N*

5.6 **Hydrochloric acid solution, 3 *N***

Components: Hydrochloric acid (HCl (aq)), concentrated, 12 *N;* RODI water

- To a 2-L glass carboy, add the following in order:
  - 1,500 mL of RODI water
  - 500 mL of 12 *N* HCl (aq)

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate

rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Dispense and dilute concentrated HCl (aq) in fume hood. Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute acid spills.

Sample jars may break due to excessive pressure, discard jars that have hairline cracks or defects.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, sieved to <2 mm, and milled to pass an 80-mesh (177-micron) sieve. The weight of air-dry soil remains relatively constant, and biological activity is low during storage.

8. Procedure

8.1 Manometer Calibration

8.1.1 Dry reagent grade $CaCO_3$ for 2 h at 110 °C. Allow to cool to room temperature in desiccator.

8.1.2 Weigh dried $CaCO_3$ in triplicate into 120-mL glass jars as follows, recording mass to nearest 0.0001:

Jar Number	Weight of $CaCO_3$
	(g)
1–3	0.0250
4–6	0.0500
7–9	0.1000
10–12	0.2000
13–15	0.3000
16–18	0.4000
19–21	0.5000
22–24	0.7500
25–27	0.000 (blank)

8.1.3 Analyze the samples by following steps 8.2.1 through 8.2.9.

8.1.4 Correct pressure readings for the pure $CaCO_3$ samples by subtracting the average of the three pressure readings for the blanks.

8.1.5 Use linear regression to relate corrected pressure to mass of pure $CaCO_3$. No more than 2 outlier points may be rejected. Reject calibration when correlation is <99.5.

8.1.6 Use validated calibration for the analysis of actual test samples.

8.2 Calcium Carbonate Equivalent (<2-mm) Basis

8.2.1 Weigh 0.5 to 2.0 g of air-dried <2-mm sample ground to 80-mesh (<180-µm) into a sample jar based on the outcome of the 1 *N,* HCl (aq) effervescence test:

8.2.1.1 Weigh 2.0 g if effervescence is none, very slight, or slight.

8.2.1.2 Weigh 1.0 g if effervescence is strong.

8.2.1.3 Weigh 0.5 g if effervescence is violent.

8.2.2 Analyze 3 blanks and a process-control sample with every batch of 24 test samples.

8.2.3 KSSL process-control sample limits are $CaCO_3$ 8.8–10.5 %. If the process-control sample is outside the control limits, investigate and resolve process failure and then re-analyze all test samples.

8.2.4 Dispense 10 mL of 3 *N* HCl (aq) into a gelatin capsule and cap it. If HCl (aq) leaks from capsule, discard and start anew.

8.2.5 Apply a thin layer of glycerin to lid O-ring before use. Place the capsule in the jar and immediately tighten lid.

8.2.6 Before capsule dissolves, equalize pressure in jar by piercing the septa with a hypodermic needle. Remove the needle after ≈5 seconds.

8.2.7 Place jars in mechanical oscillating shaker. Shake samples for 10 minutes at 140 rpm, turn off shaker, and let jars sit stationary for 40 minutes. Then shake samples at 140 rpm for an additional 10 minutes.

8.2.8 Auto-zero the manometer.

8.2.9 Measure the pressure in each jar by piercing the septum with the hypodermic needle connected to the manometer. Record the manometer readings (mm Hg).

8.3 Calcium Carbonate Equivalent (2 to <20-mm Basis)

8.3.1 Weigh 0.5 to 2.0 g of air-dried <2-mm sample ground to 80 mesh (<180 µm) into a sample jar based on the outcome of the 1 *N,* HCl (aq) effervescence test:

8.3.1.1 Weigh 2.0 g if effervescence is none, very slight, or slight.

8.3.1.2 Weigh 1.0 g if effervescence is strong.

8.3.1.3 Weigh 0.5 g if effervescence is violent.

8.3.2 Determine carbonate content by steps 8.2.1 to 8.2.9 above.

8.3.3 The carbonate in the 2- to 20-mm and <2-mm fractions are combined and converted to a <20-mm soil basis.

9. Calculations

9.1 Determine calcium carbonate equivalent (%) of <2-mm or 2- to 20-mm fractions:

$$CCE = (C / E) * R * 100$$

C = Calcium carbonate equivalent in jar, calculated from blank corrected pressure reading, g

E = Sample weight, g

R = AD/OD

100 = Units conversion factor

9.2 Report $CaCO_3$ equivalent to nearest whole percent of oven-dry soil.

9.3 Calcium carbonate equivalent <20 mm is calculated as follows:

$$CCE\ <20\text{-mm} = (C1 \times B) + (C2 \times (1-B))$$

C1= CCE in <2-mm fraction (%), calculate using 9.1

C2= CCE in 2 to 20-mm fraction (%), calculate using 9.1

B=[<20-mm fraction (g) – 2- to 20-mm fraction (g)] / <20-mm fraction (g)

9.4 Report $CaCO_3$ equivalent to the nearest whole percent of oven-dry soil.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

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Carbonate and Gypsum (4E)
Aqueous Extraction (4E2)
Precipitation in Acetone (4E2a)
Conductivity Bridge (4E2a1)
Electrical Conductivity (4E2a1a)
Gypsum, Qualitative and Quantitative (4E2a1a1)
Air-Dry, <2 mm or <20 mm (4E2a1a1a1-2)

1. Introduction to Semi-Quantitative Gypsum, Precipitation in Acetone

Gypsum content of a soil is a criterion for gypsic and petrogypsic horizons and for mineralogical class at the family level (Soil Survey Staff, 2014). Gypsum formation by precipitation of calcium sulfate ($CaSO_4$) is typically greatest at the surface layers. Soils that have a high gypsum content at depth are typically adjacent to gypsum deposits in the lower horizons of the soil profile. Exceptions exist, and leaching may disrupt this sequence.

2. Scope and Field of Application

Gypsum is a hydrated calcium sulfate mineral. Solution and removal of gypsum can result in soil subsidence that cracks building foundations, breaks irrigation canals, and makes roads uneven. Corrosion of concrete is also associated with soil gypsum. These structural failures can occur in soils with as little as 1.5% gypsum (Nelson, 1982). Typically, gypsiferous and gypseous soils have several other water-soluble minerals associated with gypsum. The gypsum content in the soil may be used to determine if reclamation of sodic soils requires chemical amendments. Refer to Elrashidi et al. (2007) for the application of Equivalent Gypsum Content (EGC) to estimate soil subsidence in gypsiferous and gypseous soils.

Analysis for gypsum content is performed at the KSSL if the electrical conductivity of a soil sample is determined to be ≥0.50 dS cm^{-1}. Gypsum is reported on both a <2-mm and a <20-mm basis.

3. Principle

An 80-mesh fine grind soil sample is mixed with water to dissolve gypsum. Acetone is added to an aliquot of extract to precipitate the dissolved gypsum. The sample is centrifuged to consolidate solid precipitate and the acetone is decanted. Water is added to re-dissolve the gypsum precipitate into solution. The electrical conductivity (EC) of the solution is read. The EC reading is used to estimate the gypsum content in weight percent. Several calculations from this test are used as final reported values (in percent), for percent corrections, or in calculations in other methods. See the calculations section (9).

3.1 Interferences

Incomplete dissolution of gypsum is possible. Samples that are <2-mm may include larger aggregates of gypsum. The fine-grind sample preparation reduces sampling errors.

Loss of the precipitated gypsum can interfere. Use care in handling the precipitated gypsum samples.

In high concentrations, Na and K sulfates can precipitate in acetone. The concentration limits for sulfates of Na and K are approximately 50 and 10 meq L^{-1}.

AD/OD results reflect gypsum water loss during sample drying and have a corrected ratio greater than 1.00. In certain cases, a corrected AD/OD result can be <1.00. Interferences should be considered. Examples include atmospheric hydration of the sample; complimentary mineral phases, such as Bassanite or Anhydrite; overall sulfur content of the sample; dissolution of other sulfates; and incomplete dissolution of gypsum during preparation.

4. Apparatus

4.1 Electronic balance, ±1.0-mg sensitivity

4.2 Bottles, 250-mL, glass or HDPE, with caps

4.3 Mechanical reciprocating shaker, 100 cycles per minute

4.4 Polypropylene wash bottle of acetone

4.5 Pipette, electronic or adjustable-volume with 5-mL,10-mL, and 20-mL pipette tips

4.6 Centrifuge capable of 2,200 rpm

4.7 Centrifuge tubes, 15-mL, conical

4.8 Conductivity meter: conductivity cell

4.9 Filter paper, folded, 185-mm diameter, Whatman 2V or equivalent

4.10 Funnel, glass or HDPE, 90-cm

4.11 Flask, Erlenmeyer, 250-mL

4.12 Vortex mixer, mini

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Acetone (C_3H_6O) (CAS# 67-64-1), purity 99%

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Acetone is highly flammable. Do not use near open flame or electrical equipment. Use a non-sparking centrifuge. Standard laboratory equipment includes fire blankets and extinguishers for use if necessary. Follow standard laboratory safety precautions.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. Subsamples are further processed via planetary ball mill to 80 mesh; this smaller size fraction is used for the test. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 To the nearest mg, weigh 5.0 g of fine-grind, air-dry soil into a 250-mL glass bottle or HDPE bottle. If a trace of gypsum is present, a 20-g sample size may be used.

8.2 Add 100 mL of RO water to each sample. Include 1 blank per sample batch.

8.3 Cap the bottle and place on reciprocating shaker at 100 cycles per minute for 1 hour at room temperature (20 ±2 °C).

8.4 Filter the suspension. The first few mL of filtrate may be cloudy and should be discarded. Collect the clear filtrate in a 250-mL flask.

8.5 Pipette 5 mL of filtrate into 15-mL conical centrifuge tube.

8.6 Pipette 5 mL of acetone into conical centrifuge tube with filtrate.

8.7 Cap tube with a polyethylene stopper and mix with vortex mixer.

8.8 Carefully release pressure within tube by loosening the stopper.

8.9 Let stand for at least 10 min to allow the precipitate to flocculate.

8.10 Use acetone wash bottle to rinse stopper (1 or 2 mL) and inside rim of tube to prevent gypsum loss.

8.11 Remove stopper and centrifuge at 2,200 rpm for 5 minutes.

8.12 Decant and discard supernatant. Invert and drain the tube on filter paper or on towel for 5 minutes. Solid sample fraction will remain in the tube.

8.13 Pipette 5 mL of acetone to the centrifuge tube. Replace stopper. Use Vortex mixer to mix sample and bring solid fraction into the column of acetone.

8.14 Use acetone wash bottle to rinse stopper (1 or 2 mL) and inside rim of tube to prevent gypsum loss.

8.15 Remove stopper and centrifuge at 2,200 rpm for 5 minutes.

8.16 Decant and discard supernatant. Invert and drain the tube on filter paper or on towel for 5 minutes. Solid sample fraction will remain in the tube.

8.17 Pipette 10 mL of RO water to centrifuge tube.

8.18 Replace stopper. Use Vortex mixer to mix sample and bring solid fraction into the column of RO water.

8.19 Calibrate the EC meter according to manufacturer's specifications.

8.20 Flush the cell and fill with RO water. Digital reading should be 0.00.

8.21 Read the EC of dissolved precipitate by drawing up solution into cell and flushing at least once.

8.22 If the EC reading is >0.85 mmhos cm^{-1}, repeat the procedure using a smaller sample size (2.5, 1.0, 0.5, 0.25, or 0.1 g).

8.23 Steps 8.1–8.22 can be followed to determine the gypsum content of 2- to 20-mm fraction using the "SK fine grind sample processing preparation."

8.23.1 Use method 1B1b2b to aggregate and process 2- to 20-mm sample fragments to <2 mm.

8.23.2 Place a <2 mm subsample in a scintillation vial and process to 80 mesh using method 1B1b2d.

8.23.3 Follow the procedure outlined in this method (4E2a1a1a1-2) for gypsum analysis. Contact the KSSL if more information is needed.

8.24 Steps 8.1–8.22 can also be followed to determine the gypsum content of a "GP sample preparation," in which the entire sample, usually composed of qualitatively homogenous, consolidated material, is disaggregated and ground to <2 mm in size.

8.23.1 Pass the entire air-dried bulk sample through a jaw-crusher adjustable plate mill until sample is <2 mm size fraction.

8.23.2 Place a <2 mm subsample in a scintillation vial and process to 80 mesh using method 1B1b2d.

8.23.3 Follow the procedure outlined in this method (4E2a1a1a1-2) for gypsum analysis. Contact the KSSL if more information is needed.

9. Calculations

9.1 Report gypsum as a percent to the nearest whole unit.

9.2 Several calculations from this test are used as final reported values (in percent), in percent corrections, or for calculations in other methods, including:

- Corrected AD/OD
- Uncorrected gypsum
- Corrected gypsum
- <2-mm fraction
- 2–20 mm fraction
- <20-mm cumulative fraction
- GP cumulative fraction
- Factor used in saturated paste calculation, method 4F2a1

9.3 Use table 4E2a–1 to convert EC reading (mmhos/cm) to gypsum content (meq/100 g). The *y* axis denotes tenths and the x axis denotes hundredths

place decimal numbers to correspond to meq/100 g in the table. For example, an EC reading of 0.53 would indicated a gypsum content of 5.38 meq L^{-1}.

Table 4E2a–1.—Convert EC Reading (mmhos cm^{-1}) to Gypsum Content (meq L^{-1}).

EC	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.0						0.40				
0.1	0.80	0.89	0.98	1.10	1.22	1.31	1.40	1.50	1.60	1.70
0.2	1.80	1.90	2.00	2.10	2.20	2.30	2.40	2.50	2.60	2.70
0.3	2.80	2.90	3.00	3.10	3.20	3.30	3.40	3.50	3.60	3.72
0.4	3.85	3.98	4.10	4.22	4.35	4.48	4.60	4.70	4.80	4.90
0.5	5.00	5.12	5.25	5.38	5.50	5.62	5.75	5.88	6.00	6.12
0.6	6.25	6.35	6.45	6.58	6.70	6.82	6.95	7.05	7.15	7.28
0.7	7.40	7.52	7.65	7.78	7.90	8.04	8.18	8.32	8.45	8.58
0.8	8.70	8.82	8.95	9.05	9.15	9.28	9.40	9.55	9.70	9.85
0.9	10.00	10.12	10.25	10.38	10.50	10.62	10.75	10.88	11.00	11.15
1.0	11.30									

9.4 The following equation can be used in place of table 4E2a–1 in spreadsheet calculations to determine uncorrected gypsum ($Gypsum_{uc}$):

Result = {{Exp {2.420384 + [1.1579713 x Log (EC − blank)]} x Water x 0.08609 x AD/OD} / (Sample Weight x 5)

9.5 Determine the uncorrected % Gypsum ($Gypsum_{uc}$) in the <2-mm sample:

% $Gypsum_{uc}$ = [Gypsum x Water x 0.08609 x AD/OD] / [Sample Weight (g) x 5]

Gypsum = meq/100 g (Gypsum determined in table 4E2a–1)

Water = 100 mL of RO water used to dissolve gypsum

0.08609 = Conversion factor (gypsum % = meq 100 g^{-1} x 0.08609)

AD/OD = Air-dry/oven-dry ratio (method 3D1)

5 = Filtrate (5 mL)

Note: When determining or correcting percent gypsum, it is important to use the associated AD/OD sample preparation. For example, a 2- to 20-mm corrected gypsum percent should be calculated using the 2- to 20-mm corrected AD/OD result.

The same equation can also be used:

- to determine the uncorrected % Gypsum of the 2- to 20-mm fraction preparation and
- to determine the uncorrected % Gypsum of the GP preparation.

9.6 Determine the corrected % Gypsum ($Gypsum_c$) in the <2-mm sample:

Note: The equation for calculating % Gypsum, corrected, assumes the crystal-water content of gypsum is 19.42% (Nelson et al., 1978) as opposed to the theoretical water content (20.21%).

$$\%\ Gypsum_c = (\%\ Gypsum_{uc}) / [1 + (0.001942 \times \%\ Gypsum_{uc})]$$

$\%\ Gypsum_{uc}$ = as determined in step 9.5

The same equation can be used:

- to determine the % Gypsum of the 2- to 20-mm fraction and
- to determine the % Gypsum of the GP sample preparation.

9.7 Determine the corrected AD/OD ratio of the <2-mm sample:

$$(AD/OD)_C = (AD/OD)_{UC} / [1 + (Gypsum \times 0.001942)]$$

$(AD/OD)_{UC}$ = Air-dry/oven-dry ratio (method 3D1)

Gypsum= % Gypsum uncorrected (step 9.5)

The AD/OD ratio is corrected to a crystal water basis when the gypsum content of the soil is ≥1%.

9.8 A cumulative % Gypsum for the <20 mm basis can be determined using the following pieces of information:

- Weight of the total air-dried, whole-soil sample
- Weight of 20- to 75-mm sieved fraction
- Weight of 5- to 20-mm sieved fraction
- Weight of 2- to 5-mm sieved fraction
- Corrected gypsum % of <2-mm fraction
- Corrected gypsum % of 2- to 20-mm fraction

9.9 Using the air-dried, whole-soil sample weight as 100%, determine the weight % fraction of each:

- Weight of 20- to 75-mm sieved fraction
- Weight of 5- to 20-mm sieved fraction
- Weight of 2- to 5-mm sieved fraction

9.10 Determine the 2- to 20-mm fraction using weight percent calculated in step 9.7:

$$(Wf_{2\text{-}5} + Wf_{5\text{-}20}) / (100.0 - Wf_{20\text{-}75})$$

$Wf_{2\text{-}5}$ = weight fraction % of 2- to 5-mm sieved from whole soil

$Wf_{5\text{-}20}$ = weight fraction % of 5- to 20-mm sieved fraction from whole soil

$Wf_{20\text{-}75}$ = weight fraction % of 20- to 75-mm sieved fraction from whole soil

9.11 Determine the <2-mm fraction using weight precents:

$$(100.0 - Wf_{2\text{-}5} - Wf_{5\text{-}20} - Wf_{20\text{-}75}) / (100.0 - Wf_{20\text{-}75})$$

9.12 Determine the <20-mm Gypsum %:

$(Gypsum_C\text{<}2 \times \text{<2-mm fraction \%}) + (Gypsum_C\text{<2-20} \times \text{2- to 20-mm fraction \%})$

$Gypsum_C$<2-mm = Corrected <2-mm Gypsum (step 9.6)

<2-mm fraction % = determined in step 9.9

$Gypsum_C$<2-20 = Corrected 2- to 20-mm Gypsum (step 9.6)

2- to 20-mm fraction %= determined in step 9.8

The <20 mm cumulative % Gypsum is reported as a weight percent.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Nelson, R.E. 1982. Carbonate and gypsum. p. 181–197. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

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Carbonate and Gypsum (4E)
Aqueous Extraction (4E2)
1:400, 24-h (4E2b)
Conductivity Bridge (4E2b1)
Electrical Conductivity (4E2b1a)
Equivalent Gypsum Content, Semiquantitative (4E2b1a1)
Air-dry, <2 mm or <20 mm (4E2b1a1a1-2)

1. Introduction to Gypsum Electrical Conductivity

Application of irrigated water on farmland in arid and semiarid areas poses engineering challenges related to gypsiferous and gypseous soils (Elrashidi et al., 2007). Typically, gypsiferous and gypseous soils have several other water-soluble minerals associated with gypsum. These salts can be concentrated through crop transpiration, evaporation, and soil leaching. The effects of these salts, such as gypsum, on crops are dependent upon plant type and soil conditions, such as composition and organic matter.

2. Scope and Field of Application

Water used to irrigate farmland throughout semiarid and arid areas commonly exhibits salt contents ranging from 150 to 900 mg/L (Garcia, 2019). Soil type, composition, and farming practices determine whether these soluble salts impair soil quality by inhibiting germination of salt-sensitive crops and creating surface crusting, or if $CaSO_4$ precipitates as a solid and becomes integrated into the soil profile as a nutrient.

Elrashidi et al. (2007) proposed estimating not solely gypsum content but also other water-soluble minerals using Equivalent Gypsum Content (EGC). EGC is defined as the quantity of gypsum and other water-soluble minerals and is expressed as a gypsum percentage (by weight) in soils. The method to estimate EGC is described herein.

3. Principle

A 0.50-g sample is weighed, and 200 mL of water is added. The sample is shaken for 24 h and allowed to settle for 15 minutes. A 20-mL sample is pipetted from the top 10-cm of the solution and filtered through a 0.45-µm filter Electrical conductivity (EC) (1:400) is measured and recorded (dS m^{-1}).

3.1 Interferences

A maximum of ≈0.5 g of gypsum can be dissolved completely in 200 mL of water. The resulting system (2.5 g L^{-1}) is considered at a saturated state. A saturated aqueous solution of gypsum has 2.6 g L^{-1} at 25 °C (Smith and Robertson, 1962; Lagewerff et al., 1965; Van Alphen and Romero, 1971; Porta, 1998).

4. Apparatus

4.1 Electronic balance, ±0.01-g sensitivity

4.2 Mechanical reciprocating shaker

4.3 Bottle, polyethylene, 250-mL

4.4 Tube, polyethylene, 50-mL

4.5 Pipette, 20-mL, 10-mL electronic digital, with tips, polypropylene

4.6 Syringe filters, 25-mm, 0.45-µm pore size

4.7 Conductivity meter and conductivity cell

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Potassium chloride (KCl) solution, 0.010 *N*

Components: Potassium chloride (KCl) (CAS# 7447-40-7), RODI water

Preparation: Dry KCl overnight in oven (110 °C). Dissolve 0.7456 g of KCl in RODI water and bring to 1-L volume. Conductivity of KCl solution at 25 °C is 1.412 mmhos cm^{-1}.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Prepare and analyze samples in duplicates. Weigh 0.50 g air-dry, <2-mm soil into 250-mL bottle.

8.2 Add 200 mL of RO water to bottle.

8.3 Shake at 100 cycles per minute for 24 hours at room temperature (20 ±2 °C).

8.4 Remove bottle from shaker and let bottle set upright 15 min, allowing soil to settle.

8.5 Pipette 20-mL sample from top 10-cm of solution and filter.

8.6 Calibrate conductivity meter using 0.010 *N* KCl solution.

8.7 Measure EC in filtrate.

8.8 If EC ≥1.0 dS m^{-1}, pipette 10 mL of soil solution and then add 20 mL of RO water into 50-mL polyethylene tube. Swirl, read, and record EC.

8.9 Rinse electrode with distilled water. Remove excess water by patting with tissue.

8.10 Report EC (1:400) to the nearest 0.1 dS m^{-1}. Report gypsum (g L^{-1}), EGC (%), and gypsum (%).

9. Calculations

9.1 Determine the Soil Equivalent Gypsum Content (EGC):

$$EGC\ (\%) = 100 \times A\ (g\ L^{-1}) \times DF \times (200\ mL / 1{,}000\ mL/L) / 0.5\ g$$

$$A = 0.998 \times EC\ (dS\ m^{-1})$$

This is the relationship between solution gypsum concentration (g/L) and EC of solution (dS m^{-1}).

DF = Dilution factor, 1 or 3, depending on whether dilution was necessary to determine "A."

9.1 Determine the Gypsum (%):

$$Gypsum\ (\%) = 0.293 + [0.830 \times EGC\ (\%)] - [0.144 \times EC_S\ (dS\ m^{-1})]$$

EC_S = Electrical conductivity of saturation paste extract (dS m^{-1}) (method 4F2b1)

If ECS is unavailable, EC1:2 may be substituted:

$$Gypsum\ (\%) = 0.294 + [0.830 \times EGC\ (\%)] - [0.318 \times EC1{:}2\ (dS\ m^{-1})]$$

EC1:2 = EC of 1:2 soil to water extract (method 4F1a1a1)

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Elrashidi, M.A., D. Hammer, C.A. Seybold, R.J. Engel, R. Burt, and P. Jones. 2007. Application of equivalent gypsum content to estimate potential subsidence of gypsiferous soils. Soil Sci. 172(3):209–224. doi:10.1097/ss.0b013e31802ff892

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van Alphen, J.G., and F.R. Romero. 1971. Gypsiferous soils: Notes on their characteristics and management. International Institute for Land Reclamation and Improvement Bulletin No. 12. ILRI, Wageningen, The Netherlands.

Carbonate and Gypsum (4E)

1 *N* HCl Treatment (4E3)

CO_2 Analysis (4E3a)

Effervescence Reading (4E3a1)

Calcium Carbonates (4E3a1a)

Air-Dry, <2 mm or <20 mm (4E3a1a1)

1. Introduction to Calcium Carbonate Effervescence

The distribution and abundance of carbonates influence soil fertility, erodibility, and available water capacity. Effervescence is not a precise indicator but a relative index of the carbonates in the soil matrix. The most common types of primary and secondary carbonates found in soils are calcite ($CaCO_3$), or a poorly crystalline equivalent, and dolomite [$CaMg(CO_3)_2$]. Less common soil carbonates include sodium carbonate (Na_2CO_3) and siderite ($FeCO_3$).

2. Scope and Field of Application

Effervescence in soils is the generation of carbon dioxide (CO_2) when dilute hydrogen chloride (HCl) interacts with primary and secondary carbonates:

$$CaCO_3 + 2HCl = H_2O + CO_2\,(g) + Ca^{2+} + 2Cl^-$$

The extent and rate of effervescence are affected by the amount of carbonates, the chemical and physical nature of the carbonates (e.g., particle size and mineralogy), the temperature and water content of the soil, and the temperature and concentration of the HCl applied to the sample.

3. Principle

A small amount of an air-dry soil sample is placed in a spot-plate well. Water is added and stirred into the soil. A similar amount of a 1 *N* HCl solution is added to the sample and any initial effervescence is observed. A final assessment of the observed effervescence is made after a 2-minute interval. The effervescence class is recorded.

3.1 Interferences

The procedure for detection of carbonates with the reaction of HCl is a subjective and qualitative test. Effervescence is not observable in all soils.

Samples are checked after 2 minutes for latent effervescence (e.g., from Dolomite).

4. Apparatus

4.1 Porcelain spot plate

4.2 Metal spatula

4.3 Task light with magnifier
4.4 Glass bottle with dropper for 1 *N* HCl
4.5 30-mL dropper bottle with RO water
4.6 Kimwipes
4.7 Timer

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type I grade of reagent water
5.2 Hydrochloric acid (HCl) (CAS# 7647-01-0), concentrated 12 *N*
5.3 **Hydrochloric acid solution, 1 *N***

Components: Concentrated hydrochloric acid (HCl), RO water

- To a 500-mL polyethylene bottle, add the following in order:
  - 458.3 mL of RO water
  - 41.7 ml of concentrated HCl
- Invert to mix.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use the fume hood when diluting concentrated HCl. Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Using a spatula, place either <2-mm or 80-mesh soil into the spot-plate well. Fill ≈25% of the well volume. Spread out the sample to remove trapped air and distribute soil evenly along the bottom of the well.
8.2 Repeat 8.1 to fill as many wells with samples as necessary. Use a Kimwipe to clean the spatula between samples.
8.3 Add 3 to 5 drops of RO water to moisten the sample and create a slurry. Using the spatula, fold and stir the mixture to dislodge trapped air. Avoid cross-contamination by using a Kimwipe to thoroughly clean the spatula between samples.

- Note: Samples that have a higher clay content may require additional drops of water to create a slurry. Clays may coat carbonate grains and thereby prevent reaction with the HCl.

8.4 Adjust the task light and magnifier to clearly illuminate the spot plate.

8.5 Working in sets of 3 samples, add 3 drops of 1 *N* HCl to each sample.

- Set a 2-minute timer and observe the 3 samples over a 30 second period for effervescence. If a sample does not effervesce, move on to the next set of 3 samples.
- After timer goes off, observe for effervescence in the sample(s) that did not initially show reaction.
- If effervescence is still not observed, use the spatula to slice through the middle of the sample. Use the magnifier to observe for effervescence.

8.6 Record effervescence class as none, very slight, slight, strong, or violent.

8.7 Clean spatula with a Kimwipe before any re-use.

9. Calculations

No calculations are required for this analysis. Report one of the following classes of effervescence for each sample:

None

- No visual effervescence. No bubbles form after 2-minute check.

Very Slight

- Bubbles rise at a few points in the sample and consistently appear at the same point in either a steady stream of tiny bubbles or in a slower stream of larger bubbles. Caution: Do not mistake trapped air for a positive test.
- Few bubbles form, usually uniform in size.
- Bubbles come from one or a few points in the well. When viewed from the side, you might see the sparkle and pop of effervescence, similar to a soda, or soft drink. Sometimes one carbonate concretion is in the soil, and a small stream of bubbles will come off of this one piece.

Slight

- More small bubbles form than with a “very slight” reaction.
- Numerous bubbles form in varying sizes.

Strong

- More bubbles than form than with the “slight” reaction. Bubbles appear immediately after the addition of the acid.
- Constant bubbles form throughout the entire well and continue to effervesce.

Violent

- One or more large bubbles appear to burst from the spot-plate well.
- Bubbles form a thick foam that appears immediately after the addition of the acid.
- Sound may be audible.
- Foam appears throughout the entire well. It continues to effervesce or may dissipate within 30 seconds.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Soil Survey Staff. 2014. Keys to soil taxonomy. 12th ed. USDA–NRCS.

Electrical Conductivity and Soluble Salts (4F)
Aqueous Extraction (4F1)
1:2 Extraction (4F1a)
Conductivity Bridge (4F1a1)
Electrical Conductivity (4F1a1a)
Salt Prediction (4F1a1a1)
Air-Dry, <2 mm (4F1a1a1a1)

1. Introduction to Electrical Conductivity Salt Prediction

Salt prediction is used to predict which soils have measurable amounts of soluble salts and also to predict the quantity and appropriate dilutions for salt analyses of those soils.

2. Scope and Field of Application

The 1:2 salt prediction determination is a screening procedure. If salt prediction or conductivity is <0.25 mmhos cm^{-1} (dS cm^{-1}), the result is considered below the limit for additional salt analyses, including saturated paste (method suite 4F2). Samples that do not qualify are only analyzed for saturated paste on request.

3. Principle

A soil sample is mixed with water and allowed to stand overnight. The electrical conductivity (EC) of the mixture is measured using a conductivity meter. The EC is used to indicate the presence of soluble salts (U.S. Salinity Laboratory Staff, 1954).

3.1 Interferences

The soil sample slurry and the reverse osmosis deionized (RODI) water used to zero and flush the conductivity cell should both be at room temperature. The extract is assumed to be at 25 °C. If the temperature deviates significantly, a correction may be required.

Provide airtight storage of KCl solution and samples to prevent soil release of alkali-earth cations.

Keep lids on samples. Exposure to air can cause gains and losses of water and dissolved gases, significantly affecting EC readings.

4. Apparatus

4.1 Electronic balance, ±1.0-mg sensitivity

4.2 Conductivity meter and conductivity cell, with automatic temperature adjustment, 25 ±0.1 °C

4.3 Plastic cups, 30-mL (1-oz), with lids

4.4 Disposable pipettes or dispenser, re-pipette or equivalent, 0 to 10 mL

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Potassium chloride solution, 0.010 *N*

Components: Potassium chloride (KCl) (CAS# 7447-40-7), RODI water

- In a 1-L volumetric flask, add the following in order:
  - 800 mL of RODI water
  - 0.7456 g of KCl dried overnight in oven (110 °C)
  - Fill to volume with RODI water.
- Conductivity of KCl solution at 25 °C is 1.412 mmhos cm^{-1}.

6. Health and Safety

Personal Protective Equipment (PPE).—Use disposable gloves with appropriate polymer rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Follow standard laboratory safety practices.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Weigh 5.0 g of <2-mm, air-dry soil in a 30-mL (1-oz) condiment cup. If samples are clayey or organic, weigh 1.0 g of soil in condiment cup; these samples absorb solution, potentially reducing the amount of solution available for testing. Reduced sample sized is accounted for in the calculation.

8.2 Pipette 10 mL of RO water to sample.

8.3 Place lid on condiment cup, shake well, and allow to stand overnight. Read after 24 hours.

8.4 Standardize the conductivity meter using RO water (blank) and 0.010 *N* KCl (1.41 mmhos cm^{-1}).

8.5 Read conductance of supernatant solution directly from the bridge. Samples with a reading of ≥0.25 dS m^{-1} are eligible for saturated paste analyses.

9. Calculations

9.1 Determine the Salt Prediction EC:

$$\text{mmhos cm}^{-1} = \text{measured EC} \times (\text{water aliquot}/10) \times (5/\text{sample weight})$$

9.2 The following equations can be used for data interpretation to estimate total soluble cation or anion concentration in the soil:

- EC (mmhos cm^{-1}) x 10 = Cation or Anion (meq L^{-1})
- EC (mmhos cm^{-1}) x 20 = Cation (meq g^{-1} soil)
- EC (mmhos cm^{-1}) x 20 = Anion (meq g^{-1} soil)

9.3 Report prediction conductance to the nearest 0.01 mmhos cm^{-1} (dS m^{-1}).

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

U.S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. L.A. Richards (ed.). USDA Agric. Handbook 60. U.S. Govt. Print. Office, Washington, DC.

Electrical Conductivity and Soluble Salts (4F)
Aqueous Extraction (4F1)
Single-Point Extraction (4F1b)
1:5, 23-h, 1-h Aqueous Extraction (4F1b1)
Conductivity Bridge (4F1b1a)
Electrical Conductivity (4F1b1a1)
Air-Dry or Field-Moist, <2 mm (4F1b1a1a-b1)

1. Introduction to Single Point Extraction Electrical Conductivity

An aliquot of water is added to a soil sample and allowed to equilibrate for 24 hours. The soil solution is extracted to measure aspects such as pH, EC, and elements in suspension. Studies at the KSSL reported a correlation between water-extractable elements for soils and their concentration in runoff from agricultural watersheds (Elrashidi et al., 2005a, 2005b).

2. Scope and Field of Application

Applied nutrients, such as phosphorus and nitrogen, in runoff from agricultural fields are leading causes of poor water quality in the United States (USEPA, 1996). When environmental impacts of conventional agricultural practices on natural water resources are evaluated, the amount of water-soluble elements and associated properties (e.g., pH, electrical conductivity) should be measured in soil under conditions similar to those present during runoff events.

3. Principle

A 7.0-g sample of soil is added to 35 mL of water in a 50-mL disposable centrifuge tube. The soil-and-water suspension is maintained at room temperature for 23 h and then shaken on a reciprocating shaker for 1 hour. The supernatant is filtered, and the EC is measured.

3.1 Interferences

The soil sample slurry and reverse osmosis deionized (RODI) water used to zero and flush the conductivity cell should both be at room temperature. The extract is assumed to be at 25 °C. If the temperature deviates significantly, a correction may be required.

Provide airtight storage of KCl solution and samples to prevent soil release of alkali-earth cations.

Keep lids on samples. Exposure to air can cause gains and losses of water and dissolved gases, significantly affecting EC readings.

4. Apparatus

4.1 Conductivity meter and conductivity cell, with automatic temperature adjustment, 25 ±0.1 °C

4.2 Plastic cups, 30-mL (1-oz), with lids

4.3 Volumetric flask, 1-L

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Potassium chloride (KCl) solution, 0.01 N

Components: Potassium chloride (KCl) (CAS# 7447-40-7), RODI water

- To a 1-L volumetric flask, add the following in order:
  - 700 mL of RODI water
  - 0.7456 g of KCl dried overnight in oven (110 °C)
  - Fill to volume with RODI water.
- Conductivity of KCl solution at 25 °C is 1.412 mmhos cm^{-1}.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. Subsamples are further processed via planetary ball mill to 80 mesh; either size fraction is appropriate for this test. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 The soil extract is prepared in using method 4D2a2.

8.2 Standardize the conductivity meter using RO water (blank) and 0.010 *N* KCl (1.41 mmhos cm^{-1}).

8.3 Measure conductance of sample extract directly from the EC meter.

8.4 Record conductance to 0.01 mmhos cm^{-1}.

9. Calculations

Report electrical conductance to the nearest 0.01 mmhos cm^{-1} (dS m^{-1}). No calculations are required for this procedure.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Elrashidi, M.A., J.D. Harder, D. Schroeder, P. Brakhage, C.A. Seybold, and C. Schaecher. 2005a. Loss of phosphorus by runoff for agricultural watersheds. Soil Sci. 170:543–558.

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Electrical Conductivity and Soluble Salts (4F)

Aqueous Extraction (4F1)

Subaqueous Soils (4F1c)

1:5 Aqueous Mixture by Volume and Estimated Porewater EC ($EC_{1:5vol}$ & EC_{pw_est}) (4F1c1)

Conductivity Meter (4F1c1a)

Electrical Conductivity (4F1c1a1)

Field-Moist, Whole-Soil (4F1c1a1b2)

1. Introduction - Soluble Salts in Subaqueous Soil

Electrical conductivity (EC) measurements are quick, simple determinations for water-soluble salts in soils. This method assumes that the salts in subaqueous soils are highly soluble chloride and sulfate salts in a dissolved state and that they include no significant contributions from minerals, such as gypsum.

2. Scope and Field of Application

For subaqueous soils, EC must be measured in a fresh, field-wet sample (moisture content at sample collection) that has been collected and sealed to exclude oxygen and refrigerated or frozen. Exposure to oxygen can cause oxidation of sulfides, forming sulfate salts, and thereby affecting (increasing) the EC value. This EC method for subaqueous soils uses a soil-to-water ratio (volume) of 1:5 ($EC_{1:5vol}$) and is measured in the supernatant, not the extract (Soil Survey Staff, 2014). Soil $EC_{1:5vol}$ is used in the “Keys to Soil taxonomy” (Soil Survey Staff, 2014) at the great group level to define freshwater subaqueous soils (Frasiwassents and Frasiwassists) from salt and brackish water subaqueous soils (Balduff, 2007; Payne, 2007).

3. Principle

A sample of subaqueous soil and in-situ water is placed in a sealed container that is completely filled with soil and ambient water to exclude any air. Samples are sealed and refrigerated or frozen until analysis. A 10-mL sample, by volume, is extracted from the bulk sample. RO water is added to the subsample, stirred for 10 seconds, and allowed to settle for no less than 10 minutes. A pH reading is recorded from the slurry and compared to the field pH to check for post-sampling sulfide oxidation. If the supernatant contains too much suspended material to obtain a reliable reading, the slurry is centrifuged and the supernatant is measured to determine EC. Water content of a duplicate sample is determined and used in calculating the estimated pore-water electrical conductivity.

3.1 Interferences

Soil samples from brackish or saltwater sites can contain sulfides. These sulfides can oxidize, forming sulfates, if (1) the sample is exposed to air, (2) testing

is not performed for several days, or (3) the sample is not kept moist, refrigerated, or frozen.

Electrical conductivity increases at approximately 1.9% per degree Celsius increase in temperature (Rhoades et al, 1999). Therefore, EC needs to be expressed at a reference temperature for purposes of comparison and accurate salinity interpretations. The commonly used reference temperature of the sample and cell is 25 ±0.5°C while EC is being measured.

$EC_{1:5vol}$ is not directly comparable to EC determined by saturated paste.

4. Apparatus

4.1 A device for extracting a 10-mL sample with minimum distortion. Examples include an open-ended syringe or a coring drill bit with a serrated-edge. The device should be able to extract a 10-mL sample without compressing or distorting the sample. The sampling device should be marked at 10-mL volume.

4.2 125-mL containers

4.3 100-mL graduated cylinder

4.4 Wooden stirring sticks

4.5 Centrifuge capable of 3,700 rpm

4.6 Centrifuge tubes, 50-mL, disposable, polyethylene

4.7 Conductivity meter and conductivity cell, with automatic temperature adjustment, 25 ±0.1 °C

4.8 Balance

4.9 Drying oven

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.2 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.3 Potassium chloride solution, 0.010 *N*

Components: Potassium chloride (KCl) (CAS# 7447-40-7), RODI water

- Dry KCl overnight in oven (110 °C).
- To a 1-L volumetric flask, add the following in order:
  - 700 mL of RODI water
  - 0.7456 g of KCl
  - Fill to volume with RODI water.
- Conductivity of KCl solution at 25 °C is 1.412 mmhos cm^{-1}.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate

rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

7. Sample Preparation

Field-moist, whole-soil cores are subsampled for this test with the objective of maintaining in-situ soil moisture content. Samples are kept in sealed containers from which all air is excluded. Ambient water is added if needed to exclude air. Samples should be frozen if stored.

8. Procedure

8.1 Samples should be analyzed immediately when received. If not, samples should be frozen.

8.2 Calibrate the pH meter using the pH 9.18, 7.00, and 4.00 buffer solutions.

8.3 Standardize the conductivity meter using RO water (blank) and 0.010 *N* KCl (1.41 mmhos cm^{-1}). Use a multi-cell probe.

8.4 Using the syringe, coring bit, or other appropriate device, extract a 10-mL subsample of moist whole soil and place into a 125 mL container.

8.5 Extract a duplicate 10-mL subsample and place into a tared container. Weigh and record.

8.6 Place the weighed sample into a drying oven at 110 °C. Remove from oven and record weight after 8 hours or when weight is stable.

8.7 Measure 10 mL of RO water into a graduated cylinder, pour water over the 10-mL soil sample in the 125-ml container, stir for 10 seconds, and allow to stand for 10 minutes.

8.8 Determine the pH of sample by carefully placing the electrode into the soil mixture. Ensure that the KCl junction and sensor membrane are in contact with the mixture.

8.9 Allow the pH meter to stabilize before recording the pH. Record the pH to the nearest 0.01 pH unit. The pH will be reported as 1:1 soil (moist)-to-water and compared to field pH to assess for oxidation of sulfides.

8.10 Add 40 mL of RO water, stir or shake for 10 seconds, and allow to stand for 10 minutes.

8.11 Use standardized conductivity meter to measure conductivity. Allow readings to stabilize. Read conductance of supernatant solution directly from the conductivity meter and record to the nearest 0.1 dS m^{-1}.

8.12 If supernatant contains too much suspended material to obtain a reliable reading, centrifuge samples in the 125 ml containers at 3,700 rpm for 8 minutes and read.

8.13 Rinse conductivity meter between samples with RODI water.

9. Calculations

9.1 Report $EC_{1:5vol}$ to the nearest 0.1 dS m^{-1}.

9.2 Calculate Estimated Porewater Electrical Conductivity as follows:

$EC_{pw\_est} = EC_{1:5vol} \times DF$ (dilution factor)

$DF = (Vs + VH_2O)/Vs$

Vs= moist sample weight−oven dry sample weight

VH_2O = volume of water added to sample (50 ml)

9.3 Report EC_{pw_est} to the nearest 0.1 dS m^{-1}.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

10.6 Compare 1:1 pH measured in step 8.9 to the field pH to ensure that there has been no significant oxidation of sulfides in the sample. The reliability of $EC_{1:5vol}$ values decreases with increasing difference between field pH and 1:1 pH. $EC_{1:5vol}$ will not be reported for samples with a difference of more than 1.5 pH units. Field pH and 1:1 pH are reported for reference.

11. References

Balduff, D.M. 2007. Pedogenesis, inventory, and utilization of subaqueous soils in Chincoteague Bay, Maryland. Ph.D. diss., University of Maryland.

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Electrical Conductivity and Soluble Salts (4F)
Saturated Paste (4F2)

"Salt-affected soils" have excessive amounts of soluble salts, exchangeable sodium (ES), or both, and are most common in arid and semi-arid regions. These soils are usually described and characterized in terms of the soluble salt concentrations, i.e., major dissolved inorganic solutes (Rhoades, 1982). Salt composition and distribution in the soil profile affect plant response, i.e., osmotic stress, specific ion effects, and nutritional imbalances. Soil texture and plant species also are factors in plant response to saline soils.

Traditionally, the classification of salt-affected soils has been based on the soluble salt concentrations in extracted soil solutions and on the exchangeable sodium percentage in the associated soil (Bohn et al., 1979). Saline soils have been defined as having a salt content >0.1% or an EC ≥4 mmhos cm^{-1}; alkali soils have an ESP (exchangeable sodium percentage) of ≥15%; and saline-alkali soils have properties of both saline and alkali soils (U.S. Salinity Laboratory Staff, 1954). In soil taxonomy, ESP and the sodium adsorption ratio (SAR) have been used as criteria for natric horizons (Soil Survey Staff, 2014). ESP and SAR are calculated in methods outlined below.

Soil salinity is conventionally defined and measured on aqueous extracts of saturated soil pastes (U.S. Salinity Laboratory Staff, 1954). The measurable absolute and relative amounts of various solutes are influenced by the soil-to-water ratio at which the soil solution extract is made. The ratio is standardized to obtain results that can be applied and interpreted universally. This standardized soil-to-water ratio is used because it is the lowest reproducible ratio at which the extract for analysis can be readily removed from the soil with common laboratory equipment, i.e., pressure or vacuum, and because this ratio is often related in a predictable manner to field measurements of soil water content (Rhoades, 1982).

The KSSL performs an initial salt prediction test to predict those soils that have measurable amounts of soluble salts and to predict the quantity and appropriate dilutions for salt analyses. The KSSL measures salinity on aqueous extracts of saturated soil pastes as described below. Extract filtered from a prepared saturated paste is used to determine:

- pH
- Soil resistivity
- Electrical conductivity
- Saturation percentage (SP)
- Water-soluble cations of Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, and NH_4^{+}
- Water-soluble anions of Br^{-}, Cl^{-}, F^{-}, NO_3^{-}, NO_2^{-}, PO_4^{3-}, and SO_4^{2-}
- Carbonate and bicarbonate concentrations
- Estimated total salt

If salt predictions or conductance are <0.25 mmhos cm^{-1}, soils are considered non-salty and no other salt analyses are performed on these soils.

The saturated percentage (SP), i.e., the amount of moisture in the saturated paste, is an important measurement. An experienced analyst should be able to repeat the saturated paste preparation to an SP within 5%. The SP can be related directly to the field-moisture range. Measurements on soils, over a considerable textural range (U.S. Salinity Laboratory Staff, 1954), indicate the following general rules of thumb:

SP ≈4 x 15-bar water

SP ≈2 x upper-end field soil moisture content

AWC ≈ SP/4

- SP = Saturation percentage
- AWC = Available water capacity

Therefore, at the upper (saturated) and lower (dry) ends of the field-moisture range, the salt concentration of the soil solution is about 4x and 2x the concentration in the saturation extract.

If the soil texture is known and the 15-bar water content has been measured, the preceding SP relationships may be redefined (U.S. Salinity Laboratory Staff, 1954) as follows:

15-Bar Water	Texture	Relationship
(%)		
2.0 to 6.5	Coarse	SP ≈6⅓ x 15-bar
6.6 to 15	Medium	SP ≈4 x 15-bar
>15	Fine	SP ≈3¼ x 15-bar
>15	Organic	SP ≈3⅔ x 15-bar

The electrical conductivity of the saturated paste (EC_S) is measured and is commonly reported as resistivity (R_S). This EC_S measurement is more closely related to plant response (U.S. Salinity Laboratory Staff, 1954). Furthermore, there is a limited correlation between EC_S and R_S, because the relationship is markedly influenced by variations in SP, salinity, and soil mineral conductivity. EC_S has been related to R_S (U.S. Laboratory Staff, 1954) by the following equation:

$EC_S \approx 0.25/R_S$

- 0.25 = Constant for Bureau of Soils electrode cup

Historically, the EC_S is adjusted to a 60 °F (15.5 °C) basis before interpretative use. EC_S and R_S increase ≈2% per °C. The KSSL determines EC_S and R_S in the methods below; the unit EC x 10^3 is mmhos cm^{-1}. The EC_S (mmhos cm^{-1}) may be

used to estimate the salt percentage (P_{sw}) in solution (U.S. Salinity Laboratory Staff, 1954) as follows:

$$P_{sw} \approx 0.064 \times EC_s \text{ (mmhos cm}^{-1}\text{)}$$

The preceding equation may be used to estimate the salt percentage in the soil (P_{ss}) (U.S. Salinity Laboratory Staff, 1954) as follows:

$$P_{ss} \approx (P_{sw} \times SP) / 100$$

The EC_s (mmhos cm^{-1}) may be used to estimate the osmotic potential (OP) in atmospheres of a solution (U.S. Salinity Laboratory Staff, 1954):

$$OP \approx 0.36 \times EC_s \text{ (mmhos cm}^{-1}\text{)}$$

The EC_s (mmhos cm^{-1}) at 25 °C may be used to estimate the total cation or anion concentration (meq L^{-1}) of the solution (U.S. Salinity Laboratory Staff, 1954) as follows:

$$\text{Total cations} \approx 10 \times EC_s \text{ (mmhos cm}^{-1}\text{)}$$

$$\text{Total anions} \approx 10 \times EC_s \text{ (mmhos cm}^{-1}\text{)}$$

A means of cross-checking chemical analyses for consistency and reliability is provided by the interrelations that exist among the various soil chemical determinations (U.S. Salinity Laboratory Staff, 1954). The saturated paste pH is the apparent pH of the soil-and-water mixture and is a key indicator in many of these interrelations. The saturated-paste pH is dependent upon the dissolved CO_2 concentration; moisture content of the mixture; exchangeable cation composition; soluble-salt composition and concentration; and the presence and amount of gypsum and alkaline-earth carbonates. Some general rules of thumb that apply to the saturated paste (U.S. Salinity Laboratory Staff, 1954) are as follows:

Total Cation and Anion Concentrations

- Total cations ≈ Total anions, expressed on equivalent basis.

pH and Ca and Mg Concentrations

- Concentrations of Ca^{2+} and Mg^{2+} are seldom >2 meq L^{-1} at pH >9.

pH and Carbonate and Bicarbonate Concentrations

- Carbonate concentration (meq L^{-1}) is measurable only if pH >9.
- Bicarbonate concentration is rarely >10 meq L^{-1} in absence of carbonates.
- Bicarbonate concentration is seldom >3 or 4 meq L^{-1} if pH <7.

Gypsum

- Gypsum is rarely present if pH >8.2.
- Gypsum has variable solubility in saline solutions (20 to 50 meq L^{-1}).
- Check for the presence of gypsum if Ca concentration >20 meq L^{-1} and pH ≤8.2.

pH, ESP, and Alkaline-Earth Carbonates

- Alkaline-earth CO_3^- and ESP ≥15 are indicated if pH ≥8.5.
- ESP ≤15 may or may not be indicated if pH <8.5.
- No alkaline-earth CO_3^- are indicated if pH <7.5.

pH and Exchangeable Acidity

- Significant amounts of exchangeable acidity are indicated if pH <7.0.

The commonly determined soluble cations and anions in the saturation extract include calcium, magnesium, sodium, potassium, chloride, sulfate, nitrate, fluoride, carbonate, bicarbonate, and nitrite. The less commonly analyzed cations and anions include iron, aluminum, manganese, lithium, strontium, rubidium, cesium, hydronium, phosphate, borate, silicate, bromide, selenate, selenite, arsenate, and arsenite.

The effect of soluble cations upon the exchangeable cation determination is to increase the cation concentration in the extracting solution, i.e., NH_4OAc, buffered at pH 7.0 (method 4B1a1b1-4). The dissolution of salts by the extractant necessitates an independent determination of soluble cations and a correction to the exchangeable cations. Therefore, in soils with soluble salts or carbonates, the soluble cations (meq L^{-1} solution) must be measured separately and the results subtracted from the extractable bases for determination of exchangeable bases as follows:

$$\text{Exchangeable} = \text{Extractable} - \text{Soluble}$$

The presence of alkaline-earth carbonates prevents accurate determination of exchangeable Ca and Mg.

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Electrical Conductivity and Soluble Salts (4F)
Saturated Paste (4F2)
Gravimetric (4F2a)
Saturated Paste Water Percentage (4F2a1)
Air-Dry, <2 mm (4F2a1a1)

1. Introduction to Saturated Paste Water Percentage

Soil salinity is conventionally defined and measured on aqueous extracts of saturated soil pastes (U.S. Salinity Laboratory Staff, 1954). The soil-to-water ratio is often related in a predictable manner to field soil-water contents (Rhoades, 1982) and is standardized to obtain results that can be applied and interpreted universally.

2. Scope and Field of Application

In the saturated paste water percentage (SP) measurement, the measurable absolute and relative amounts of various solutes are influenced by the soil-to-water ratio at which the soil solution extract is made. The SP serves as the lowest reproducible ratio at which the extract for analysis can be readily removed from the soil with common laboratory equipment, i.e., pressure or vacuum. Measurements on soils over a considerable textural range (U.S. Salinity Laboratory Staff, 1954) indicate the following general rules of thumb:

SP ≈ 4 x 15-bar water

SP ≈ 2 x upper-end field soil moisture content

AWC ≈ SP/4

- SP = Saturation percentage
- AWC = Available water capacity

3. Principle

The saturated soil paste is an analyst-defined mixture of soil and water. An experienced analyst should be able to repeat the saturated paste preparation to a saturation percentage within 5%. Saturated paste is prepared by adding water to a soil sample while stirring the mixture until the soil paste meets the saturation criteria. The saturation criteria are then rechecked several hours later. If the mixture fails to meet these criteria, more water or soil is added until criteria are met. The mixture is covered and allowed to stand overnight.

An aqueous extract is obtained from the saturated paste. Subsamples are used to determine the moisture content, i.e., saturated paste water percentage (SP), and for chemical analyses, e.g., electrical conductivity and major anion and cation concentrations in solution.

3.1 Interferences

Dry peat and muck soils, especially if coarse textured or woody, require overnight wetting to obtain a definite end point for the saturated paste. Special precautions must be taken for peat and muck soils and for very fine or very coarse textured soils (Rhoades, 1982). After the first wetting, pastes of these soils usually stiffen and lose their glisten. Adding water and remixing, the paste usually retains the saturated paste characteristics.

With fine-textured soils, enough water should be added immediately, with a minimum of mixing, to bring the sample nearly to saturation.

The presence of free water on the surface of the paste after standing is an indication of oversaturation in the coarse-textured soils (Rhoades, 1982).

4. Apparatus

4.1 Aluminum cans, drying

4.2 Spatulas, stainless steel, hardwood handles

4.3 Electronic balance, ±1-mg sensitivity

4.4 Oven, thermostatically controlled, 110 °C

4.5 Thermometer, 0 to 200 °C

4.6 Plastic containers, 1,920-mL (16-oz), with recessed lids

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

6. Health and Safety

Personal Protective Equipment (PPE).—Disposable gloves with appropriate polymer rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron should be used when appropriate.

Use heat-resistant gloves to remove hot moisture cans from the oven. Follow standard laboratory safety practices.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

Saturated Soil Paste Preparation

8.1 Place a <2-mm, air-dry, 250-g soil sample in the plastic container.

8.2 Add enough RO water to bring the sample nearly to saturation. Even and complete hydration is key. Suggestions for achieving paste consistency:

- Use smaller stirring strokes.
- Cut through the sample with the spatula edge.
- Try not to whip or introduce air to the sample. Air can create clay skins and lumps of dry, clay-rich soil.
- If the paste becomes too wet, add more dry soil. If more soil is not available, place sample in front of a fan or in fume hood for 5 minutes to drive off standing water; check and re-stir sample.

8.3 At saturation, the paste meets the following criteria. Allow to stand for at least 4 h and recheck the saturation criteria.

- The soil paste glistens as it reflects light.
- It flows slightly when the container is tipped.
- It slides freely and cleanly off the spatula unless the soil has a high clay content.

8.4 Recheck saturation criteria: Within minutes of stirring, free water should not collect on the soil surface, paste should not stiffen markedly, and paste should not lose its glisten upon standing.

8.5 If the paste does not meet the saturation criteria, remix the paste with more RO water or dry soil.

8.6 Cover the container and allow the sample to stand overnight.

Saturated Paste Water Percentage Determination

8.7 Record a tare weight for each moisture can and lid (TC). Label each moisture can with the appropriate sample number.

8.8 Add ≈20 to 40 g of the saturated soil paste to the moisture can.

8.9 Place lid on can and collect moist sample weight (WMS). Record the weight to the nearest mg.

8.10 Remove the can lid, place the can in a vented drying oven at 110 °C, and leave in the oven overnight. A drying period of 24 h or longer is recommended. Do not place moist samples in the oven with other samples that are drying, unless these samples have been in the oven at least 12 to 16 h. Do not overcrowd the drying oven with samples.

8.11 Remove the cans from the oven. Allow the cans to cool for 1 h.

8.12 Weigh the oven-dry paste samples and lids and record the weight (WDS). Do not use the dried subsample for other analyses.

9. Calculations

9.1 Determine the sample weights of saturated paste and oven-dried sample:

$$Wt_{SP} = WMS - TC$$

$$Wt_{OD} = WDS - TC$$

WMS = Moist weight

WDS = Oven-dry sample weight

TC = Sample can and lid weight

9.2 Determine the saturated paste water percentage (SP):

$$SP = [(Wt_{SP} - Wt_{OD}) / (Wt_{OD})] \times 100$$

Wt_{SP} = Weight of saturated paste

Wt_{OD} = Weight of oven-dry soil

9.3 When a sample contains gypsum, the oven-dry weight and saturation percentage must be corrected based upon the gypsum content. Oven drying removes both water held in the sample and crystal water held in gypsum. The calculation for the oven dried weight correction (OD_c) is:

$$OD_{c=} OD_u / (1 - (Gyp\%_c * 0.1942)$$

OD_c = Corrected weight

OD_u = Uncorrected weight

$Gyp\%_c$ = Corrected gypsum value as determined from gypsum method 4E2a1a1

0.1942 = Crystal water content of gypsum used at the KSSL (Nelson et al., 1978)

9.4 The corrected oven-dry weight is used to calculate a corrected SP value:

$$SP_c = (Wt_{water} / OD_c) \times 100$$

SP_c = Saturation percentage, corrected

$Wt_{water} = Wt_{SP} - OD_u$

9.5 Report the saturated paste water percentage to the nearest 0.1%.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Rhoades, J.D. 1982. Soluble Salts. p. 167–179. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

U.S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. L.A. Richards (ed.). USDA Agric. Handbook 60. U.S. Govt. Print. Office, Washington, DC.

Electrical Conductivity and Soluble Salts (4F)
Saturated Paste (4F2)
Conductivity Meter (4F2b)
Electrical Conductivity (4F2b1)
Air-Dry, <2 mm (4F2b1a1)

1. Introduction to Saturated Paste Electrical Conductivity

Traditionally, the classification of salt-affected soils has been based on the soluble salt concentrations in extracted soil solutions and the exchangeable sodium percentage in the associated soil (Bohn et al., 1979).

2. Scope and Field of Application

Saline soils have been defined as having a salt content >0.1% or an EC ≥4 mmhos cm^{-1}; alkali soils have an ESP (exchangeable sodium percentage) of ≥15%; and saline-alkali soils have properties of both saline and alkali soils (U.S. Salinity Laboratory Staff, 1954). The electrical conductivity of the saturation extract (EC_S) is used as a criterion for classifying a soil as saline. Other uses of this measurement include the estimation of the total cation concentration in the extract, salt percentage in solution (P_{SW}), salt percentage in soil (P_{SS}), and osmotic pressure (OP).

The unit EC x 10^3 is also mmhos cm^{-1}.

- For solutions with a low EC_S, i.e., dilute solutions, the EC_S (mmhos cm^{-1}) x 10 ≈ cation concentration (meq L^{-1}) (U.S. Salinity Laboratory Staff, 1954).
- The EC_S (mmhos cm^{-1}) x 0.064 ≈ (P_{SW}); the (P_{SW} x SP) / 100 ≈ P_{SS}; and the EC_S (mmhos cm^{-1}) x 0.36 ≈ OP in atmospheres (U.S. Salinity Laboratory Staff, 1954).

Historically, the EC_S is adjusted to a 60 °F (15.5 °C) basis before interpretative use. This EC_S measurement is more closely related to plant response (U.S. Salinity Laboratory Staff, 1954).

3. Principle

The EC_S of the saturation extract that is prepared in method 4F2 is measured using a conductivity cell and a direct reading digital meter. The cell constant is set using a standard solution.

3.1 Interferences

Reverse osmosis deionized water is used to zero and flush the conductivity cell. The extract temperature is assumed to be 25 °C. If the temperature deviates significantly, a correction may be required.

Provide airtight storage of KCl solution and samples to prevent soil release of alkali-earth cations. Exposure to air can cause gains and losses of water and dissolved gases, significantly affecting EC readings.

4. Apparatus

4.1 Conductivity meter and conductivity cell, with automatic temperature adjustment, 25 ±0.1 °C

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.2 Potassium chloride solution, 0.010 *N*

Components: Potassium chloride (KCl) (CAS# 7447-40-7), RODI water

- To a 1-L volumetric flask, add the following in order:
  - 750 mL of RODI water
  - 0.7456 g of KCl (dried overnight in oven at 110 °C)
  - Fill to volume with RODI water.
- Invert to mix.
- Conductivity of KCl solution at 25 °C is 1.412 mmhos cm^{-1}.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. This test uses the saturated paste created from the <2-mm dry sample.

8. Procedure

8.1 Calibrate the conductivity meter and cell by drawing the 0.010 *N* KCl solution into the cell.

8.2 Read the electrical conductivity of saturation extract (EC_S) by drawing up the extract into the cell.

8.3 When the reading has stabilized, record the EC_S. Rinse the cell with RODI water and ensure that the conductivity reading falls to zero.

9. Calculations

Report EC_S to the nearest 0.01 mmhos cm^{-1} (dS m^{-1}). No calculations are required for this procedure.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

U.S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. L.A. Richards (ed.). USDA Agric. Handbook 60. U.S. Govt. Print. Office, Washington, DC.

Electrical Conductivity and Soluble Salts (4F)
Saturated Paste (4F2)
Conductivity Bridge (4F2b)
Resistivity (4F2b2)
Air-Dry, <2 mm (4F2b2a1)

1. Introduction to Saturated Paste Resistivity

The resistivity of the soil paste is used to estimate the salt content in the soil. The apparatus is simple and rugged, the measurements can be made quickly, and the results are reproducible. Many agencies use the Bureau of Soils electrode cup to estimate the soluble salt content in soils (Davis and Bryan, 1910; Soil Survey Staff, 1951).

2. Scope and Field of Application

The correlation between saturated paste electrical conductivity (EC_S) and saturated past resistivity (R_S) is limited because the relationship is markedly influenced by variations in saturated paste water percentage (SP), salinity, and soil mineral conductivity. The following equation relates EC_S to R_S (U.S. Laboratory Staff, 1954):

$$EC_S \approx 0.25/R_S$$

- 0.25 = Constant for Bureau of Soils electrode cup

EC_S and R_S increase ≈2% per °C. There is no simple method to convert saturation extract electrical conductivity to soil paste resistivity or vice versa.

3. Principle

A saturated paste that is prepared in method 4F2 is placed in an electrode cup. The temperature and resistance of the paste are measured. The resistance (ohms) is converted to a 60 °F (15.5 °C) basis using a fourth-order equation (Benham, 2003).

3.1 Interferences

No significant interferences are known to affect the saturated paste resistivity measurement.

4. Apparatus

4.1 Resistivity meter

4.2 Thermometer, 0 to 100 °C

5. Chemicals

No reagents or consumables are used in this procedure.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents, especially concentrated acids and bases, use disposable gloves with appropriate polymer rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Follow standard laboratory safety practices.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. This test uses the saturated paste created from the <2-mm dry sample.

8. Procedure

8.1 Fill the electrode cup or cell with the saturated paste prepared for method 4F2.

8.2 Record the resistivity.

8.3 Place a thermometer in the saturated paste. When the temperature is stabilized, record the temperature.

9. Calculations

9.1 Use table 4F2b–1 to convert measured resistance to specific resistance at 60 °F (15.5 °C).

$$\text{Resistivity (ohms cm}^{-1}\text{)} = \text{ohms @ 60 °F} \times \text{electrode cup cell factor}$$

9.2 The following equation may be used to reduce soil paste resistance readings to values at 60 °F. Report final results to 4 significant figures.

$$\text{Resistance (ohms) corrected to 60 °F} = (-0.013840786 + 0.028627073\ B - 0.00037976971\ B2 + 3.7891593e^{-06}\ B3 - 1.2020657e^{-08}\ B4) \times C \times D \times E$$

B = Temperature (°F) at which the resistance was measured

C = Resistance (ohms) measured at temperature B

D = Electrode cup cell factor

E = Scale (range multiplier)

9.3 Report saturated paste resistivity in units of ohms at 60 °F (15.5 °C) to the nearest whole number.

Table 4F2b–1.—Bureau of Soils Data for Reducing Soil Paste Resistance Readings to Values at 60 °F (Whitney and Means, 1897).

Temp	Ohms								
°F	1000	2000	3000	4000	5000	6000	7000	8000	9000
40	735	1470	2205	2940	3675	4410	5145	5880	6615
42	763	1526	2289	3052	3815	4578	5341	6104	6867
44	788	1576	2364	3152	3940	4728	5516	6304	7092
46	814	1628	2442	3256	4070	4884	5698	6512	7326
48	843	1686	2529	3372	4215	5058	5901	6744	7587
50	867	1734	2601	3468	4335	5202	6069	6936	7803
52	893	1786	2679	3572	4465	5358	6251	7144	8037
54	917	1834	2751	3668	4585	5502	6419	7336	8253
56	947	1894	2841	3788	4735	5682	6629	7576	8523
58	974	1948	2922	3896	4870	5844	6818	7792	8766
60	1000	2000	3000	4000	5000	6000	7000	8000	9000
62	1027	2054	3081	4108	5135	6162	7189	8216	9243
64	1054	2108	3162	4216	5270	6324	7378	8432	9486
66	1081	2162	3243	4324	5405	6486	7567	8648	9729
68	1110	2220	3330	4440	5550	6660	7770	8880	9990
70	1140	2280	3420	4560	5700	6840	7980	9120	10,260
72	1170	2340	3510	4680	5850	7020	8190	9360	10,530
74	1201	2402	3603	4804	6005	7206	8407	9608	10,809
76	1230	2460	3690	4920	6150	7380	8610	9840	11,070
78	1261	2522	3783	5044	6305	7566	8827	10,088	11,349
80	1294	2588	3882	5176	6470	7764	9058	10,352	11,646
82	1327	2654	3981	5308	6635	7962	9289	10,616	11,943
84	1359	2718	4077	5436	6795	8154	9513	10,872	12,231
86	1393	2786	4179	5572	6965	8358	9751	11,144	12,537
88	1427	2854	4281	5708	7135	8562	9989	11,416	12,843
90	1460	2920	4380	5840	7300	8760	10,220	11,680	13,140
92	1495	2990	4485	5980	7475	8970	10,465	11,960	13,455
94	1532	3064	4596	6128	7660	9192	10,724	12,256	13,788
96	1570	3140	4710	6280	7850	9420	10,990	12,560	14,130
98	1611	3222	4833	6444	8055	9666	11,277	12,888	14,499

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

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Electrical Conductivity and Soluble Salts (4F)
Saturated Paste (4F2)
Saturated Paste Extraction (4F2c)
Automatic Extractor (4F2c1)

1. Introduction to Saturated Paste Extraction

The saturated paste extract is an important aqueous solution because many soil properties have been related to the composition of the saturation extract, e.g., soluble salt composition and electrical conductivity. These soil properties or characteristics are related in turn to plant response to salinity (U.S. Salinity Laboratory Staff, 1954).

2. Scope and field of application.

Soil salinity is conventionally defined and measured on aqueous extracts of saturated soil pastes (U.S. Salinity Laboratory Staff, 1954). The measurable absolute and relative amounts of various solutes are influenced by the soil-to-water ratio at which the soil solution extract is made. This ratio is standardized to obtain results that can be applied and interpreted universally. This soil-to-water ratio is used because it is the lowest reproducible ratio at which the extract for analysis can be readily removed from the soil with common laboratory equipment, i.e., pressure or vacuum, and because this ratio is often related in a predictable manner to field soil-water contents (Rhoades, 1982).

3. Principle

The saturated paste (prepared in method 4F2) is transferred to a plastic filter funnel fitted with filter paper. The funnel is placed on a mechanical vacuum extractor (Holmgren et al., 1977), and the saturated paste is extracted. The extract is used in subsequent chemical analyses, e.g., water-soluble cations and water-soluble anions.

3.1 Interferences

Repeated extractions may be necessary to obtain sufficient quantities of extract. Some saturated pastes are difficult to extract because of soil dispersion. High speed centrifuging or filtration of the extract may be necessary.

4. Apparatus

4.1 Mechanical vacuum extractor, 24-place (See images in method 4B1a1a1a1.)

4.2 Paste extraction funnel cups, 9-cm diameter, for mechanical vacuum extractors

4.3 Syringes, disposable, 60-mL, polypropylene, for extraction

4.4 Rubber tubing, 3.2 ID x 1.6 OD x 6.4 mm (⅛" ID x 1/16" OD x 1")

4.5 Polycons, hinged lid, plastic

4.6 Syringe filters, 0.2-µm pore size

4.7 Filter paper, 3- and 9-cm diameter, Whatman 40 or equivalent

5. Chemicals

Reverse osmosis (RO) water, ASTM Type III grade of reagent water

6. Health and Safety

Personal Protective Equipment (PPE).—Use disposable gloves with appropriate polymer rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling samples. Follow standard laboratory procedures.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. This test uses the saturated paste created from the <2-mm dry sample.

8. Procedure

8.1 Place a 3-cm diameter filter-paper circle over the center of the cup followed by two 9-cm diameter filter-paper circles. Slightly moisten the filter paper to ensure that it remains in place. Ensure no air is trapped between the two 9-cm filter-paper circles. If air bubbles are present, smooth the two filter papers from center to edge.

8.2 Stir prepared saturated paste (from method 4FC) to ensure homogenous texture.

8.3 Fill extraction funnel cup three-fourths full of prepared saturated paste. Gently tap the cup to remove entrapped air in the paste.

8.4 Place the funnel cup on the upper tier of the mechanical vacuum extractor. Place extraction syringe on the tier below the funnel and connect to sample funnel with rubber tubing.

8.5 When all cups are ready to extract, a plastic cover or watch glass may be placed over the extraction cup to prevent evaporation.

8.6 Turn on the extractor. Set the extraction time to 45 minutes.

8.7 When the extractor stops, turn off the power.

8.8 Carefully remove the syringe containing the extract. Leave the rubber tubing on the sample funnel.

8.9 Filter the paste extract by connecting the syringe to a 0.2-µm diameter syringe, and filter into a plastic lidded polycon.

8.10 If insufficient extract has been obtained, additional extraction will be required. Suggestions include:

- Re-extract by resetting the vacuum extractor to the starting configuration.
    - If more sample is available, take out the dried soil in the bottom of the cup and replace with fresh sample.
    - Periodically stir the paste in the sample funnel, introducing saturated sample near the suction and reorienting clays.
    - The extraction may need to be slowed to an overnight extraction.
    - High speed centrifuging by placing paste in a two-part filter and cup or a 60-mL centrifuge tube. Centrifuge at 4,000 rpm for 15 minutes.

8.11 If extracts are not to be analyzed immediately after collection, store samples at 4 °C and analyze within 72 hrs.

9. Calculations

No calculations are required for this procedure.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Holmgren, G.G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Am. J. 41:1207–1208.

U.S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. L.A. Richards (ed.). USDA Agric. Handbook 60. U.S. Govt. Print. Office, Washington, DC.

Electrical Conductivity and Soluble Salts (4F)

Saturated Paste (4F2)

Saturated Paste Extraction (4F2c)

Automatic Extractor (4F2c1)

Ion Chromatograph (4F2c1b)

Conductivity Detector (4F2c1b1)

Self-Regeneration Suppressor (4F2c1b1a)

Bromide, Chloride, Fluoride, Nitrate, Nitrite, Phosphate, Sodium, Ammonium, Potassium, Magnesium, Calcium, and Sulfate (4F2c1b1a1-12)

Air-Dry, <2 mm (4F2c1b1a1-12a1)

1. Introduction to Ion Chromatography and Saturated Paste Extracts

A prepared soil sample is saturated with water and allowed to stand overnight. The solute is drawn off and filtered to obtain a clear extract. This extract is analyzed by ion chromatography to determine the concentration of the following anions (-) and cations (+): fluoride, acetate, chloride nitrite, nitrate, sulfate, phosphate, sodium, ammonium, potassium, magnesium, and calcium. Sulfate and chloride are the most abundant ions typically found in soil.

2. Scope and Field of Application

Soils having excessive amounts of soluble salts, exchangeable sodium (ES), or both are common in arid and semi-arid regions. Soluble salt composition and distribution in the soil profile can an influence plant response due to osmotic stress, specific ion effects, and nutritional imbalances. Soil salinity also plays a role in soil texture and may restrict the number of plant species or limit plant species to salt-tolerant varieties.

Classification of salt-affected soils is based on the soluble salt concentrations in extracted soil solutions and on the exchangeable sodium percentage (ESP) in the associated soil (Bohn et al., 1979).

In general, saline soils have been defined as having a salt content >0.1% or an EC ≥4 mmhos cm^{-1}; alkali soils have an ESP of ≥15%; and saline-alkali soils have properties of both saline and alkali soils (U.S. Salinity Laboratory Staff, 1954). In soil taxonomy, ESP and the sodium adsorption ratio (SAR) have been used as criteria for natric horizons (Soil Survey Staff, 2014). ESP and SAR are calculated in methods 4F3a1 and 4F3b, respectively.

3. Principle

The soil saturation extract is diluted based on its electrical conductivity (EC_S). The diluted sample is injected into the ion chromatograph. The anions and cations are separated and then measured by conductivity. Standard concentrations

of anions and cations are used to calibrate the system. A calibration curve is determined, and the ion concentrations are calculated. The extracted anions F^-, CH_3COO^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, and PO_4^{3-} are reported in mmol (−) L^{-1}. The cations Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+} are reported in mmol (+) L^{-1}. This same method may also be used for water analysis.

3.1 Interferences

Some saturation extracts contain suspended solids. Filtering after extraction removes the particles.

Organic anions that have low molecular weight will co-elute with inorganic anions from the column.

4. Apparatus

4.1 Ion chromatograph

4.2 Digital diluter/dispenser, with syringes, 10,000-µL and 1,000-µL

4.3 1.5-mL polypropylene vial with septa cap

4.4 Centrifuge tubes, 15-mL

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.2 Helium gas. De-gas RODI water used in eluent generation for at least 15 minutes.

5.3 **Primary stock standards**; commercially made, high purity:

1,000 mg/L Br^-, Bromide Standard
1,000 mg/L Cl^-, Chloride Standard
1,000 mg/L F^-, Fluoride Standard
1,000 mg/L NO^{3-}, Nitrate Standard
1,000 mg/L NO^{2-}, Nitrite Standard
1,000 mg/L SO_4^{2-}, Sulfate Standard
1,000 mg/L PO_4^{3-}, Phosphate Standard
1,000 mg/L CH_3COO^-, Acetate Standard
1,000 mg/L Na^+, Sodium Standard
1,000 mg/L NH_4^+, Ammonium Standard
1,000 mg/L K^+, Potassium Standard
1,000 mg/L Mg^{2+}, Magnesium Standard
1,000 mg/L Ca^{2+}, Calcium Standard

5.4 **Anion and cation calibration standards**

Components: Primary stock standards 1,000 mg L^{-1}, RODI water

- Refer to table 4F2c–1 for anion mixing instructions.
- Refer to table 4F2c–2 for anion concentrations.
- Refer to table 4F2c–3 for cation mixing instructions.
- Refer to table 4F2c–4 for cation concentrations.
- Make fresh weekly.
- Cation calibration standards are used as a quality control for anion balances and results. Cations are tested in addition to the anions to verify charge balance. Cations are tested as a means of quality control, even though only percent sulfate is reported.

5.4.1 Anion 4

- To a 500-mL glass volumetric flask, add the following in order:
  - 200 mL of RODI water
  - 0.5 mL of Fluoride Standard
  - 5.0 mL of Acetate Standard
  - 20.0 mL of Chloride Standard
  - 5.0 mL of Nitrite Standard
  - 20.0 mL of Nitrate Standard
  - 20 mL of Sulfate Standard
  - 20 mL of Phosphate Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.4.2 Anion 3

- To a 500-mL glass volumetric flask, add the following in order:
  - 200 mL of RODI water
  - 0.25 mL of Fluoride Standard
  - 2.5 mL of Acetate Standard
  - 10.0 mL of Chloride Standard
  - 2.5 mL of Nitrite Standard
  - 10.0 mL of Nitrate Standard
  - 10 mL of Sulfate Standard
  - 10 mL of Phosphate Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.4.3 Anion 2

- To a 500-mL glass volumetric flask, add the following in order:
  - 200 mL of RODI water
  - 50 mL of Anion 4 Standard

- Fill to volume with RODI water.
- Invert to mix.

5.4.4 Anion 1

- To a 500-mL glass volumetric flask, add the following in order:
  - 200 mL of RODI water
  - 25 mL of Anion 4 Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.4.5 Anion CVS

- To a 500-mL glass volumetric flask, add the following in order:
  - 200 mL of RODI water
  - 0.1 mL of Fluoride Standard
  - 1.0 mL of Acetate Standard
  - 4.0 mL of Chloride Standard
  - 1.0 mL of Nitrite Standard
  - 4.0 mL of Nitrate Standard
  - 4.0 mL of Sulfate Standard
  - 4.0 mL of Phosphate Standard
  - Fill to volume with RODI water.
- Invert to mix.

Table 4F2c–1.—Preparation of Anion Calibration Standards Anion 1–Anion 4 and Calibration Verification Standard. (Prepare in 500-mL volumetric flasks.)

Calibration Std.	Fluoride	Acetate	Chloride	Nitrite	Nitrate	Sulfate	Phosphate	RODI Water
	(mL)	*(mL)*	*(mL)*	*(mL)*	*(mL)*	*(mL)*	*(mL)*	
Anion 4 (High)	0.5	5	20	5	20	20	20	Fill to 500 mL with RODI water
Anion 3 (Mid)	0.25	2.5	10	2.5	10	10	10	
Anion 2 (Low)	Add 50 mL of Anion 4 standard to 500-mL flask							
Anion 1 (Low Low)	Add 25 mL of Anion 4 standard to 500-mL flask							
Anion CVS	0.1	1	4	1	4	4	4	

Table 4F2c–2.—Concentrations of Anion Calibration Standards Anion 1–Anion 4 and Calibration Verification Standard.

Calibration Std.	Fluoride	Acetate	Chloride	Nitrite	Nitrate	Sulfate	Phos-phate
	(ppm)	*(ppm)*	*(ppm)*	*(ppm)*	*(ppm)*	*(ppm)*	*(ppm)*
Anion 4 (High)	1	10	40	10	40	40	40
Anion 3 (Mid)	0.5	5	20	5	20	20	20
Anion 2 (Low)	0.1	1	4	1	4	4	4
Anion 1 (Low Low)	0.05	0.5	2	0.5	2	2	2
Anion CVS	0.2	2	8	2	8	8	8

5.4.6 Cation 4

- To a 500-mL glass volumetric flask, add the following in order:
  - 200 mL of RODI water
  - 15 mL of Sodium Standard
  - 5.0 mL of Ammonium Standard
  - 2.5 mL of Potassium Standard
  - 5.0 mL of Magnesium Standard
  - 15.0 mL of Calcium Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.4.7 Cation 3

- To a 500-mL glass volumetric flask, add the following in order:
  - 200 mL of RODI water
  - 7.5 mL of Sodium Standard
  - 2.5 mL of Ammonium Standard
  - 1.25 mL of Potassium Standard
  - 2.5 mL of Magnesium Standard
  - 7.5 mL of Calcium Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.4.8 Cation 2

- To a 500-mL glass volumetric flask, add the following in order:

- 200 mL of RODI water
- 50 mL of Cation 4 Standard
- Fill to volume with RODI water.

- Invert to mix.

5.4.9 Cation 1

- To a 500-mL glass volumetric flask, add the following in order:
  - 200 mL of RODI water
  - 25 mL of Cation 4 Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.4.10 Cation CVS

- To a 500-mL glass volumetric flask, add the following in order:
  - 200 mL of RODI water
  - 3.0 mL of Sodium Standard
  - 1.0 mL of Ammonium Standard
  - 0.5 mL of Potassium Standard
  - 1.0 mL of Magnesium Standard
  - 3.0 mL of Calcium Standard
  - Fill to volume with RODI water.
- Invert to mix.

Table 4F2c–3.—Preparation of Cation Calibration Standards Cation 1–Cation 4 and Calibration Verification Standard. (Prepare in 500-mL volumetric flasks.)

Calibration Std.	Sodium	Ammoni-um	Potassium	Magnesium	Calcium	RODI Water
	(mL)	*(mL)*	*(mL)*	*(mL)*	*(mL)*	
Cation 4 (High)	15	5	2.5	5	15	Fill to 500 mL with RODI water
Cation 3 (Mid)	7.5	2.5	1.25	2.5	7.5	
Cation 2 (Low)	Add 50 mL of Cation 4 standard to 500-mL flask					
Cation 1 (Low Low)	Add 25 mL of Cation 4 standard to 500-mL flask					
Cation CVS	3	1	0.5	1	3	

Table 4F2c–4.—Concentrations of Cation Calibration Standards Cation 1–Cation 4 and Calibration Verification Standard.

Calibration Std.	Sodium	Ammonium	Potassium	Magnesium	Calcium
	(ppm)	*(ppm)*	*(ppm)*	*(ppm)*	*(ppm)*
Cation 4 (High)	30	10	5	10	30
Cation 3 (Mid)	15	5	2.5	5	15
Cation 2 (Low)	3	1	0.5	1	3
Cation 1 (Low Low)	1.5	0.5	0.25	0.5	1.5
Cation CVS	6	2	1	2	6

6. Health and Safety

Warning.—Many metal salts are extremely toxic and may be fatal if ingested.

Personal Protective Equipment (PPE).—When preparing reagents, especially concentrated acids and bases, use disposable gloves with appropriate polymer rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids. Dispense concentrated acids and base in fume hood.

Follow the manufacturer's safety precautions when using the ion chromatograph.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Set-up and operation of ion chromatograph (IC).—Refer to the manufacturer's manual for the set-up and operation of the chromatograph. Tables 4F2c–5 and 4F2c–6 show examples of instrument parameters, ranges, and typical settings.

Table 4F2c–5.—Example of Instrument Anion Parameters.

Anion Parameters	Range and/or Typical Setting
Calibration model	Peak Area
Detector	Conductivity
Column type	Dionex Ionpac CS12A
Gradient program	Gradient
Column program	Hold 13 mmol KOH, 9 min/linear increase to 55 mmol KOH, 9–16 min/hold 55 mmol KOH, 16–20 min
Pump flow setting	0.9 mL/min
Pump pressure	≈2,700 psi
Injection volume	25 µL
Column temperature	30 ºC
Suppressor current	112 mA

Table 4F2c–6.—Example of Instrument Cation Parameters.

Cation Parameters	Range and/or Typical Setting
Calibration model	Peak Area
Detector	Conductivity
Column type	Dionex Ionpac CS12A
Gradient program	Isocratic
Column program	20 mmol Methane Sulfonic Acid
Pump flow setting	0.9 mL/min
Pump pressure	≈2,700 psi
Injection volume	25 µL
Column temperature	30 ºC
Suppressor current	53 mA

8.2 Dilution of sample extracts.—Dilute samples according to table 4F2c–7 based on saturated paste electrical conductivity (EC).

8.3 IC Calibration and Analysis

8.3.1 Calibrate the chromatograph and analyze samples according to the instrument method. Analyze a CVS for both anions and cations every 12 samples. If the CVS is outside the accepted range (+/- 10%), recalibrate and re-analyze from the last passing CVS.

Table 4F2c–7.—Paste Extracts and Dilution Factors.

EC of Saturated Paste Extract		Dilution Factor
From	To	
138.5	250	6,000
100.3	138.5	3,000
56.5	100.3	1,500
27.6	56.5	800
13.3	27.6	400
7.1	13.3	200
4.1	7.1	100
2.5	4.1	50
1.6	2.5	20
1.1	1.6	10
0.9	1.1	5
0.0	0.9	3

8.3.2 If samples are outside the calibration range for one or more analytes, further dilution of the sample extract is required. Dilute sample extracts with RODI water and re-analyze.

8.3.3 Perform one quality control using Anion CVS and Cation CVS for every 12 samples. If reading is not within the accepted range (+/- 10%), recalibrate and re-analyze from the last CVS that is within range.

8.4 Record analyte readings to 0.01 mg L^{-1}.

9. Calculations

9.1 Concentrations are converted from mg L^{-1} to mmol (−) L^{-1} for anions and to mmol (+) L^{-1} for cations.

9.2 Analyte Concentration in Soil (mmol L^{-1}) = (A x B) / C

A = Analyte (F^-, CH_3COO^-, Cl^-, NO^{2-}, NO^{3-}, $SO4^{2-}$, PO_4^{3-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) concentration in extract (mg L^{-1})

B = Dilution ratio, if needed

C = Equivalent weight

Equivalent Weight	
Analyte	**mg mmol L^{-1}**
F^-	19.00
CH_3COO^-	59.04
Cl^-	35.45
NO_2^-	46.01
NO_3^-	62.00
SO_4^{2-}	48.03
PO_4^{3-}	31.66
Na^+	22.99
NH_4^+	18.04
K^+	39.10
Mg^{2+}	12.20
Ca^{2+}	20.04

9.3 Report the saturation extraction anions (F^-, CH_3COO^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-} to the nearest 0.1 (mmol (−) L^{-1}) and cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) to the nearest 0.1 (mmol (+) L^{-1}).

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist for final review.

10.6 Compare individual results to method detection limits (MDL) and practical quantitation limits (PQL) before reporting analysis results.

10.6.1 Report numerical values for results that are above the PQL.

10.6.2 Report “trace” for results that are between the MDL and PQL.

10.6.3 Report “non-detect” for results that are below the MDL.

MDL and PQL in Reporting Units

Analyte	MDL	PQL
	(mg kg^{-1} of oven-dried soil)	*(mg kg^{-1} of oven-dried soil)*

11. References

Khym, J.X. 1974. Analytical ion-exchange procedures in chemistry and biology: Theory, equipment, techniques. Prentice-Hall, Inc., Englewood Cliffs, NJ.

U.S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. L.A. Richards (ed.). USDA Agric. Handbook 60. U.S. Govt. Print. Office, Washington, DC.

Electrical Conductivity and Soluble Salts (4F)

Saturated Paste (4F2)

Saturated Paste Extraction (4F2c)

Automatic Extractor (4F2c1)

Automatic Titrator (4F2c1c)

Combination pH-Reference Electrode (4F2c1c1)

Acid Titration, H_2SO_4 (4F2c1c1a)

Carbonate and Bicarbonate (4F2c1c1a1-2)

Air-Dry, <2 mm (4F2c1c1a1-2a1)

1. Introduction to Saturated Paste Carbonate/Bicarbonate

Carbonate and bicarbonate anions are among those ions that are most dependent upon soil moisture. The total dissolved ion amounts generally increase with increasing soil moisture content. Interpretations about carbonate and bicarbonate ions in soil solution are highly dependent upon soil solution conditions.

2. Scope and Field of Application

The water-soluble anions that usually are determined in saturation extracts are carbonate, bicarbonate, sulfate, chloride, nitrate, nitrite, fluoride, and phosphate. Carbonate and bicarbonate are analyzed by titration.

- In saturation extracts, carbonate is measurable if the pH >9 (U.S. Salinity Laboratory Staff, 1954).
- The bicarbonate concentration is seldom >10 meq L^{-1} in the absence of carbonate anions (U.S. Salinity Laboratory Staff, 1954).
- The bicarbonate concentration at pH ≤7 seldom exceeds 3 or 4 meq L^{-1} (U.S. Salinity Laboratory Staff, 1954).

3. Principle

An aliquot of the saturation extract is titrated on an automatic titrator to pH 8.25 (carbonate) and pH 4.60 (bicarbonate) end points. The carbonate and bicarbonate are calculated from the titers, aliquot volume, blank titer, and acid normality. Carbonate and bicarbonate are reported in mmol (-) L^{-1} (meq L^{-1}).

3.1 Interferences

Wiping the electrode dry with a cloth, laboratory tissue, or similar material may cause electrode polarization. Clean the pH electrode by rinsing with reverse osmosis (RO) water.

Slow electrode response may cause the end point to be overshot. Proper cleaning with RODI water only and appropriate storage are critical for electrode accuracy. If damage or contamination is suspected, change the electrode.

Blanks may not titrate properly because some sources of reverse osmosis (RO) water have a low pH.

4. Apparatus

4.1 Automatic titrator, with control unit, sample changer, dispenser, and software

4.2 Combination pH-reference electrode

4.3 Pipettes, electronic digital, 5-mL, with tips

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Sulfuric acid (H_2SO_4) (CAS# 7664-93-9), concentrated, 36 *N*

5.3 Helium gas helium (minimum purity 99.999%)

5.4 **Sulfuric acid solution, 0.0240 *N,* standardized**

Components: Concentrated sulfuric acid (H_2SO_4), RODI water, degassed (≈15 min)

- In a 5-L polyethylene carboy, add the following in order:
  - 4 L degassed RODI water
  - 2.67 mL of concentrated sulfuric acid
- Standardize the acid after preparation. Refer to: Standardization of Acids (method 4A).

5.5 Buffers, pH 4.00, 7.00, and 9.18

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Dispense concentrated acids in a fume hood. Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids.

Follow the manufacturer's safety precautions when using the automatic titrator.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. This test uses the saturated paste extract obtained in method 4F2c: Saturated Paste Extraction.

8. Procedure

8.1 Pipette 3 mL of the saturated paste extract into a 250-mL titration beaker.

8.2 Add 72 mL of RO water into the titration beaker. Final volume is 75 mL for

blanks and samples. Run 8 to 12 blanks of RO water through the titration procedure.

8.3 Refer to manufacturer's manual for operation of the automatic titrator.

8.4 Calibrate automatic titrator with pH 4.00, 7.00, and 9.18 buffers.

8.5 Place the 250-mL titration beakers in the sample changer and begin titration.

- Carbonate titration end point is pH 8.25.
- Bicarbonate titration end point is pH 4.60.

8.6 Record titer and other titration parameters.

9. Calculations

9.1 Determine carbonate

$$CO_3^{2-}(\text{mmol}\ (-)\ L^{-1}) = [2 \times T_{8.25} \times N] / V$$

9.2 Determine bicarbonate

$$HCO_3^{-}(\text{mmol}\ (-)\ L^{-1}) = [(T_{4.60} - T_{8.25} - B) \times N] / V$$

$T_{8.25}$ = Titer for $CO_3^{2-} \rightarrow HCO_3^{-}$ (mL)

$T_{4.60}$ = Titer for $HCO_3^{-} \rightarrow H_2CO_3$ (mL)

N = Normality of H_2SO_4 (mmol(+)/mL)

B = Average titer of blank solution (mL)

V = Volume of saturation extract titrated (L)

2 = Multiplier to calculate CO_3^{2-}(mmol (−) L^{-1}) from $T_{8.25}$

9.3 Report saturation extract CO_3^{2-} and HCO_3^{-} concentrations to the nearest 0.1 mmol (−) L^{-1}.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

U.S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. L.A. Richards (ed.). USDA Agric. Handbook 60. U.S. Govt. Print. Office, Washington, DC.

Electrical Conductivity and Soluble Salts (4F)
Ratios and Estimates Related to Soluble Salts (4F3)
Exchangeable Sodium Percentage (ESP), NH_4OAc, pH 7.0 (4F3a)
ESP, Calculated without Saturated Paste Extraction (4F3a1)

$$ESP = (ES / CEC–7) \times 100$$

- ESP = Exchangeable sodium percentage
- ES = Extractable sodium (NH_4OAc extractable Na^+, (cmol (+) kg^{-1}))
- CEC–7 = CEC by NH_4OAc, pH 7.0 (cmol (+) kg^{-1})

The equation above may be used when the saturation extract is not prepared. Compute the exchangeable sodium percentage (ESP) by dividing the exchangeable sodium (ES) by CEC–7 (the CEC by NH_4OAc, pH 7.0) and multiplying by 100 (method 4F3a1). The ES is calculated by subtracting the water-soluble Na^+ determined in method 4F2c1a4 from the NH_4OAc extractable Na^+ determined in method 4B1a1b4 (U.S. Salinity Laboratory Staff, 1954). The CEC–7 is determined in method 4B1a1a1a1. In soil taxonomy, an ESP ≥15% is a criterion for natric horizons (Soil Survey Staff, 2014).

Electrical Conductivity and Soluble Salts (4F)
Ratios and Estimates Related to Soluble Salts (4F3)
Exchangeable Sodium Percentage (ESP), NH_4OAc, pH 7.0 (4F3a)
ESP, Calculated with Saturated Paste Extraction (4F3a2)

$$ESP = 100 \times \{Na_{ex} - [Na_{ws} \times (H_2O_{ws} / 1{,}000)]\} / CEC–7$$

- ESP = Exchangeable sodium percentage
- Na_{ex} = Extractable Na (NH_4OAc extractable Na^+, (cmol (+) kg^{-1}))
- Na_{ws} = Water-soluble Na (mmol (+) L^{-1})
- H_2O_{ws} = Water saturation percentage
- CEC–7 = CEC by NH_4OAc, pH 7.0 (cmol (+) kg^{-1})
- 1,000 = Conversion factor to (cmol (+) kg^{-1})
- 100 = Conversion factor to percent

When the saturation extract is prepared, the KSSL calculates the ESP by method 4F3a2 and the equation above. Exchangeable Na is computed with acceptable accuracy unless salt contents are >20 mmhos cm^{-1} (dS m^{-1}) at 25 °C. Exchangeable Na equals extractable Na minus saturation-extract Na multiplied by saturation percentage. Saturation percentage is the water percentage in the saturated paste divided by 1,000. Exchangeable Na can be determined with greater accuracy than the other cations in the presence of gypsum or carbonates. If exchangeable K is negligible compared to exchangeable Ca and Mg, then exchangeable Ca plus Mg equals CEC (NH_4OAc, pH 7.0) minus

exchangeable Na. This approximation is suitably reproducible for comparison between soils and for soil classification. Exchangeable Ca can be computed in the same manner as exchangeable Na. Results are not as satisfactory for exchangeable Ca when computed in the presence of carbonates or large amounts of gypsum.

Electrical Conductivity and Soluble Salts (4F)
Ratios and Estimates Related to Soluble Salts (4F3)
Sodium Adsorption Ratio (SAR) (4F3b)

$$SAR = \frac{[Na^{+}]}{\sqrt{\frac{[Ca^{++}]+[Mg^{++}]}{2}}}$$

SAR = Sodium Adsorption Ratio

- Na^{+} = Water soluble Na^{+} (mmol (+) L^{-1})
- Ca^{2+} = Water soluble Ca^{2+} (mmol (+) L^{-1})
- Mg^{2+} = Water soluble Mg^{2+} (mmol (+) L^{-1})

Compute the sodium adsorption ratio (SAR) by dividing the molar concentration of the monovalent cation Na^{+} by the square root of the molar concentration of the divalent cations Ca^{2+} and Mg^{2+} (U.S. Salinity Laboratory Staff, 1954). The water soluble Ca^{2+}, Mg^{2+}, and Na^{+} are determined in methods 4F2c1a1, 4F2c1a2, and 4F2c1a4, respectively. The SAR was developed as a measurement of the quality of irrigation water, particularly when the water is used for irrigating soils that are salt- or sodium-affected (U.S. Salinity Laboratory Staff, 1954). In soil taxonomy, a SAR ≥13 is a criterion for natric horizons (Soil Survey Staff, 2014). The KSSL calculates the sodium adsorption ratio by method 4F3b.

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Soil Survey Staff. 2014. Keys to soil taxonomy. 12th ed. USDA–NRCS.

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Electrical Conductivity and Soluble Salts (4F)
Ratios and Estimates Related to Soluble Salts (4F3)
Estimated Total Salt (4F3c)

Use the charts and graphs available in U.S. Salinity Laboratory Staff (1954) to estimate total salt content (4F3c) from the electrical conductivity (EC_S) of the

saturation extract (method 4F2b1). The essential relations are summarized in the following equation:

$$\text{Total Salt in Soil (ppm)} = [-4.2333 + (12.2347 \times EC_S)_+ (0.058 \times EC_S^2) - (0.0003 \times EC_S^3)] \times 0.000064 \times SP$$

- EC_S = Electrical conductivity of saturation extract
- SP = Saturation percentage of saturation paste

The following equations were previously used to estimate total salt content.

$$\text{Log Total Salt in Soil (ppm)} = 0.81 + [1.08 \times \text{Log } EC_S \text{ (mmhos cm}^{-1})] + \text{Log SP}$$

- EC_S = Electrical conductivity of saturation extract
- SP = Saturation percentage of saturation paste

$$\text{Total Salt in Soil (\%)} = \text{Total salt (ppm)} \times 10^{-4}$$

The previously used equations are applicable to saturation extracts with an EC_S <20 mmhos cm^{-1}. Deviations occur at higher concentrations of salt.

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Soil Survey Staff. 2014. Keys to soil taxonomy. 12th ed. USDA–NRCS.

U.S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. L.A. Richards (ed.). USDA Agric. Handbook 60. U.S. Govt. Print. Office, Washington, DC.

Selective Dissolutions (4G)

Selective dissolution data have been used extensively in the study of the noncrystalline material content of soils and sediments. The continuum of crystalline order ranges from no long-range order through paracrystalline and poorly crystalline to well crystalline (Follet et al., 1965). Over the years, various terms have been used to describe broad groupings of soil components; e.g., crystalline phyllosilicates, amorphous, poorly crystalline, paracrystalline, noncrystalline, allophane, imogolite, short-range-order minerals (SROMs), and others (Jackson et al., 1986). These groupings have been related, in part, to various laboratory analyses and have thereby been operationally defined quantitatively and semiquantitatively by these analyses (Jackson et al., 1986).

Selective dissolution data are necessary for independent determinations of various inorganic constituents of soils. The data are needed because many physical analytical methods have difficulty in estimating (or even recognizing) the presence of noncrystalline and paracrystalline free oxides or aluminosilicates mixed with crystalline soil components (Jackson et al., 1986). Crystalline free oxides and phyllosilicates of soils can be identified qualitatively and estimated semiquantitatively by x-ray diffraction analysis. Those soils containing hydroxyls (-OH groups), e.g., kaolinite, gibbsite, and goethite, can sometimes be determined quantitatively by differential thermal analysis (DTA), differential scanning colorimetry (DCS), and thermogravimetric analysis (TGA). Refer to additional discussion on x-ray diffraction and thermal analysis in the mineralogy section (7) of this manual.

Chemical methods cannot perfectly distinguish the degrees of crystallinity; selective chemical dissolution data present difficulties and some caution is required in the interpretation of these analytical data (van Wambeke, 1992). Refer to Wada (1989) regarding the dissolution of Al, Fe, and Si in various clay constituents and organic complexes by treatment with different reagents.

The KSSL routinely performs three selective chemical dissolutions: dithionite-citrate (method 4G1a1-3), ammonium oxalate (method 4G2a1a1-5), and sodium pyrophosphate (method 4G3a1-3).

Dithionite-Citrate Extraction

- Dithionite-citrate extractable Fe (Fe_d) is considered a measure of “free iron” in soils and, as such, is pedogenically significant. “Free iron” is also considered an important factor in P-fixation and soil aggregate stability.
- Data regarding dithionite-citrate extractable Fe are of interest in studies of soil genesis and classification because of its increasing concentration with increasing weathering and its effect on soil colors (Schwertmann, 1992).
- The dithionite-citrate extraction originally had two objectives. The first was to determine the free Fe oxides. The second was to remove the amorphous coatings and crystals of free Fe oxide, which were acting as

cementing agents, for subsequent physical and chemical analysis of soils, sediments, and clay minerals (Weaver et al., 1968; Jackson, 1969; Jackson et al., 1986).

Sodium Pyrophosphate Extraction

- Sodium pyrophosphate extracting solutions tend to selectively extract mainly Fe and Al associated with organic compounds.
- Numerous evaluations have indicated that the pyrophosphate extraction does not necessarily correlate with organic-bound Fe and Al (Schuppli et al., 1983; Kassim et al., 1984; Parfitt and Childs, 1988; Birkeland et al., 1989). At one time, sodium-pyrophosphate extractable Fe and Al in conjunction with dithionite-citrate data were used to help identify translocated Al and Fe humus complexes in spodic horizons (Soil Survey Staff, 1975).
- Pyrophosphate not only extracts organic-bound Fe but also peptizes solid particles of ferrihydrite and in some instances even goethite (Yuan et al., 1993).
- At one time, sodium pyrophosphate extract data in conjunction with dithionite-citrate data were chemical requirements for spodic horizons and were referred to as spodic horizon criteria on the KSSL data sheets. These data have been replaced by other criteria (Soil Survey Staff, 2014).

Ammonium Oxalate Extraction

- Ammonium oxalate extraction measures the quantities of poorly crystalline materials in the soil. However, chemical methods cannot distinguish degrees of crystallinity, and some caution must be exercised in the interpretation of the analytical data (van Wambeke, 1992).
- The ammonium oxalate extraction is assumed to dissolve selectively “active” Al and Fe components that are present in noncrystalline materials as well as associated or independent, poorly crystalline silica. The method also extracts allophane, imogolite, Al+Fe humus complexes, and amorphous or poorly crystallized oxides and hydroxides. Opaline Si is not dissolved by this method (Wada, 1977; Higashi and Ikeda, 1974; Hodges and Zelazny, 1980; Schwertmann, 1959, 1964; McKeague and Day, 1966; McKeague et al., 1971; Fey and LeRoux, 1976).
- The data on the effect of this procedure on clay minerals have been conflicting. In general, however, the ammonium oxalate treatment is considered to have very little effect on phyllosilicates (kaolinite, montmorillonite, and illite) or gibbsite.

Application, Ratios, and Estimates

- The Fe_o/Fe_d ratio is often calculated because it is considered an

approximation of the relative proportion of ferrihydrite in soils (Schwertmann, 1985).

- Fe_d is considered a measure of the total pedogenic Fe (e.g., goethite, hematite, lepidocrocite, and ferrihydrite).
- Ammonium oxalate extractable Fe (Fe_o), probably ferrihydrite, is a measure of the paracrystalline Fe (Birkeland et al., 1989).

- The weight of Fe atoms is approximately twice that of Al atoms. In evaluating the relative proportion of Fe and Al atoms solubilized by ammonium oxalate, the weight percent of Fe must be divided by two; i.e., AlO+½FeO. Refer to the Soil Survey Staff (2014, 2011) for more detailed discussion of these taxonomic criteria.
- Mn_d is considered the "easily reducible Mn."
- Al_d and Al_o are pedogenically significant.
  - The Al_d represents the Al substituted in Fe oxides, which can have an upper limit of 33 percent mole substitution (Schwertmann et al., 1977; Schwertmann and Taylor, 1989).
  - The Al_o is generally an estimate of the total pedogenic Al in soils dominated by allophane, imogolite, and organically-bound Al (Wada, 1977).
  - The Al_d extract is commonly less than the Al_o (Birkeland et al., 1989) and so does not necessarily represent the total pedogenic Al (Wada, 1977).
- Allophane in soils can be estimated from the Al_o and Si_o and the pyrophosphate extractable Al (Al_p) (Parfitt and Henmi, 1982; Parfitt and Wilson, 1985; Parfitt, 1990). The Al_o represents the Al dissolved from allophane, imogolite, and Al-humus complexes, and the Al_p is the Al from the Al-humus complexes alone (Parfitt and Kimble, 1989). The Al_o minus the Al_p gives an estimate of the Al in allophane and imogolite, whereas the Si_o gives an estimate of the Si in allophane and imogolite. The $(Al_o - Al_p)/Si_o$ times the molar ratio (28/27, which represents the atomic weights of Al and Si) is an estimate of the Al/Si ratio of allophane and imogolite in the soil.
- An optical density of ammonium oxalate extract (ODOE) of ≥0.25 is used as a chemical criterion for spodic materials (Soil Survey Staff, 2014). An increase in ODOE is used as an indicator of the accumulation of translocated organic materials in an illuvial horizon (Soil Survey Staff, 2014).

Selective chemical dissolution data are used as taxonomic criteria for mineralogy classes. For example, ammonium oxalate Fe and Si are used for the amorphic and ferrihydritic mineralogy classes and dithionite-citrate Fe is used for the ferritic mineralogy class. Ammonium oxalate extractable Al_o plus 0.5 Fe_o is also used as a taxonomic criterion for andic soil properties (Soil Survey Staff, 2014).

Terms describing selective dissolution have not been used consistently in the literature. In addition, there is not always a clear delineation between dissolution data, either conceptually or operationally. For more detailed discussion of the various soil terms and the application of selective chemical extractions, refer to Wada (1989) and Soil Survey Staff (2011).

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Selective Dissolutions (4G)
Dithionite-Citrate Extraction (4G1)
Inductively Coupled Plasma-Atomic Emission Spectrophotometer (4G1b)
Aluminum, Iron, Manganese, and Silicon (4G1b1-4)
Air-Dry or Field-Moist, <2 mm (4G1b1-4a-b1)

1. Introduction to CD Extraction Analysis via ICP–AES

Dithionite-citrate extractable Fe (Fe_d) is considered a measure of "free iron" in soils and, as such, is pedogenically significant. "Free iron" is also considered an important factor in P-fixation and soil aggregate stability. Data regarding dithionite-citrate extractable Fe are of interest in studies of soil genesis and classification because of its increasing concentration with increasing weathering and its effect on soil colors (Schwertmann, 1992).

2. Scope and Field of Application

Dithionite-citrate (CD) causes selective dissolution and extraction of Fe from ferric oxides (i.e., hematite and magnetite) and iron oxyhydroxides (i.e., goethite). Aluminum substituted into these minerals is extracted simultaneously with iron. Dithionite reduces ferric iron (Fe^{3+}), and citrate stabilizes it by chelation. Organically bound iron and aluminum are extracted if the citrate in the extracting solution is a stronger chelator than the organic molecules binding the Fe and Al. Manganese may also be extracted by this procedure. Iron extracted by citrate dithionite is related to the distribution of clay within the profile and is used to define anthric saturation; the ferritic, ferruginous, sesquic, and parasesquic mineralogy classes; and ferrihumic soil material.

3. Principle

The CD extracted aluminum, iron, manganese, and silica are measured by an inductively coupled plasma-atomic emission spectrophotometer (ICP–AES). The CD extractable Al, Fe, Mn, and Si are reported in percent.

3.1 Interferences

ICP–AES interferences are element dependent and are minimized or eliminated through wavelength selection, background correction, matrix matching, and use of internal standards as appropriate.

In general, gem tip, crossflow nebulizers are less sensitive to matrix matching effects as compared to other style nebulizers. If other nebulizer types are used, such as Meinhard, then the calibration standard matrix may need to be adjusted.

Filtered extracts can yield different recoveries of Fe, Mn, Al, and Si relative to unfiltered extracts.

4. Apparatus

4.1 Electronic balance, ±1.0-mg sensitivity

4.2 Mechanical reciprocating shaker, 200 oscillations min^{-1}, 1½-in strokes

4.3 ICP–AES using a gem tip, cross flow nebulizer, and Scott type spray chamber

4.4 Centrifuge capable of 4,000 rpm

4.5 Vortexer, mini

4.6 1-mL and 10-mL electronic pipettes

4.7 Bottle top dispenser, 30-mL

4.8 Test tubes, 15-mL

4.9 Volumetric flasks, class A, 250-mL, 500-mL, and 1,000-mL

4.10 Measuring scoop, handmade, 0.4 g calibrated

4.11 Centrifuge tubes, 50-mL, disposable

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade reagent water

5.2 Compressed argon (minimum purity 99.99%)

5.3 Compressed nitrogen (minimum purity 99.99%)

5.4 Sodium citrate dihydrate ($Na_3C_6H_5O_7•2H_2O$) (CAS# 6132-04-3)

5.5 Sodium dithionite ($Na_2S_2O_4$) (CAS# 7775-14-6), purified powder

5.6 **Primary stock standards;** commercially made, high purity

1,000 mg/L Al, Aluminum Standard

1,000 mg/L Fe, Iron Standard

1,000 mg/L Mn, Manganese Standard

1,000 mg/L Si, Silica Standard

1,000 mg/L Lu, Lutetium Standard

5.7 **Sodium citrate solution, 0.57 M**

Components: Sodium citrate dihydrate ($Na_3C_6H_5O_7•2H_2O$), RODI water

- To a 2-L glass volumetric, add the following in order:
  - 1 L of RODI water
  - 336 g sodium citrate dihydrate
  - Fill to volume with RODI water.
- Invert to mix.

5.8 **ICP–AES calibration standards (Reagents CD1-CD3)**

5.8.1 Reagent CD3 (High)

- To a 500-mL glass volumetric flask, add the following in order:

- 200 mL of RODI water
- 25 mL of sodium citrate solution
- 5 mL of 1,000 mg/L Al, Aluminum Standard
- 25 mL of 1,000 mg/L Fe, Iron Standard
- 1 mL of 1,000 mg/L Mn, Manganese Standard
- 2.5 mL of 1,000 mg/L Si, Silicon Standard
- Fill to volume with RODI water.

- Invert to mix.

5.8.2 Reagent CD2 (Low)

- To a 500-mL glass volumetric flask, add the following in order:
  - 200 mL of RODI water
  - 25 mL of sodium citrate solution
  - 2.5 mL of 1,000 mg/L Al, Aluminum Standard
  - 12.5 mL of 1,000 mg/L Fe, Iron Standard
  - 0.5 mL of 1,000 mg/L Mn, Manganese Standard
  - 1.25 mL of 1,000 mg/L Si, Silicon Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.8.3 Reagent CD1 (Internal standard)

- To a 500-mL glass volumetric flask, add the following in order:
  - 200 mL of RODI water
  - 5 mL of 1,000 mg/L Lu, Lutetium Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.8.4 Blank

- To a 500-mL glass volumetric flask, add the following in order:
  - 200 mL of RODI water
  - 25 mL of sodium citrate solution
  - Fill to volume with RODI water.
- Invert to mix.

5.9 Independent calibration verification standards

Components: Sodium citrate solution, high purity element standards, RODI water

Note: The calibration verification standard needs to be prepared independently of calibration Reagents CD1–CD3.

- Use different (brand, lot, or bottle) primary stock standards than those used for preparing the calibration standard Reagents CD1–CD3.

- To a 500-mL volumetric flask, add the following in order:
  - 200 mL of RODI water
  - 25 mL of 0.57 *M* sodium citrate solution
  - 3.5 mL of 1,000 mg/L Al, Aluminum Standard
  - 12.5 mL of 1,000 mg/L Fe, Iron Standard
  - 0.5 mL of 1,000 mg/L Mn, Manganese Standard
  - 1.25 mL of 1,000 mg/L Si, Silicon Standard
  - Fill to volume with RODI water.
- Invert to mix.

Table 4G1b–1.—Preparation of ICP–AES Calibration Standards CD1–CD3 and Calibration Verification Standard. (Prepare in 500-mL volumetric flasks.)

Element or Component	Blank	CD1 Internal Standard	CD2 Low	CD3 High
	(mL)	*(mL)*	*(mL)*	*(mL)*
Sodium citrate solution (CVS)	25	--	25	25
Al	--	--	2.5	5
Fe	--	--	12.5	25
Mn	--	--	0.5	1
Si	--	--	1.25	2.5
Lu	--	5	--	--
RODI water	Fill to volume	200 mL initially, fill to volume		

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids. Dispense concentrated acids and bases in fume hood.

Sodium dithionite may spontaneously ignite if allowed to become moist, even by atmospheric moisture. Keep dithionite in a fume hood.

Gas cylinders should be chained or bolted in an upright position following standard KSSL laboratory safety procedures.

Follow the manufacturer's safety precautions when using the ICP–AES.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Extraction of Al, Fe, Mn, and Si

8.1.1 Weigh 0.75 g of <2-mm or fine-grind, air-dry soil sample to the nearest mg and place in a 50-mL centrifuge tube. If sample is moist, weigh enough soil to achieve ≈0.75 g of air-dry soil.

8.1.2 To each sample add 0.4 g of sodium dithionite, use one calibrated scoop.

8.1.3 Using a 30-mL bottle top dispenser, add 25 mL of 0.57 *M* sodium citrate solution to each sample.

8.1.4 Cap tubes and shake briefly by hand to dislodge soil from tube bottom. Place tubes in rack.

8.1.5 Place rack in shaker and shake overnight (12 to 16 h) at 200 oscillations min^{-1} at room temperature (20 ±2 °C).

8.1.6 Remove tubes from shaker and manually shake tubes to dislodge any soil from cap. Allow samples to sit overnight.

8.1.7 The following day, centrifuge at 4,000 rpm for 15 minutes. The Fe, Mn, Al, and Si are determined by ICP–AES from a clear aliquot of solution.

8.1.8 Samples need to be poured off after centrifuging to prevent continued extraction of iron from the sample.

8.2 Dilution of Sample Extracts

8.2.1 Using electronic pipettes, dilute the samples 1:20 with RODI (0.5 mL of sample, 9.5 mL of RODI).

8.2.2 Calibrate the ICP–AES according to the instrument method and analyze samples.

Table 4G1b–2.—ICP–AES Reporting Wavelengths and Calibration Standards.

		Blank	CD Low	CD High	CD CVS	Estimated PQL for Element
			mg/L	*mg/L*	*mg/L*	*mg/L*
Reporting wavelengths	Al: 396.153	0	5	10	7	0.2
	Fe: 259.939	0	25	50	25	0.05
	Mn: 259.372	0	1	2	1	0.01
	Si: 251.611	0	2.5	5	2.5	0.2
Reference wavelengths	Al: 394.401	--				
	Fe: 238.204					
	Mn: 257.610					
	Si: 212.412					

8.2.3 If the solution concentration of the sample exceeds the high standard for a given element by 10x or greater, then an additional dilution is required. Dilute the out of range sample another 1:5 using RODI as the diluent to give a final dilution of 1:100. Re-analyze.

9. Calculations

9.1 Convert analyte concentrations (mg L^{-1}) to percent in soil as follows:

$$\text{Soil Al, Fe, Mn, Si (\%)} = (A \times B \times C \times R \times 100) / (E \times 1{,}000)$$

A = Sample extract reading (mg L^{-1})

B = Extract Volume (L)

C = Dilution, required

R = Air-dry/oven-dry ratio (method 3D1) or field-moist/oven-dry ratio (method 3D2)

E = Sample weight (g)

100 = Conversion factor to 100-g basis

1,000 = mg g^{-1}

9.2 Report percent CD extractable Al, Fe, Mn, and Si to the nearest 0.1 of a percent.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist for final review.

10.6 Compare individual results to method detection limits (MDL) and practical quantitation limits (PQL) before reporting analysis results.

10.6.1 Report numerical values for results that are above the PQL.

10.6.2 Report "trace" for results that are between the MDL and PQL.

10.6.3 Report "non-detect" for results that are below the MDL.

MDL and PQL in Reporting Units

Analyte	MDL	PQL
	(mg kg^{-1} of oven-dried soil)	*(mg kg^{-1} of oven-dried soil)*

11. References

Aguilera, N.H., and M.L. Jackson. 1953. Iron oxide removal from soils and clays. Soil Sci. Soc. Am. Proc. 17:359–364.

Jackson, M.L. 1969. Soil chemical analysis—Advanced course. 2nd ed. Univ. Wisconsin, Madison.

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Selective Dissolutions (4G)
Ammonium Oxalate Extraction (4G2)
Automatic Extractor (4G2a)
Inductively Coupled Plasma Atomic Emission Spectrophotometer (4G2a1)
Radial Mode (4G2a1a)
Aluminum, Iron, Manganese, Phosphorus, and Silicon (4G2a1a1-5)
Air-Dry or Field-Moist, <2 mm (4G2a1a1-5a-b1)

UV-Visible Spectrophotometer, Dual Beam (4G2a2)
Absorbance (4G2a2a)
Optical Density (4G2a2a1)
Air-Dry or Field-Moist, <2 mm (4G2a2a1a-b1)

1. Introduction to Ammonium Oxalate Extract Analysis via ICP–AES

Ammonium oxalate is used in the selective dissolution and extraction of organically complexed Fe and Al, non-crystalline hydrous oxides of Fe and Al, allophane, and amorphous aluminosilicates (Wada, 1989). This extraction is also sometimes referred to as “acid ammonium oxalate,” “acid oxalate,” “oxalate-oxalic acid,” or “oxalic acid-ammonium oxalate.”

2. Scope and Field of Application

Ammonium oxalate used in conjunction with citrate-dithionite can be used to identify sources of iron and aluminum in the soil. The value for oxalate extractable aluminum plus one-half the extractable iron is used in the identification of andic soil properties. The optical density of the extracted solution is used to identify spodic material. The relative amount of oxalate extractable iron and silicon is used to define amporphic and ferrihydritic mineralogy classes.

3. Principle

A soil sample is treated with an ammonium oxalate extraction solution. The Al, Fe, Mn, P, and Si extracted by the ammonium oxalate are measured by inductively coupled plasma atomic emission spectrophotometry (ICP–AES). Results for Al, Fe, and Si are reported as percent. Results for Mn and P are reported in mg kg^{-1}. In method 4G2a2a1, the optical density of the extract is measured with a UV spectrophotometer at 430 nm.

3.1 Interferences

ICP–AES interferences are element dependent and are minimized or eliminated through wavelength selection, background correction, matrix matching, and use of internal standards as appropriate.

The ammonium oxalate extraction is sensitive to UV light. Covering the samples during extraction reduces the dissolution effect that ammonium oxalate has on crystalline oxides and clay minerals. If the sample contains large amounts of amorphous material (>2% Al), an alternate sample treatment should be used, such as shaking with 0.275 *M* ammonium oxalate, pH 3.25, 1:100 soil to extractant.

4. Apparatus

4.1 Electronic balance, ±1.0-mg sensitivity
4.2 Dispenser, 50-mL
4.3 Pipettes, electronic digital, 50-mL, 10,000-µL and 1,000-µL
4.4 Centrifuge
4.5 Containers, polyethylene
4.6 Inductively coupled plasma atomic emission spectrophotometer (ICP–AES)
4.7 Test tubes, 15-mL, 16 mm x 100 mm
4.8 Vortexer, mini
4.9 Spectrophotometer
4.10 Cuvettes, plastic, 4.5-mL, 1-cm light path
4.11 Centrifuge tubes, 50-mL, disposable

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water
5.2 Argon gas, purity 99.9%
5.3 Nitrogen, purity 99.9%
5.4 Ammonium oxalate ($(NH_4)_2C_2O_4 \cdot 2H_2O$) (CAS# 6009-70-7)
5.5 Oxalic acid ($H_2C_2O_4 \cdot H_2O$) (CAS # 6153-56-6)
5.6 pH buffers, 4.00, 7.00, and 9.18
5.7 **Primary stock standards;** commercially made, high purity:

1,000 mg/L Fe, Iron Standard
1,000 mg/L Al, Aluminum Standard
1,000 mg/L Mn, Manganese Standard
1,000 mg/L P, Phosphorus Standard
1,000 mg/L Lu, Lutetium Standard
1,000 mg/L Si, Silicon Standard

5.8 **Ammonium oxalate extracting solution, 0.2 M, pH 3.0**

Components: Ammonium oxalate ($(NH_4)_2C_2O_4 \cdot 2H_2O$), oxalic acid ($H_2C_2O_4 \cdot H_2O$), RODI water

- This solution is prepared in two parts.
- Solution A (base): To a 10-L carboy, add the following in order:
  - 10 L of RODI water
  - 284 g of ammonium oxalate
- Swirl to mix.
- Solution B (acid): To a 10-L carboy, add the following in order:
  - 10 L of RODI water
  - 252 g of oxalic acid
- Swirl to mix.
- Mix 4 parts Solution A with 3 parts Solution B.
- The resulting ammonium oxalate solution should be pH 3. If not, adjust the pH by adding either more solution A (base) or solution B (acid).
- Store in a polypropylene bottle.

5.9 Internal standard

Components: 1,000 mg/L Lu, Lutetium Standard; RODI water

- To a 500-mL glass volumetric flask, add the following in order:
  - 300 mL of RODI water
  - 5 mL of 1,000 mg/L Lu, Lutetium Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.10 Elemental calibration and verification standard solutions (Reagents OX1–OX5)

Components: Ammonium oxalate extracting solution; high purity standards: Fe, Si, Al, Mn, and P; RODI water

- Mixing instructions are outlined in 4G2a–1.
- Store in polyethylene bottles.
- Store in refrigerator.
- Final standard concentrations are in table 4G2a–2.

5.10.1 Reagent OX 1 (Very Low Si)

- To a 1 L volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 100 mL of ammonium oxalate extracting solution
  - 2 mL of 1,000 mg/L Si, Silicon Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.10.2 Reagent OX 2 (Low Si)

- To a 1 L volumetric flask, add the following in order:

- 500 mL of RODI water
- 100 mL of ammonium oxalate extracting solution
- 5 mL of 1,000 mg/L Si, Silicon Standard
- Fill to volume with RODI water.

- Invert to mix.

5.10.3 Reagent OX 3 (Low)

- To a 1 L volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 100 mL of ammonium oxalate extracting solution
  - 10 mL of 1,000 mg/L Si, Silicon Standard
  - 10 mL of 1,000 mg/L Fe, Iron Standard
  - 10 mL of 1,000 mg/L Al, Aluminum Standard
  - 2 mL of 1,000 mg/L Mn, Manganese Standard
  - 3 mL of 1,000 mg/L P; Phosphorus Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.10.4 Reagent OX 4 (Mid)

- To a 1 L volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 100 mL of ammonium oxalate extracting solution
  - 30 mL of 1,000 mg/L Si, Silicon Standard
  - 30 mL of 1,000 mg/L Fe, Iron Standard
  - 30 mL of 1,000 mg/L Al, Aluminum Standard
  - 5 mL of 1,000 mg/L Mn, Manganese Standard
  - 10 mL of 1,000 mg/L P, Phosphorus Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.10.5 Reagent OX 5 (High)

- To a 1 L volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 100 mL of ammonium oxalate extracting solution
  - 60 mL of 1,000 mg/L Si, Silicon Standard
  - 60 mL of 1,000 mg/L Fe, Iron Standard
  - 60 mL of 1,000 mg/L Al, Aluminum Standard
  - 10 mL of 1,000 mg/L Mn, Manganese Standard
  - 20 mL of 1,000 mg/L P, Phosphorus Standard

- Fill to volume with RODI water.
- Invert to mix.

5.10.6 OX CVS

- To a 1 L volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 100 mL of ammonium oxalate extracting solution
  - 5 mL of 1,000 mg/L Si, Silicon Standard
  - 6 mL of 1,000 mg/L Fe, Iron Standard
  - 10 mL of 1,000 mg/L Al, Aluminum Standard
  - 0.5 mL of 1,000 mg/L Mn, Manganese Standard
  - 1.0 mL of 1,000 mg/L P, Phosphorus Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.10.7 OX Calibration blank

- The calibration blank is prepared fresh daily prior to analysis.
- To a 50-mL conical centrifuge tube, add the following in order:
  - 5 mL of ammonium oxalate extracting solution
  - 45 mL of RODI water.
- Invert to mix.

Table 4G2a–1.—Elemental Calibration and Verification Standard Solutions. (Prepared in 1-L volumetric flasks.)

Component or High Purity Standard	OX 1 Very Low Si	OX 2 Low Si	OX 3 Low	OX 4 Medium	OX 5 High	OX CVS
	(mL)	*(mL)*	*(mL)*	*(mL)*	*(mL)*	*(mL)*
Si	2	5	10	30	60	5
Fe	---	---	10	30	60	6
Al	---	---	10	30	60	10
Mn	---	---	2	5	10	0.5
P	---	---	3	10	20	1
0.2 *M* Ammonium oxalate	100	100	100	100	100	100
RODI water	Bring to 1 L with RODI water					

Table 4G2a–2.—Concentrations of Elemental Calibration and Verification Standard Solutions.

Component	OX 1 Very Low Si	OX 2 Low Si	OX 3 Low	OX 4 Medium	OX 5 High	OX CVS
	(mg L^{-1})	*(mg L^{-1})*	*(mg L^{-1})*	*(mg L^{-1})*	*(mg L^{-1})*	*(mg L^{-1})*
Si	2	5	10	30	60	5
Fe	---	---	10	30	60	6
Al	---	---	10	30	60	10
Mn	---	---	2	5	10	0.5
P	---	---	3	10	20	1

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Extraction of Fe, Mn, Al, Si, and P

8.1.1 Weigh 0.5 g of <2-mm, air-dry or 80-meshed (fine grind) soil to the nearest mg and place in 50-mL centrifuge tube. If sample is moist, weigh enough soil to achieve ≈0.5 g. Prepare one reagent blank (no sample in tube) and one soil standard per set of 24 samples.

8.1.2 Using a 50-mL electronic pipette, dispense 50 mL of ammonium oxalate extracting solution into each tube.

8.1.3 Cap the tubes and ensure the samples are thoroughly wetted. Shaking, swirling, or stirring may be required to wet organic samples. Cover samples with a black plastic bag to exclude light.

8.1.4 Shake samples a minimum of 4 hours (no longer than 5 hours) at 200 oscillations/minute.

8.1.5 After shaking, tap down samples to knock soil from the cap of the tube.

8.1.6 Centrifuge 15 minutes at 3,700 rpm.

8.1.7 Fill a 5-mL disposable tube with extract solution. This solution is reserved for determination of Fe, Mn, Al, Si, and P. If extracts will not be analyzed immediately after collection, then store samples at 4 °C.

8.2 Determination of Optical Density of Extract

8.2.1 For each sample extracted, fill a disposable cuvette with sample extract solution. Properly discard excess solution. Keep extracts covered to prevent further color development.

8.2.2 Place 4 mL of ammonium oxalate reagent blank in a disposable cuvette.

8.2.3 On the spectrophotometer, select 430-nm wavelength. Refer to manufacturer's manual for operation of the spectrophotometer.

8.2.4 Use the ammonium oxalate reagent blank to zero the spectrophotometer.

8.2.5 Record optical density of ammonium oxalate extract to nearest 0.001 unit.

8.2.6 If a sample has an absorbance higher than 2.0, a dilution is required. Dilute the sample 1:2, pipette 2 mL of sample and 2 mL of oxalate blank into a disposable cup, swirl the cup to mix and pour diluted sample into a clean cuvette. Read the diluted sample on the spectrophotometer and record the dilution in LIMS.

8.3 Dilution of Sample Extracts for ICP–AES Analysis

8.3.1 Dilute ammonium oxalate sample extracts (1:10) with RODI water.

8.3.2 Dilute 1-part ammonium oxalate sample extract with 9 parts ammonium oxalate extracting solution.

8.3.3 Pipette 0.5 mL of sample extract and 4.5 mL of RODI water into a 15-mL test tube. Vortex to mix sample and diluent.

8.4 ICP–AES Set-up and Operation

8.4.1 Refer to the manufacturer's manual for set-up and operation of the ICP–AES.

8.4.2 Analyte data are reported at the wavelengths shown in table 4G2a–3.

Table 4G2a–3.—Elemental Reporting Wavelengths.

Element	Reporting Wavelength
	(nm)
Fe	259.94
Al	394.40
Si	251.61
Mn	257.61
P	213.61

8.5 ICP–AES Calibration and Analysis

8.5.1 Calibrate the ICP–AES according to the instrument method. Analyze a CVS (calibration verification standard) after calibrating and every 12 samples. If the CVS falls within the range of the method (±10%), proceed with sample analysis. If the CVS is outside the range, recalibrate and re-analyze from the last passing CVS.

8.5.2 If a sample analyte exceeds the calibration range by 5 times or more, then the sample needs to be diluted.

8.5.2.1 Dilute 1:5 (1 mL of sample extract with 4 mL of 0.02 *M* ammonium oxalate extracting solution), followed by a 1:10 (1 mL of 1:5 solution with 9 mL of RODI water). This makes for a 1:50 dilution.

8.5.3 Using Reagent CVS (calibration verification standard), perform one quality control check every 12 samples. If reading is not within 10%, recalibrate and re-analyze starting from the last CVS that was within 10%.

8.6 Record analyte readings to the nearest 0.01 mg L^{-1}.

9. Calculations

9.1 Instrument readings give analyte concentrations in: mg L^{-1} Fe, Mn, Al, Si, and P.

9.2 Soil Fe, Al, Si (%) = (A x B1 x C1 x C2 x R x 100) / (B2 x E x 1,000 x 1,000)

A = Sample extract reading (mg L^{-1})

B_1 = Mass of 50 mL, 0.2 *M* ammonium oxalate added to sample tube

B_2 = Density of 0.2 *M* ammonium oxalate solution at 20 °C (1.007 g mL^{-1})

C_1 = Dilution, required

C_2 = Dilution, if performed

R = Air-dry/oven-dry ratio (method 3D1) or field-moist/oven-dry ratio (method 3D2)

E = Sample mass (g)

100 = Conversion factor to 100-g basis

1,000 = Factor in denominator (mL L^{-1})

1,000 = Factor in denominator (mg g^{-1})

9.3 Soil Mn, P (mg kg^{-1}) = $(A \times B_1 \times C_1 \times C_2 \times R \times 1{,}000) / (B_2 \times E \times 1{,}000)$

A = Sample extract reading (mg L^{-1})

B_1 = Mass of 50 mL, 0.2 *M* ammonium oxalate added to sample tube

B_2 = Density of 0.2 *M* ammonium oxalate solution at 20 °C (1.007 g mL^{-1})

C_1 = Dilution, required

C_2 = Dilution, if performed

R = Air-dry/oven-dry ratio (method 3D1) or field-moist/oven-dry ratio (method 3D2)

1,000 = Conversion factor in numerator to kg-basis

E = Sample mass (g)

9.4 Report the percent ammonium oxalate extractable Al, Fe, and Si to the nearest 0.01%.

9.5 Report the concentration of ammonium oxalate extractable Mn and P to the nearest mg kg^{-1} soil. Report the optical density of the ammonium oxalate extract to the nearest 0.01 unit.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist for final review.

10.6 Compare individual results to method detection limits (MDL) and practical quantitation limits (PQL) before reporting analysis results.

10.6.1 Report numerical values for results that are above the PQL.

10.6.2 Report “trace” for results that are between the MDL and PQL.

10.6.3 Report “non-detect” for results that are below the MDL.

MDL and PQL in Reporting Units

Analyte	MDL	PQL
	(mg kg^{-1} of oven-dried soil)	*(mg kg^{-1} of oven-dried soil)*

11. References

Aguilera, N.H., and M.L. Jackson. 1953. Iron oxide removal from soils and clays. Soil Sci. Soc. Am. Proc. 17:359–364.

Holmgren, G.G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Am. J. 41:1207–1208.

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Selective Dissolutions (4G)

Ammonium Oxalate (4G2)

Ratios and Estimates Related to Ammonium Oxalate Extraction (4G2b)

Al+½Fe (4G2b1)

The ratio using ammonium oxalate extractable Al plus ½ Fe determined in method 4G2a1a1-5 is used as a taxonomic criterion for andic soil properties. Refer to Soil Survey Staff (2011, 2014) for more detailed information on the application of this ratio.

References

Soil Survey Staff. 2014. Keys to soil taxonomy. 12th ed. USDA–NRCS.

Soil Survey Staff. 2011. Soil survey laboratory information manual. Version 2.0. USDA–NRCS. Soil Survey Investigations Report No. 45. U.S. Govt. Print. Office, Washington, DC.

Total Analysis (4H)

Trace Metals Acid Digestion (4H1)

HNO_3+HCl Digestion (4H1a)

Microwave (4H1a1)

Inductively Coupled Plasma Mass Spectrophotometer (4H1a1b)

Antimony, Arsenic, Barium, Beryllium, Cadmium, Cobalt, Chromium, Copper, Lead, Manganese, Mercury, Molybdenum, Nickel, Phosphorus, Selenium, Silver, Strontium, Tin, Tungsten, Vanadium, and Zinc (4H1a1b1-21)

Air-Dry, <2 mm (4H1a1b1-21a1)

1. Introduction to Trace Metal Analysis via ICP–MS

The term “trace metals” is applied to many elements typically found at low or background levels in the environment. Knowledge of these background levels is important in understanding the impact that increased concentrations of trace metals may have on an ecosystem (Tiller, 1989; Holmgren et al., 1993).

Trace metal data has many applications in soil survey, including understanding differences between natural and human-induced distribution, the relationship of trace metals with other soil properties, and the fate and transport of anthropogenic elements. Such knowledge expands the utility and application of soil survey information in areas of environmental concern, such as urban soils, mine spoil reclamation, smelter emissions, and agricultural waste applications (Burt et al., 2002, 2003, 2011, 2013).

2. Scope and Field of Application

Trace elements may become elevated in concentration due to natural activities (e.g., magmatic activity, mineral weathering, and translocation through the soil or landscape) or due to human activities (e.g., pesticides, mining, smelting, and manufacturing). The relative reactivity or bioavailability of these elements in soils is governed by a variety of chemical factors, including pH, redox potential, organic material, and oxides (Pierzynski and Schwab, 1993; Gambrell, 1994; Keller and Vedy, 1994).

3. Principle

A 500-mg, <2-mm soil separate that has been air-dried and ground to <200 mesh (75 µm) is weighed; nitric and hydrochloric acids are added; and microwave digestion of the sample is conducted. The concentration is determined for Ag, As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, Sr, V, W, and Zn using an inductively coupled plasma mass spectrometer (ICP–MS).

The approach of this digestion methodology is to maximize the extractable concentration of elements in digested soils while minimizing the matrix interferences.

3.1 Interferences

Analyte-specific interferences are corrected or minimized by using matrix matching, internal standards, collision/reaction cell technology, and careful selection of specific masses for data reporting.

4. Apparatus

4.1 Electronic balance, ±1.0-mg sensitivity

4.2 Bottle top dispensers, 10-mL and 50-mL capacity

4.3 Laboratory grade microwave oven

4.4 Volumetric flasks, 1-L, 500-mL, 250-mL, and 50-mL, class A glass

4.5 Containers, 500-mL, polypropylene, with screw caps

4.6 Centrifuge tubes, 50-mL, disposable

4.7 Disposable borosilicate glass tubes, 15-mL

4.8 Pipettes, electronic digital, 1-mL and 10-mL

4.9 Inductively coupled plasma mass spectrophotometer (ICP–MS)

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.2 Compressed argon (minimum purity 99.99%)

5.3 Compressed hydrogen (minimum purity 99.999%)

5.4 Compressed helium (minimum purity 99.999%)

5.5 Concentrated hydrochloric acid (HCl) (CAS# 7647-01-0), 12 *N,* trace pure grade

5.6 Concentrated nitric acid (HNO_3) (CAS # 7697-37-2), 16 *N,* trace pure grade

5.7 **Trace metals in drinking water (TMDW) stock,** commercially prepared certified reference material (CRM) containing:

2 µg/L Ag
10 µg/L Sb, Cd, and Se
20 µg/L Be, Cr, and Cu
25 µg/L Co
30 µg/L V
40 µg/L Pb and Mn
50 µg/L Ba
60 µg/L Ni
70 µg/L Zn
80 µg/L As
100 µg/L Fe and Mo

120 µg/L Al
250 µg/L Sr
9,000 µg/L Mg

5.8 Stock A: Trace method stock, commercially prepared solution containing:

10 µg/mL Mn, P, and Sr

5.9 Stock C: Trace method stock; commercially prepared solution containing:

1 µg/mL Ag
10.0 g/mL As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mo, Ni, Sb, Se, Sn, W, V, and Zn

5.10 High purity concentrated elements

Individual high purity primary standards, commercially prepared, individual solutions containing:

1,000 mg/L Al, Aluminum Standard
1,000 mg/L Au, Gold Standard
1,000 mg/L Ba, Barium Standard
1,000 mg/L Be, Beryllium Standard
1,000 mg/L Bi, Bismuth Standard
1,000 mg/L Ce, Cerium Standard
1,000 mg/L Co, Cobalt Standard
1,000 mg/L Cu, Copper Standard
1,000 mg/L Fe, Iron Standard
1,000 mg/L Ge, Germanium Standard
100 mg/L Hg, Mercury Standard
1,000 mg /L Hg, Mercury Standard
1,000 mg/L In, Indium Standard
1,000 mg/L Li^6, $Lithium^6$ Standard
1,000 mg/L Mg, Magnesium Standard
1,000 mg/L Mn, Manganese Standard
1,000 mg/L Ni, Nickel Standard
1,000 mg/L P, Phosphorus Standard
1,000 mg/L Pb, Lead Standard
1,000 mg/L Sc, Scandium Standard
1,000 mg/L Sn, Tin Standard
1,000 mg/L Tb, Terbium Standard
1,000 mg/L U, Uranium Standard
1,000 mg/L W, Tungsten Standard
1,000 mg/L Zn, Zinc Standard

5.11 ICP–MS tuning solutions

Components: Nitric acid (HNO_3), RODI water, 1,000 µg/L primary standards (see 5.10 above)

5.11.1 Tuning stock solution; 1 mg/L tune solution

- To a 1-L glass volumetric flask, add the following in order:
  - Approximately 500 mL of RODI water
  - 1.0 mL of 1,000 mg/L Be, Beryllium Standard
  - 1.0 mL of 1,000 mg/L Ce, Cerium Standard
  - 1.0 mL of 1,000 mg/L Fe, Iron Standard
  - 1.0 mL of 1,000 mg/L In, Indium Standard
  - 1.0 mL of 1,000 mg/L Li^6, $Lithium^6$ Standard
  - 1.0 mL of 1,000 mg/L Mg, Magnesium Standard
  - 1.0 mL of 1,000 mg/L Pb, Lead Standard
  - 1.0 mL of 1,000 mg/L U; Uranium Standard
  - Fill to volume with RODI water.
- Mix thoroughly.

5.11.2 Daily tuning solution

- To a 1-L glass volumetric flask, add the following in order:
  - Approximately 500 mL of RODI water
  - 18 mL of concentrated HNO_3
  - 1 mL of tuning stock solution (see 5.11.1 above)
  - Fill to volume with RODI water.
- Mix thoroughly.

5.11.3 Monthly tuning solution (dual detector)

- To a 1-L glass volumetric flask, add the following in order:
  - Approximately 500 mL of RODI water
  - 18 mL of HNO_3
  - 6 mL of HCl
  - 0.2 mL each of 1,000 mg/L primary standards: Al, Ba, Ce, Co, Cu, In, Li^6, Mg, Mn, Ni, Pb, Tb, U, and Zn
  - Fill to volume with RODI water.
- Mix thoroughly.

5.12 Calibration verification (CVS) and internal standard (IS) solutions

Components: Nitric acid (HNO_3), RODI water, 1,000 µg/L primary standards (see 5.10 above), hydrochloric acid (HCl)

5.12.1 Internal standard solution

- To a 2-L glass volumetric flask, add the following in order:
  - Approximately 500 mL of RODI water
  - 18 mL of HNO_3
  - 6 mL of HCl

- 0.250 mL of 1,000 mg/L Au, Gold Standard
- 1 mL each of 1,000 mg/L primary standards: Li_6, Sc, Ge, Y, In, Tb, and Bi
- Fill to volume with RODI water.

- Mix thoroughly.

5.12.2 Standard matrix

- To a 1-L glass volumetric flask, add the following in order:
  - Approximately 500 mL of RODI water
  - 0.250 mL of 1,000 mg/L Au, Gold Standard
  - 18 mL of HNO_3
  - Fill to volume with RODI water.
- Mix thoroughly.

5.12.3 TMDW CVS, 1:10 dilution

- To a 50-mL centrifuge tube, add the following in order:
  - 27 mL of standard matrix (see 5.12.2 above)
  - 3 mL of TMDW stock (see 5.7 above)
- Mix thoroughly.

5.12.4 Hg stock CVS, 1,000 µg/L Hg

- To a 1-L glass volumetric flask, add the following in order:
  - Approximately 500 mL of RODI water
  - 1 mL of 1,000 mg/L Hg, Mercury Standard
  - Fill to volume with RODI water.
- Mix thoroughly.

5.12.5 Hg CVS 1 µg/L Hg

- To a 1-L glass volumetric flask, add the following in order:
  - Approximately 500 mL of RODI water
  - 18 mL of HNO_3
  - 6 mL of HCl
  - 0.250 mL of 1,000 mg/L Au, Gold Standard
  - 1 mL of Hg stock CVS solution (see 5.12.4 above)
  - Fill to volume with RODI water.
- Mix thoroughly.

5.12.6 SnW stock CVS, 1,000 µg/L

- To a 1-L glass volumetric flask, add the following in order:
  - Approximately 500 mL of RODI water
  - 1 mL of 1,000 mg/L Sn, Tin Standard
  - 1 mL of 1,000 mg/L W, Tungsten Standard
  - Fill to volume with RODI water.
- Mix thoroughly.

5.12.7 PSnW CVS

- To a 1-L glass volumetric flask, add the following in order:
  - Approximately 500 mL of RODI water
  - 18 mL of NHO_3
  - 0.250 mL of 1,000 mg/L P
  - 5 mL of 1,000 µg/L SnW stock CVS solution
  - Fill to volume with RODI water.
- Mix thoroughly.

5.13 ICP–MS calibration standards: TM-4, TM-3, TM-2, TM-1, TM-0

Components: Stock C (see 5.9 above), nitric acid (HNO_3), hydrochloric acid (HCl), RODI water, 1,000 µg/L primary standards (see 5.10 above)

- Refer to table 4H1a–1 below for mixing instructions.
- TM-2 and TM-1 solutions are serial dilutions created from T-4 solution.
- Table 4H1a–3 lists solution concentrations.

5.13.1 Standard matrix

- To a 1-L glass volumetric flask, add the following in order:
  - Approximately 500 mL of RODI water
  - 0.250 mL of 1,000 mg/L Au, Gold Standard
  - 18 mL of HNO_3
  - Fill to volume with RODI water.
- Mix thoroughly.

5.13.2 TM-4 (Mixed elements—high)

- To a 500-mL glass volumetric flask, add the following in order:
  - Approximately 300 mL of RODI water
  - 3 mL of HCl
  - 9 mL of HNO_3
  - 0.125 mL of 1,000 µg/mL Au, Gold Standard
  - 0.500 mL of Stock C solution
  - Fill to volume with RODI water.
- Mix thoroughly.

5.13.3 TM-3 (Mixed elements—mid)

- To a 500-mL glass volumetric flask, add the following in order:
  - Approximately 300 mL of RODI water
  - 3 mL of HCl
  - 9 mL of HNO_3
  - 0.125 mL of 1,000 µg/mL Au, Gold Standard
  - 0.250 mL of stock C
  - Fill to volume with RODI water.
- Mix thoroughly.

5.13.4 TM-2 (Mixed elements—low)

- To a 500-mL glass volumetric flask, add the following in order:
  - Approximately 300 mL of standard matrix
  - 50 mL of TM-4 solution
  - Fill to volume with standard matrix.
- Mix thoroughly.

5.13.5 TM-1 (Mixed elements—very low)

- To a 500-mL glass volumetric flask, add the following in order:
  - Approximately 300 mL of standard matrix
  - 50 mL of TM-2 solution
  - Fill to volume with standard matrix.
- Mix thoroughly.

5.13.6 TM-0 (blank)

- To a 500-mL glass volumetric flask, add the following in order:
  - Approximately 300 mL of RODI water
  - 9 mL of HNO_3
  - 3 mL of HCl
  - 0.125 mL of 1,000 mg/L Au, Gold Standard
  - Fill to volume with RODI water.

Table 4H1a–1.—Preparation of Calibration Standards TM-4, TM-3, TM-2, TM-1, and TM-0. (Prepare in 500-mL volumetric flasks.)

Reagent	TM-4	TM-3	TM-2	TM-1	TM-0
	(mL)	*(mL)*	*(mL)*	*(mL)*	*(mL)*
Hydrochloric acid (HCl)	3	3	---	---	3
Nitric acid (HNO_3)	9	9			9
1,000 mg/L Au	0.125	0.125			0.125
Trace method stock C	0.5	0.25			---
TM-4 solution	---	---	50		
TM-2 solution	---	---	---	50	
RODI water	300 mL initially, fill to volume	300 mL initially, fill to volume	---	---	300 mL initially, fill to volume
Standard matrix	---	---	300 mL initially, fill to volume	300 mL initially, fill to volume	---

5.14 ICP–MS calibration standards: TM-8, TM-7, TM-6, TM-5

Components: Hydrochloric acid (HCl), nitric acid (HNO_3), Trace Method Stock A solution, RODI water

- Refer to table 4H1a–2 below for mixing instructions.
- Table 4H1a–3 lists solution concentrations.

5.14.1 TM-8 (P, Mn, Sr; high)

- To a 500-mL glass volumetric flask, add the following in order:
  - Approximately 300 mL of RODI water
  - 50 mL of Trace Method Stock A solution (see 5.8 above)
  - 9 mL of HNO_3
  - 3 mL of HCl
  - Fill to volume with RODI water.
- Mix thoroughly.

5.14.2 TM-7 (P, Mn, Sr; mid)

- To a 500-mL glass volumetric flask, add the following in order:
  - Approximately 300 mL of RODI water
  - 37.5 mL of Trace Method Stock A solution (see 5.8 above)
  - 9 mL of HNO_3
  - 3 mL of HCl
  - Fill to volume with RODI water.
- Mix thoroughly.

5.14.3 TM-6 (P, Mn, Sr; low)

- To a 500-mL glass volumetric flask, add the following in order:
  - Approximately 300 mL of RODI water
  - 12.5 mL of Trace Method Stock A solution (see 5.8 above)
  - 9 mL of HNO_3
  - 3 mL of HCl
  - Fill to volume with RODI water.
- Mix thoroughly.

5.14.4 TM-5 (P, Mn, Sr; very low)

- To a 500-mL glass volumetric flask, add the following in order:
  - Approximately 300 mL of RODI water
  - 1.25 mL of Trace Method Stock A solution (see 5.8 above)
  - 9 mL of HNO_3
  - 3 mL of HCl
  - Fill to volume with RODI water.
- Mix thoroughly.

Table 4H1a–2.—Preparation of Calibration Standards TM-8, TM-7, TM-6, and TM-5. (Prepare in 500-mL volumetric flasks.)

Reagent	TM-8	TM-7	TM-6	TM-5
	(mL)	*(mL)*	*(mL)*	*(mL)*
Trace method stock A	50	37.5	12.5	1.25
Nitric acid (NHO_3)	9	9	9	9
Hydrochloric acid (HCl)	3	3	3	3
RODI water	300 mL initially, fill to volume with RODI water			

5.14.5 Stock Hg solution, 1 mg/L Hg

- To a 100-mL glass volumetric flask, add the following in order:
  - Approximately 30 mL of RODI water
  - 1 mL of 100 mg/L Hg, Mercury Standard
  - Fill to volume with RODI water.
- Mix thoroughly.

5.14.6 TM-9 (Hg; low)

- To a 1-L glass volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 18 mL of HNO_3
  - 6 mL of HCl
  - 0.250 mL of 1,000 µg/mL Au, Gold Standard
  - 0.5 mL of stock Hg solution (see 5.14.5 above)
  - Fill to volume with RODI water.
- Mix thoroughly.

5.14.7 TM-10 (Hg; high)

- To a 100-mL glass volumetric flask, add the following in order:
  - Approximately 500 mL of RODI water
  - 18 mL of HNO_3
  - 6 mL of HCl
  - 0.250 mL of 1,000 µg/mL Au, Gold Standard
  - 1 mL of stock Hg solution (see 5.14.5 above)
  - Fill to volume with RODI water.
- Mix thoroughly.

5.14.8 TM-11 (Ba; high)

- To a 1-L glass volumetric flask, add the following in order:

- Approximately 500 mL of RODI water
- 18 mL of HNO_3
- 6 mL of HCl
- 0.250 mL of 1,000 mg/L Au, Gold Standard
- 0.5 mL of 1,000 mg/L Ba, Barium Standard
- Fill to volume with RODI water.

- Mix thoroughly.

Table 4H1a–3.—Preparation of Calibration Standards TM-9, TM-10, and TM-11. (Prepare in 1-L glass volumetric flasks.)

Reagent	TM-9	TM-10	TM-11
	(mL)	*(mL)*	*(mL)*
Stock Hg solution	0.5	1.0	---
1,000 mg/L Ba	---	---	0.5
1,000 mg/L Au	0.25	0.25	0.25
Nitric acid (NHO_3)	18	18	18
Hydrochloric acid (HCl)	6	6	6
RODI water	500 mL initially, fill to volume with RODI water		

5.15 Sample diluent

- To a 1-L glass volumetric flask, add the following in order:
  - Approximately 500 mL of RODI water
  - 277 µL of 1,000 mg/L Au, Gold Standard
  - Fill to volume with RODI water.
- Mix thoroughly.

5.16 Rinse solution for ICP–MS sample introduction

Components: Nitric acid (HNO_3); hydrochloric acid (HCl); 1,000 mg/mL Au, Gold Primary Standard; RODI water

- To a 2-L polypropylene jug, add the following in order:
  - 500 mL of RODI water
  - 2 mL of 1,000 mg/L Au, Gold Standard
  - 63 mL of HNO_3
  - 45 mL of HCl
  - Fill to volume with RODI water.
- Mix thoroughly.

5.17 Standard concentrations in µg/mL for each element are in table 4H1a–4.

Table 4H1a–4.—Standard Concentrations of Trace Method Solutions.

Calibration Standards TM-0 through TM-11 Element Concentrations (µg/L)												
Element	TM-0	TM-1	TM-2	TM-3	TM-4	TM-5	TM-6	TM-7	TM-8	TM-9	TM-10	TM-11
Ba	0	--	--	5	10							
Be	0	0.1	1	5	10	--	--	--	--	--	--	--
Li	0	--	--	--	--	--	--	--	--	--	--	--
Cr	0	0.1	1	5	10	--	--	--	--	--	--	--
V	0	--	--	5	10	--	--	--	--	--	--	--
As	0	--	1	5	10	--	--	--	--	--	--	--
C	0	0.1	1	5	10	--	--	--	--	--	--	--
Co	0	0.1	1	5	10	--	--	--	--	--	--	--
Ni	0	0.1	1	5	10	--	--	--	--	--	--	--
Zn	0	0.1	1	5	10	--	--	--	--	--	--	--
Se	0	0.1	1	5	10	--	--	--	--	--	--	--
Sb	0	0.1	1	5	10	--	--	--	--	--	--	--
Ag	0	--	0.1	0.5	1	--	--	--	--	--	--	--
Mo	0	0.1	1	5	10	--	--	--	--	--	--	--
Cd	0	0.1	1	5	10	--	--	--	--	--	--	--
Sn	0	0.1	1	5	10	--	--	--	--	--	--	--
W	0	0.1	1	5	10	--	--	--	--	--	--	--
Pb	0	0.1	1	5	10	--	--	--	--	--	--	--
P	0	0	--	--	--	25	250	750	1,000	--	--	--
Mn	0	--	--	--	--	25	250	750	1,000	--	--	--
Sr	0	--	--	--	--	25	250	750	1,000	--	--	--
Hg	0	--	--	--	--	--	--	--	--	0.5	1	--
Ba	0	--	--	--	--	--	--	--	--	--	--	500

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or

apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids. Dispense concentrated acids in fume hood.

Dewars of liquefied argon should be maintained in an upright position following standard KSSL laboratory safety procedures.

Follow the manufacturer's safety precautions when using the ICP–MS.

Warning.—Filling the digestion vessel to >25 percent of the free volume or adding organic reagents or oxidizing agents to the cup may result in excessive venting or explosion of the digestion vessel.

7. Sample Preparation

For trace element analysis, the field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm (1B1b2). Air-dry is generally the optimum water content for handling and processing soil. In addition, the weight of air-dry soil remains relatively constant, and biological activity is low during storage. For routine soil analyses, most U.S. and Canadian laboratories homogenize and process samples to pass a 2-mm sieve (Bates, 1993).

8. Procedure

8.1 Refer to the manufacturer's manual for use and operation of the microwave.

8.2 Weigh 0.5 g of air dried <2-mm sample that has been ground to 200-mesh (<74 µm) into a microwave digestion vessel. For O horizons or samples with a significant amount of organic matter, weigh 0.25 g of sample. Prepare two quality-control check samples and either a blank or inter-batch duplicate per set of 24 samples.

8.3 In a fume hood, dispense 9.0 mL of HNO_3 and 3.0 mL of HCl into each digestion vessel. All soil should be wetted. Swirling may be required to wet organic samples.

8.4 If a strong reaction is observed due to such sample constituents as carbonates or organic material, allow acids and sample to react for ≈10 min in a fume hood with the vessel open.

8.5 Heat samples in microwave, applying 1,800 watts at 100 percent power for 15 min or until samples reach 175 °C. Maintain at 175 °C for 15 minutes.

8.6 Allow samples to cool before removing from the microwave.

8.7 In a fume hood, carefully transfer all the contents of each vessel to 50-mL disposable centrifuge tubes. Add 38 mL of RODI water to each sample for a total extract volume of 50 mL.

8.8 Let samples settle 24 hours before analysis.

8.9 Dilute samples 1:10 with sample diluent (see 5.15 above) into 15-mL glass tubes. Vortex to mix.

Note: Additional dilution may be required for specific analytes that are out of the working range of the ICP–MS.

8.10 ICP–MS set-up and operation: Refer to the manufacturer's manual for operating the ICP–MS. General instrument set-up parameters are as follows: Meinhardt nebulizer, cyclonic spray chamber, 1,600 watts, neb flow 1 L/min, aux flow 1.2 L/min, plasma flow 18 L/min. See table 4H1a–5 for reported masses, internal standards, and cell gas.

Table 4H1a–5.—General Instrument Set-Up and Analysis Conditions.

Analyte	m/z Measured	Internal Standard	Cell Gas
Be	9	Li^6	Ar
Cr	52	Sc	He
V	51	Sc	He
As	75	Ge	He
Cu	63	Ge	He
Co	59	Ge	He
Ni	60	Ge	He
Zn	66	Ge	Ar
Se	78	Ge	H_2
Sb	121	In	Ar
Ag	107	In	Ar
Mo	98	In	Ar
Cd	111	In	He
Sn	118	In	He
W	184	Tb	Ar
Pb	208	Bi	Ar
P	31	Sc	He
Mn	55	Ge	He
Sr	88	In	Ar
Hg	202	Bi	Ar
Ba	209	Tb	Ar

8.11 Calibrate the instrument using calibration standards from tables 4H1a–1, –2, and –3. Analyze TMDW 1:10, SnPW, and Hg CVS once after calibration and then every 12 test samples. If the CVS fails, recalibrate and re-analyze test samples from the last passing CVS. Recalibrate every 24 samples.

8.12 Analyze two SRM process-control samples and either a process-control blank or inter-batch duplicate with every batch of 24 samples.

8.13 If results from process-control samples are outside the acceptable range, re-analyze the process-control sample to confirm the results. If confirmed, re-analyze all associated test samples from beginning of method.

8.14 If a test sample analyte exceeds three times the high calibration standard concentration, dilute sample 1:100.

8.15 Record analyte readings to 0.1 unit. The instrument readings for analyte concentration are measured in units of mg L^{-1}, which are converted to a soil basis.

8.16 Establish detection limits using the blank standard solution. Instrumental detection limits are calculated by using 3 times the standard deviation of 10 readings of the blank. These values establish the lower detection limits for each element. Report analyzed values lower than the detection limits as "ND" or non-detected.

9. Calculations

9.1 Determine element concentration (mg kg^{-1})

$$mg\ kg^{-1} = (A * B * C * R * 1{,}000_1) / (E * 1{,}000_2)$$

A = Analyte concentration in extract (µg $/L^{-1}$)

B = Extract volume (L)

C = Dilution, if performed

R = Air-dry/oven-dry ratio (method 3D1)

$1{,}000_1$ = Conversion factor in numerator to produce units of kg^{-1}

E = Sample weight (g)

$1{,}000_2$ = Conversion factor in denominator to produce units of mg

9.2 Data are reported to the nearest 0.01 mg kg^{-1}.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist for final review.

10.6 Compare individual results to method detection limits (MDL) and practical quantitation limits (PQL) before reporting analysis results.

10.6.1 Report numerical values for results that are above the PQL.

10.6.2 Report "trace" for results that are between the MDL and PQL.

10.6.3 Report "non-detect" for results that are below the MDL.

MDL and PQL in Reporting Units

Analyte	MDL	PQL
	(mg kg^{-1} of oven-dried soil)	*(mg kg^{-1} of oven-dried soil)*

11. References

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Total Analysis (4H)
Acid Digestion (4H1)
$HF+HNO_3+HCl$ Digestion (4H1b)
Microwave (4H1b1)
Boric Acid (4H1b1a)
Inductively Coupled Plasma Atomic Emission Spectrometer (4H1b1a1)
Radial Mode (4H1b1a1a)
Aluminum, Calcium, Iron, Potassium, Magnesium, Manganese, Sodium, Phosphorus, Silicon, Strontium, Zirconium, and Titanium (4H1b1a1a1-12)
Air-Dry, <2 mm (4H1b1a1a1-12a1)
Oven-Dry, <2 µm (4H1b1a1a1-12c3)

1. Introduction to Total Analysis via ICP–OES

A combination of nitric, hydrochloric, and hydrofluoric acids (HNO_3, HCl, and HF) are used to digest soil material prior to analysis. The analysis is performed by inductively coupled plasma optical emission spectrometry (ICP–OES). The method is referred to as total analysis due to complete digestion and dissolution of the entire sample by the action of HF. Prior to the development of modern analytical techniques (e.g., x-ray diffraction and thermal analysis), identification of minerals was based on elemental analysis and optical properties (Washington, 1930; Bain and Smith, 1994). Chemical analysis is still essential for determining mineral structural formulas and for identifying and quantifying specific mineral species through elemental allocation to minerals. Many clay mineral groups are subdivided based on composition.

2. Scope and Field of Application

Analysis of the fine-earth (<2-mm) fraction provides information on parent material uniformity, pedon development, and mineral weathering within or between pedons. This interpretation is determined from differences between horizons or pedons. It compares elemental concentrations; elemental ratios, such as Si/Al, Si/Al+Fe, or Ti/Zr; or total elemental concentrations to concentrations determined by selective dissolution techniques.

The inherent fertility of a soil derived from its parent material can be examined by determination of the basic cations relative to the Si or Al content. Phosphorus fertility of a soil and potential water quality problems can be better understood by measurements of total P than by other P measurements, such as water-soluble P or Bray-1 extractable P.

3. Principle

A 0.25 g sample of 200-mesh (74 µm) soil material is weighed into a digestion vessel. A combination of concentrated acids (HNO_3, HCl, and HF) are added to the sample, which is then digested in a laboratory grade microwave digestion system. A second digestion step is required. In the second step, boric acid solution is added to the sample to facilitate dissolution of metal fluorides (e.g., AlF_3). The concentration of Al, Ca, Fe, K, Mg, Mn, Na, P, Si, Sr, Ti, and Zr are determined by ICP–OES.

3.1 Interferences

Insoluble fluorides of various metals may form. Formation of SiF_4 results in gaseous losses of Si. Additions of boric acid limit formation of this molecule and dissolve other metal fluorides.

Spectral and matrix interferences exist. Careful selection of specific wavelengths for data reporting is important.

4. Apparatus

4.1 Electronic balance, ±1.0-mg sensitivity

4.2 Bottle top dispenser, 10-mL capacity (to dispense HNO_3 and HCl)

4.3 Laboratory grade microwave oven

4.4 Microwave digestion vessels. Consult manufacturer for vessesls that are appropriate for this application.

4.5 Volumetric flasks, 1-L, 500-mL, 250-mL, and 100-mL, HDPE

4.6 Containers, 500-mL, polypropylene, with screw caps

4.7 Pipettes, electronic digital, 1,000-µL and 10-mL

4.8 Inductively coupled plasma optical emission spectrometer (ICP–OES)

4.9 HF bottle top safety dispenser, 5-mL

4.10 4-L sized carboy, HDPE

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.2 Compressed gasses, argon (minimum purity 99.996%) and nitrogen (minimum purity 99.999%)

5.3 Hydrofluoric acid (HF) (CAS# 7664-39-3), 48%, low trace-metal content

5.4 Concentrated hydrochloric acid (HCl) (CAS# 7647-01-0), 12 *N,* trace pure grade

5.5 Concentrated nitric acid (HNO_3) (CAS # 7697-37-2), 16 *N,* trace pure grade

5.6 Boric acid (H_3BO_3) (CAS# 10043-35-3), granular, low trace-metal content

5.7 Boric acid solution, 4.5%

Components: Boric acid (H_3BO_3), RODI water

- To a 1-L glass beaker, add the following in order:
  - 800 mL of RODI water
  - 45.0 g boric acid
- Place beaker on hotplate on low heat. Stir periodically until boric acid is dissolved.
- Remove from heat, decant into 1-L volumetric flask.
  - Fill to volume with RODI water.
- Invert to mix.

5.8 Boric acid solution, 1.9%

Components: Boric acid (H_3BO_3), RODI water

- To a 4-L HDPE carboy, add the following in order:
  - 2 L of RODI water
  - 76.0 g of low trace-metal, granular boric acid (H_3BO_3)
  - Fill to volume with RODI water.
- Swirl to mix.

5.9 High purity primary standards: 1,000 mg L^{-1} concentrated elements, commercially prepared:

1,000 mg/L Ca, Calcium Standard
1,000 mg/L Mg, Magnesium Standard
1,000 mg/L Mn, Manganese Standard
1,000 mg/L K, Potassium Standard
1,000 mg/L Al, Aluminum Standard
1,000 mg/L Fe, Iron Standard
1,000 mg/L Ti, Titanium Standard
1,000 mg/L Zr, Zirconium Standard
1,000 mg/L Na, Sodium Standard
1,000 mg/L Si, Silicon Standard
1,000 mg/L P, Phosphorous Standard
1,000 mg/L Sr, Strontium Standard
1,000 mg/L Lu, Lutetium Standard

5.10 Calibration verification standard (CVS) solutions

Components: Hydrofluoric acid (HF); hydrochloric acid (HCl); nitric acid (HNO_3); 4.5% boric acid solution; 1.9% boric acid solution; 1,000 mg/L primary standards: Al, Ca, Fe, K, Mg, Mn, Na, P, Si, Sr, Ti, and Zr; RODI water

- Refer to tables 4H1b–1, –2, and –3 for mixing instructions.
- Refer to table 4H1b–4 for standard solution concentrations.

5.10.1 Instrument calibration standard, calcium (high)

- To a 250-mL polyethylene volumetric flask, add the following in order:
  - 50 mL of 4.5% boric acid solution
  - 22.5 mL of nitric acid (HNO_3)
  - 37.50 mL of 1,000 µg/mL Ca, Calcium Standard
  - 12.50 mL of 1,000 µg/mL K, Potassium Standard
  - 10.0 mL of 1,000 µg/mL Mg, Magnesium Standard
  - 5.0 mL of 1,000 µg/mL Mn, Manganese Standard
  - Fill to volume with 1.9% boric acid solution.
- Invert to mix.

5.10.2 Instrument calibration standard, calcium (low)

- To a 250-mL polyethylene volumetric flask, add the following in order:
  - 50 mL of 4.5% boric acid solution
  - 22.5 mL of nitric acid (HNO_3)
  - 18.75 mL of 1,000 µg/mL Ca, Calcium Standard
  - 6.25 mL of 1,000 µg/mL K, Potassium Standard
  - 5.0 mL of 1,000 µg/mL Mg, Magnesium Standard
  - 2.5 mL of 1,000 µg/mL Mn, Manganese Standard
  - Fill to volume with 1.9% boric acid solution.
- Invert to mix.

Table 4H1b–1.—Preparation of ICP Calcium Mixed Calibration Standards. (Prepare in 250-mL volumetric flasks.)

Element or Component	Low	High
	(mL)	*(mL)*
Ca 1,000 µg/mL	18.75	37.5
K 1,000 µg/mL	6.25	12.5
Mg 1,000 µg/mL	5.0	10
Mn 1,000 µg/mL	2.5	5
Hydrofluoric acid (HF)	10	10
Hydrochloric acid (HCl)	7.5	7.5
Nitric acid (HNO_3)	22.5	22.5
Boric acid solution, 4.5%	50 mL initially	50 mL
Boric acid solution, 1.9%	Fill to volume	Fill to volume

5.10.3 Instrument calibration standard, aluminum (high)

- To a 250-mL polyethylene volumetric flask, add the following in order:
  - 50 mL of 4.5% boric acid solution
  - 22.5 mL of nitric acid (HNO_3)
  - 50.0 mL of 1,000 µg/mL Al, Aluminum Standard
  - 37.5 mL of 1,000 µg/mL Fe, Iron Standard
  - 2.5 mL of 1,000 µg/mL Ti, Titanium Standard
  - 2.5 mL of 1,000 µg/mL Zr, Zirconium Standard
  - 12.5 mL of 1,000 µg/mL Na, Sodium Standard
  - 10 mL of hydrofluoric acid (HF)
  - 7.5 mL of hydrochloric acid (HCl)
  - Fill to volume with 1.9% boric acid solution.
- Invert to mix.

5.10.4 Instrument calibration standard, aluminum (low)

- To a 250-mL polyethylene volumetric flask, add the following in order:
  - 50 mL of 4.5% boric acid solution
  - 22.5 mL of nitric acid (HNO_3)
  - 25.0 mL of 1,000 µg/mL Al, Aluminum Standard
  - 18.75 mL of 1,000 µg/mL Fe, Iron Standard
  - 1.25 mL of 1,000 µg/mL Ti, Titanium Standard
  - 1.25 mL of 1,000 µg/mL Zr, Zirconium Standard
  - 12.5 mL of 1,000 µg/mL Na, Sodium Standard
  - 10 mL of hydrofluoric acid (HF)
  - 7.5 mL of hydrochloric acid (HCl)
  - Fill to volume with 1.9% boric acid solution.
- Invert to mix.

Table 4H1b–2.—Preparation of ICP Aluminum Mixed Calibration Standards. (Prepare in 250-mL volumetric flasks.)

Element or Component	Low	High
	(mL)	*(mL)*
Al 1,000 µg/mL	25	50
Fe 1,000 µg/mL	18.75	37.5

Table 4H1b–2.—Continued

Element or Component	Low	High
Ti 1,000 µg/mL	1.25	2.5
Zr 1,000 µg/mL	1.25	2.5
Na 1,000 µg/mL	6.25	12.5
Hydrofluoric acid (HF)	10	10
Hydrochloric acid (HCl)	7.5	7.5
Nitric acid (HNO_3)	22.5	22.5
Boric acid solution, 4.5%	50 mL	50 mL
Boric acid solution, 1.9%	Fill to volume	Fill to volume

5.10.5 Instrument calibration standard, silicon (low)

- To a 250-mL polyethylene volumetric flask, add the following in order:
  - 50 mL of 4.5% boric acid solution
  - 22.5 mL of nitric acid (HNO_3)
  - 56.25 mL of 1,000 µg/mL Si, Silicon Standard
  - 1.25 mL of 1,000 µg/mL P, Phosphorus Standard
  - 0.375 mL of 1,000 µg/mL Sr, Strontium Standard
  - 10 mL of hydrofluoric acid (HF)
  - 7.5 mL of hydrochloric acid (HCl)
  - Fill to volume with 1.9% boric acid solution.
- Invert to mix.

5.10.6 Instrument calibration standard, silicon (high)

- To a 250-mL polyethylene volumetric flask, add the following in order:
  - 50 mL of 4.5% boric acid solution
  - 22.5 mL of nitric acid
  - 112.50 mL of 1,000 µg/mL Si, Silicon Standard
  - 2.50 mL of 1,000 µg/mL P, Phosphorus Standard
  - 3.75 mL of 1,000 µg/mL Sr, Strontium Standard
  - 10 mL of hydrofluoric acid (HF)
  - 7.5 mL of hydrochloric acid (HCl)
  - Fill to volume with 1.9% boric acid solution.
- Invert to mix.

Table 4H1b–3.—Instrument Calibration Standard Solutions, Silicon.

ICP Silicon Mixed Calibration Standards (Prepare in 250-mL volumetric flask.)		
Element or Component	**Low**	**High**
	(mL)	*(mL)*
Si 1,000 µg/mL	56.25	112.5
P 1,000 µg/mL	1.25	2.5
Sr 1,000 µg/mL	0.375	3.75
Hydrofluoric acid (HF)	10	10
Hydrochloric acid (HCl)	7.5	7.5
Nitric acid (HNO_3)	22.5	22.5
Boric acid solution, 4.5%	50 mL	50 mL
Boric acid solution, 1.9%	Fill to volume	Fill to volume

Table 4H1b–4.—Concentrations of Standard Calibration Solutions.

Equipment Calibration Standards Concentrations		
Solution	**Low**	**High**
	(mg L^{-1})	*(mg L^{-1})*
Ca	75	150
K	25	50
Mg	20	40
Mn	10	20
Al	100	200
Fe	75	150
Ti	5	10
Zr	5	10
Na	25	50
Si	225	450
P	5	10
Sr	1.5	15

5.11 Calibration verification blank solution

Components: Hydrofluoric acid (HF), hydrochloric acid (HCl), nitric acid (HNO_3), 4.5% boric acid solution, 1.9% boric acid solution

- To a 500-mL polyethylene flask, add the following in order:
  - 20 mL of hydrofluoric acid (HF)
  - 45 mL of hydrochloric acid (HCl)
  - 15 mL of nitric acid (HNO_3)
  - 100 mL of 4.5% boric acid solution
  - Fill to volume with 1.9% boric acid solution.
- Invert to mix.

6. Health and Safety

Warning.—Filling the digestion vessel to >25 percent of the free volume or adding organic reagents or oxidizing agents to the digestate may result in rupture or explosion of the digestion vessel. Always follow manufacturer recommendations and safety guidelines.

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids.

7. Sample Preparation

For major element analysis, the field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm (1B1b2). Air-dry is generally the optimum water content to handle and to process soil. In addition, the weight of air-dry soil remains relatively constant and biological activity is low during storage. For routine soil analyses, most U.S. and Canadian laboratories homogenize and process samples to pass a 2-mm sieve (Bates, 1993).

8. Procedure

8.1 Refer to the manufacturer's manual for use and operation of the microwave.

8.2 Weigh 0.25 g of air-dried <2-mm sample that has been ground to 200-mesh (<74 µm) into a microwave digestion vessel. Prepare two quality-control check samples and either a blank or inter-batch duplicate per set of 24 samples.

8.3 In a fume hood, use a bottle-top dispenser to add 9.0 mL HNO_3, 3.0 mL HCl, and 4 mL HF into each digestion vessel. All soil should be wetted. Swirling may be required to wet organic samples.

8.4 If a strong reaction is observed due to sample constituents, such as carbonates or organic material, allow acids and sample to react for ≈10 min in a fume hood with the vessel open.

8.5 Heat samples in microwave, applying 1,800 watts at 100 percent power for 20 min or until samples reach 180 °C. Maintain at 180 °C for 10 min.

8.6 Allow sample to cool before removing from the microwave.

8.7 Add 20 mL of 4.5% boric acid solution to each digestion vessel.

8.8 Heat samples in microwave, applying 1,800 watts at 100 percent power for 20 min or until samples reach 170 °C. Maintain at 170 °C for 10 min.

8.9 In a fume hood, carefully transfer the contents of each vessel to a 100 mL HDPE volumetric flask.

8.10 Allow samples to cool completely before filling to the mark with 1.9% boric acid.

8.11 ICP–OES Calibration Set-up and Operation

8.11.1 Refer to the manufacturer's manual for operating the ICP-OES. General instrument set-up parameters are as follows: radial mode, gem tip crossflow nebulizer, Scott type spray chamber, 1450 watts, neb flow 0.75 L/min, aux flow 0.2 L/min, and plasma flow 15 L/min. See table 4H1b–5 for recommended reporting and reference wavelengths.

8.11.2 Use the ICP-OES in radial mode and analyze for the following elements: Fe, Mn, Al, Ca, Mg, Na, K, P, Si, Sr, Zr, and Ti.

8.11.3 No initial dilutions of samples are necessary prior to analysis. Perform instrument checks, calibrations, alignment, and gas pressure checks prior to analysis as discussed in operation manual of instrument.

8.11.4 Analyses are generally performed at two or more wavelengths for each element. The selected wavelengths are as shown in table 4H1b–5 (reported wavelength listed first):

Table 4H1b–5.—Reporting and Reference Elemental Wavelengths.

Element	Wavelength	
	Reporting	Reference
	(nm)	*(nm)*
Al	308.215	396.157
Ca	315.887	317.932
Fe	259.939	238.205
K	766.490	---

Table 4H1b–5.—Continued

Element	Wavelength	
	Reporting	Reference
Mg	280.271	279.075
Mn	257.610	260.570
Na	589.592	588.995
P	178.221	213.620
Si	212.412	251.612
Sr	407.747	421.523
Ti	334.940	368.522
Zr	339.197	343.818

8.11.5 Use the blank standard solution to dilute those samples with solution concentrations greater than 5 times the high standard. Rerun all elements and use only the data needed from the diluted analysis.

8.11.6 Establish detection limits using the blank standard solution. Instrument detection limits are calculated by multiplying the standard deviation of 10 readings of the blank by 3. These values establish the lower detection limits for each element. Analyzed values lower than the detection limits are set equal to zero.

9. Calculations

9.1 The calculation of mg kg^{-1} of an element in the soil from mg L^{-1} in solution is as follows:

Analyte concentration in soil (mg kg^{-1}) = (A x B x C x R x 1,000) / E

A = Sample extract reading (mg L^{-1})

B = Extract volume (L)

C = Dilution, if performed

R = Air-dry/oven-dry ratio

1,000 = Conversion factor in numerator to kg-basis

E = Sample weight (g)

9.2 Data are recorded on an elemental basis. Often, users request data for an oxide form. The factor for converting from an elemental form to an oxide form is based on the atomic weights of the element and oxygen. An example is as follows:

Atomic weight Si = 28.09

Atomic Weight O = 16.0

Molecular weight SiO_2 = 60.09

9.2.1 Calculate percent Si in SiO_2 as follows:

$$Si\ (\%) = (28.09/60.09) \times 100 = 46.7\%$$

There is 46.7 percent Si in SiO_2.

9.2.2 To convert elemental concentrations from ppm to percent oxide in the soil divide by 10,000, then, divide the percent by the proportion of the element in the oxide according to values in 4H1b– 6.

9.2.3 Elemental percentages for various oxides are shown below in table 4H1b–6.

Table 4H1b–6.—Elemental Oxides and Elemental Proportions.

Element	Oxide Form	Elemental Proportion in Oxide
Si	SiO_2	0.467
Al	Al_2O_3	0.529
Fe	Fe_2O_3	0.699
Mg	MgO	0.603
Mn	MnO	0.774
K	K_2O	0.830
Ti	TiO_2	0.599
Ca	CaO	0.715
Zr	ZrO_2	0.740
P	P_2O_5	0.436
Na	Na_2O	0.742

9.3 Analyses are generally performed at two or more wavelengths for each element, with one wavelength selected for reporting purposes.

9.4 Data are reported to the nearest mg kg^{-1}.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist for final review.

10.6 Compare individual results to method detection limits (MDL) and practical quantitation limits (PQL) before reporting analysis results.

10.6.1 Report numerical values for results that are above the PQL.

10.6.2 Report "trace" for results that are between the MDL and PQL.

10.6.3 Report "non-detect" for results that are below the MDL.

MDL and PQL in Reporting Units

Analyte	MDL	PQL
	(mg kg^{-1} of oven-dried soil)	*(mg kg^{-1} of oven-dried soil)*

11. References

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Introduction to Carbon, Nitrogen, and Sulfur Analyses (4H)

Total Analysis (4H)
Dry Combustion (4H2)

Organic Matter and Organic Carbon

Soil organic matter has been defined as the organic fraction of the soil exclusive of undecayed plant and animal residues and has been used synonymously with "humus" (Soil Science Society of America, 1997). For laboratory analyses, however, the soil organic matter generally includes only those organic materials that accompany soil particles through a 2-mm sieve (Nelson and Sommers, 1982). The organic matter content influences many soil properties, including water retention capacity; extractable bases; capacity to supply N, P, and micronutrients; stability of soil aggregates; and soil aeration (Nelson and Sommers, 1996).

Organic C is a major component of soil organic matter. Organic C consists of the cells of microorganisms; plant and animal residues at various stages of decomposition; stable "humus" synthesized from residues; and nearly inert and highly carbonized compounds, such as charcoal, graphite, and coal (Nelson and Sommers, 1982). Because organic C is the major component of soil organic matter, a measurement of organic C can serve as an indirect determination of organic matter. Organic C determination is by either wet or dry combustion. In the past, the KSSL used the now-obsolete wet combustion method 6A1c: Walkley-Black modified acid-dichromate digestion, $FeSO_4$ titration, automatic titrator.

Values for organic C are multiplied by the "Van Bemmelen factor" (1.724) to calculate organic matter. This factor assumes that organic matter contains 58% organic C. The proportion of organic C in soil organic matter for a range of soils is highly variable. Any constant factor that is selected is only an approximation. Studies have indicated that subsoils have a higher factor than surface soils (Broadbent, 1953). Surface soils rarely have a factor <1.8 and usually range from 1.8 to 2.0. The subsoil factor may average ≈2.5. The preference is to report organic C rather than to convert the organic C to organic matter through use of an approximate correction factor.

The KSSL also uses a direct determination of soil organic matter. In this determination, the organic matter is destroyed and then the loss in weight of the soil is taken as a measure of the organic matter content (section 5A). The percent organic matter lost on ignition (400 °C) can be used in place of organic matter estimates by the Walkley-Black organic C method.

Total Carbon

Total carbon is the sum of organic and inorganic C. Most of the organic C is associated with the organic matter fraction, and the inorganic C is generally with

carbonate minerals. The organic C in mineral soils generally ranges from 0 to 12% (Nelson and Sommers, 1996).

Total C is quantified by two basic methods: wet or dry combustion. The KSSL uses dry combustion (method 4H2a1). In total C determinations, all forms of C in a soil are converted to CO_2 followed by a quantification of the evolved CO_2. Total C can be used to estimate the organic C content of a soil. The difference between total and inorganic C is an estimate of the organic C. The inorganic C should be approximately equivalent to carbonate values measured by CO_2 evolution with strong acid (Nelson and Sommers, 1996). In KSSL method 4E1a1a1, the amount of carbonate in a soil is determined by treating a sample with HCl followed by a manometric measurement of the evolved CO_2. The amount of carbonate is then calculated as a $CaCO_3$ equivalent basis. Organic C defines mineral and organic soils. In soil taxonomy, organic C is also used at lower taxonomic levels; e.g., ustollic and fluventic subgroups (Soil Survey Staff, 2014).

Total Nitrogen

Total N includes organic and inorganic forms. The total N content of the soil may be <0.02% in subsoils, 2.5% in peats, and 0.06 to 0.5% in surface layers of many cultivated soils (Bremner and Mulvaney, 1982). The total N data many be used to determine the soil C:N ratio, the soil potential to supply N for plant growth, and the N distribution in the soil profile. The C:N ratio generally ranges from 10 to 12. Variations in the C:N ratio may serve as an indicator of the amount of soil inorganic N. Uncultivated soils typically have higher C:N ratios than those of cultivated soils.

Soils that have large amounts of illites or vermiculites can “fix” significant amounts of N compared to those soils dominated by smectites or kaolinites (Young and Aldag, 1982; Nommik and Vahtras, 1982). Because the content of organic C of may soils diminishes with depth and the level of “fixed” N remains constant or increases, the C:N ratio narrows (Young and Aldag, 1982). The potential to “fix” N has important fertility implications as the “fixed” N is slowly available for plant growth.

Two methods of analysis of total N have gained acceptance for the determination of total N in soils. These are the Kjeldahl (1883) method, which is essentially a wet oxidation procedure, and the Dumas (1831) method, which is fundamentally a dry oxidation (i.e., combustion) procedure (Bremner, 1996). The KSSL uses the combustion technique for analysis of total N (method 4H2a2).

Total Sulfur

Organic and inorganic forms of sulfur are found in soils. The organic fraction accounts for >95% of the total S in most soils from humid and semi-humid areas (Tabatabai, 1996). Mineralization of organic S and its conversion to sulfate by chemical and biological activity may serve as a source of plant-available S. Total S typically ranges from 0.01 to 0.05% in most mineral soils. In organic soils, total

S may be >0.05%. The ratio of organic to inorganic S in a soil sample varies widely according to soil type and depth of sampling (Tabatabai, 1996).

In well drained, well aerated soils, most of the inorganic S normally occurs as sulfate. Marine tidal flats, other anaerobic marine sediments, and mine spoils usually have large amounts of reduced S compounds that oxidize to sulfuric acid upon exposure to the air. In arid regions, significant amounts of inorganic S are found as sulfates, such as gypsum and barite (Tabatabai, 1996).

The typical use of total S analysis is to index the total reserves of this element, which may be converted to plant-available S. The KSSL uses the combustion technique for analysis of total S. Extractable sulfate S (SO_4^{2-} S) is an index of readily plant-available S. Reagents that have been used for measuring SO_4^{2-} S include water, hot water, ammonium acetate, sodium carbonate, other carbonates, ammonium chloride, other chlorides, potassium phosphate, other phosphates, and ammonium fluoride (Bray-1). Extractable SO_4^{2-} S does not include the labile fraction of soil organic S that is mineralized during the growing season (Tabatabai, 1996). Extraction reagents for organic S include hydrogen peroxide, sodium bicarbonate, sodium hydroxide, sodium oxalate, sodium peroxide, and sodium pyrophosphate. Other methods are available for determination of S, especially for total S and SO_4^{2-} S. Refer to the review by Beaton et al. (1968). For detailed discussion of the application of total C, N, and S, refer to Soil Survey Staff (2011).

Total Analysis (4H)
Dry Combustion (4H2)
Thermal Conductivity Detector (4H2a)
Total Carbon, Nitrogen, and Sulfur (4H2a1-3)
Air-Dry, <2 mm (4H2a1-3a1)

1. Introduction to Carbon, Nitrogen, and Sulfur Analyses

The organic fraction of the soil that is made up of decayed plant and animal residues and is synonymous with “humus” (Soil Science Society of America, 1987) influences many soil properties. Examples include water retention; extractable bases; source of N, P, and micronutrients; stability of soil aggregates; and soil aeration (Nelson and Sommers, 1996). Non-decayed plant and animal material, however, are not considered part of the soil organic fraction because laboratory analysis samples generally include only those organic materials that pass a 2-mm sieve along with soil particles (Nelson and Sommers, 1982).

Organic and inorganic forms of carbon, nitrogen, and sulfur are measured by dry combustion analysis. An air-dry, 80-mesh (<180-µm) sample is introduced into an oxygen enriched furnace that combusts the sample. Upon combustion, carbon dioxide (CO_2), nitrogen (N_2 and NO_x), and sulfur (SO_2 and SO_3) gases are released. The combustion compounds are measured as CO_2, N_2, and SO_2, which are reported as percent total carbon, nitrogen, and sulfur of the soil.

2. Scope and Field of Application

The Kellogg Soil Survey Laboratory (KSSL) measures total carbon, nitrogen, and sulfur by combustion analysis that assesses both organic and inorganic forms of each element in the sample.

Organic carbon is typically associated with the organic matter fraction of the soil, and inorganic carbon is generally found as carbonate minerals. The content of organic carbon in mineral soils generally ranges from 0 to 12% (Nelson and Sommers, 1996). Organic carbon can be determined indirectly by measuring the inorganic carbon (carbonate) and subtracting from the total carbon value. Organic carbon is used in many places in soil taxonomy. Examples include the definitions of mineral and organic soil material; characteristics of diagnostic surface horizons, such as “Histic;” and criteria for taxa with horizons that have a high content of organic matter, such as the Humults suborder (Soil Survey Staff, 2014).

Total nitrogen data is used to determine the soil carbon to nitrogen ratio, the potential supply of nitrogen available for plant growth, and nitrogen distribution through the soil profile.

Organic sulfur typically accounts for >95% of the total sulfur in soils from humid and semi-humid areas (Tabatabai, 1996). Total sulfur is used, along with 1:1 water pH, as a criterion in the required characteristics for sulfidic materials. Total sulfur is used as an index of plant-available sulfur. In well drained and aerated soils,

most of the inorganic sulfur occurs as sulfate. Marine tidal flats, other anaerobic marine sediments, and mine spoils usually have large amounts of reduced sulfur compounds that oxidize to sulfuric acid upon exposure to the air. In arid regions, significant amounts of inorganic sulfur are found as sulfates, such as gypsum and barite (Tabatabai, 1996).

3. Principle

Organic and inorganic forms of carbon, nitrogen, and sulfur are measured using a combustion analyzer. An air-dry, 80-mesh (<180-µm) sample is packed in tin foil, weighed, pelletized, and analyzed for total C, N, and S by an elemental analyzer (methods 4H2a1, 4H2a2, and 4H2a3, respectively). The elemental analyzer works according to the principle of catalytic tube combustion in an oxygen enriched helium stream at 1,140 °C. Upon combustion, carbon dioxide (CO_2), nitrogen (N_2 and NO_x), and sulfur (SO_2 and SO_3) gases are released. The helium carrier gas transfers the combustion products to a reduction tube where nitrogen and sulfur compounds are reduced to N_2 and SO_2. The desired components (N_2, CO_2, and SO_2) are determined in succession with a calibrated thermal conductivity detector for N_2 and CO_2 and with a calibrated infrared detector for SO_2. Total carbon, nitrogen, and sulfur are reported as percentages of oven-dry soil.

3.1 Interferences

Gloves should be worn when handling samples to prevent contamination.

The sample should be compressed to remove air from the sample and thereby ensure valid N_2 results.

4. Apparatus

4.1 Combustion analyzer

4.2 Electronic balance (±0.001 mg-sensitivity)

5. Chemicals

5.1 Sulfanilamide ($H_2NC_6H_4SO_2NH_2$) (CAS# 63-74-1), daily factor standard

5.2 Sulfanilic acid ($H_2NC_6H_4SO_3H$) (CAS# 121-57-3), instrument calibration

5.3 Acetanilide ($C_6H_5NHCOCH_3$) (CAS# 103-84-4), instrument calibration

5.4 0.5-mm copper (CAS# 7440-50-8), wire-sticks

5.5 Corundum balls, high purity (Al_2O_3) (CAS# 1344-28-1), spheres, 3–5 mm

5.6 Tungsten (VI) oxide powder (WO_3) (CAS# 12036-22-5)

5.7 Tungsten (VI) oxide granules (WO_3) (CAS# 1314-35-8)

5.8 Quartz wool (CAS# 60676-86-0)

5.9 Silver wool (CAS# 7440-22-4)

5.10 Alumina wool (Al_2O_3) (CAS# 1344-28-1)

5.11 Helium (CAS# 7440-59-7), 99.999% purity, carrier gas

5.12 Oxygen (CAS# 7782-44-7), 99.996% purity, combustion gas

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Follow the manufacturer's safety precautions when operating the combustion analyzer.

7. Sample Preparation

For CNS analysis, the field sample is air-dried at 30 to 35 °C, crushed, sieved to <2 mm, and milled to pass an 80-mesh (177-micron) sieve. The weight of air-dry soil remains relatively constant, and biological activity is low during storage.

8. Procedure

8.1 Set-up and Operation of the Combustion Analyzer

8.1.1 Refer to the manufacturer's manuals for operational parameters and maintenance of the combustion analyzer.

8.1.2 The combustion tube is packed with layers of the following materials according to the manufacturer's specification:

- Corundum balls
- Tungsten oxide granules (WO_3)
- Quartz wool

8.1.3 The reduction tube is packed with layers of the following materials according to the manufacturer's specification:

- Quartz wool
- Copper wire
- Corundum balls
- Silver wool

8.1.4 Tube temperatures during analysis:

- Combustion tube 1,140 °C
- Reduction tube 850 °C

8.2 Instrument response is calibrated against known masses of acetanilide and sulfanilamide that cover the desired working range for each element (0.10–20.00 mg carbon, 0.02–3.00 mg nitrogen, and 0.050–2.00 mg sulfur).

8.3 Prior to analysis, a ≈2 mg sample of sulfanilamide is analyzed to verify instrument calibration and adjust the slope of the calibration curves to

compensate for any drift. Instrument recalibration is recommended if the sulfanilamide results are more than 10% different from expected values.

8.4 Weigh out 5 to 30 mg of air-dried, 80-mesh (<180-µm) sample into a tin foil cup. Sample weight is generally based on anticipated organic material content.

- Organic soils are typically weighed at 10–15 mg.
- Mineral horizons are typically weighed at 25–30 mg.
- Samples that have a high content of gypsum are typically weighed at 5–10 mg.

8.5 Add ≈100 mg tungsten (VI) oxide powder (WO_3) to the sample. WO_3 aids combustion by delivering additional oxygen and by binding alkaline and alkaline-earth elements to help prevent formation of non-volatile sulfates.

8.6 Press the foil cup around the soil and WO_3 into a pellet.

8.7 Two process-control samples are analyzed for every 70 samples. One sample is a certified reference material (CRM). Note:

- CRM control limits: Carbon 5.90–6.40 %, nitrogen 1.03–1.17 %, sulfur 0.48–0.52 %
- KSSL control-sample limits: Carbon 3.02–3.20 %, nitrogen 0.16–0.20 %, sulfur 0.00–0.04 %

8.8 If result from a process-control sample is outside the acceptable range, re-analyze all test samples since the last acceptable process control.

Example Instrument Calibration Table

Mass	Reagent	N	C	S
(mg)		*(mg)*	*(mg)*	*(mg)*
30.005	acetanilide	3.109	21.329	
28.235	acetanilide	2.925	20.071	
26.089	acetanilide	2.703	18.545	
24.167	acetanilide	2.504	17.179	
22.048	acetanilide	2.284	15.673	
19.961	acetanilide	2.068	14.189	
17.98	acetanilide	1.863	12.781	
16.051	acetanilide	1.663	11.410	
14.079	acetanilide	1.459	10.008	
12.099	acetanilide	1.253	8.601	
10.217	acetanilide	1.058	7.263	
8.026	acetanilide	0.831	5.705	
6.003	acetanilide	0.622	4.267	
4.99	acetanilide	0.517	3.547	

Example Instrument Calibration Table—Continued

Mass	Reagent	N	C	S
(mg)		*(mg)*	*(mg)*	*(mg)*
11.194	sulfanilic acid	0.905	4.658	2.072
9.025	sulfanilic acid	0.730	3.755	1.671
7.225	sulfanilic acid	0.584	3.006	1.338
5.962	sulfanilic acid	0.482	2.481	1.104
5.045	sulfanilic acid	0.408	2.099	0.934
4.535	sulfanilic acid	0.367	1.887	0.840
4.008	sulfanilic acid	0.324	1.668	0.742
3.477	sulfanilic acid	0.281	1.447	0.644
2.933	sulfanilic acid	0.237	1.220	0.543
2.471	sulfanilic acid	0.200	1.028	0.457
2.027	sulfanilic acid	0.164	0.843	0.375
1.77	sulfanilic acid	0.143	0.736	0.328
1.577	sulfanilic acid	0.128	0.656	0.292
1.237	sulfanilic acid	0.100	0.515	0.229
1.024	sulfanilic acid	0.083	0.426	0.190
0.746	sulfanilic acid	0.060	0.310	0.138
0.506	sulfanilic acid	0.041	0.211	0.094
0.41	sulfanilic acid	0.033	0.171	0.076
0.31	sulfanilic acid	0.025	0.129	0.057
0.212	sulfanilic acid	0.017	0.088	0.039
0.138	sulfanilic acid	0.011	0.057	0.026

9. Calculations

9.1 Total Carbon (%) = 100 * (C * R) / E

C = mg carbon (instrument reading)

R = Air-dry/oven-dry ratio

E = Sample mass (mg)

9.2 Total Nitrogen (%) = 100 * (N * R) / E

N = mg nitrogen (instrument reading)

R = Air-dry/oven-dry ratio

E = Sample mass (mg)

9.3 Total Sulfur (%) = 100 * (S * R) / E

S = mg sulfur (instrument reading)

R = Air-dry/oven-dry ratio

E = Sample mass (mg)

9.4 Report total C, N, and S percentages to the nearest 0.01%.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist for final review.

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Ground and Surface Water Analysis (4l)
Hydrogen-Ion Activity (4l1)
Electrode (4l1a)
Standard Glass Body Combination (4l1a1)
Digital pH/Ion Meter (4l1a1a)
pH (4l1a1a1)

1. Introduction to Surface Water pH

USDA–NRCS projects requiring collection of water samples are usually completed in conjunction with pedon sampling or for specific research projects. Choice of the water-sampling site depends not only on the purpose of the investigation but also on local conditions, depth, and frequency of sampling (Velthorst, 1996). Sample filtration using a 0.45-µm membrane separates dissolved from suspended material, and water analyses are performed as promptly as possible.

2. Scope and Field of Application

The pH of a water sample is commonly determined and is one of the most indicative measurements of water chemical properties. The acidity, neutrality, or basicity is a key factor in the evaluation of water quality.

3. Principle

The pH of the water sample is measured using a digital pH meter with a calibrated combination electrode.

3.1 Interferences

Water pH needs to be measured immediately upon arrival at the laboratory to maintain optimal preservation of sample (Velthorst, 1996).

4. Apparatus

4.1 Syringe filters, 25-mm, 0.45-µm pore size

4.2 Tubes, 50-mL, with caps

4.3 Digital pH/ion meter

4.4 Combination pH-reference electrode

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Buffers, pH 4.00, 7.00, and 9.18

6. Health and Safety

Personal Protective Equipment (PPE).—Use disposable gloves with appropriate polymer rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Follow standard laboratory safety practices.

7. Sample Preparation

Surface water samples are collected from study site. If sample pH is not to be analyzed immediately after collection, store samples at 4 °C. Analyze samples within 72 hours.

8. Procedure

8.1 Filter water sample into a 50-mL tube.

8.2 Calibrate the pH meter with pH 4.00, 7.00, and 9.18 buffer solutions.

8.3 After equipment calibration, gently wash the electrode with RO water. Dry the electrode. Do not wipe the electrode with a tissue as this may cause a static charge on the electrode.

8.4 Gently lower the electrode in the water sample until the KCl junction of the electrode is beneath the water surface.

8.5 Allow the pH meter to stabilize before recording the pH. Record pH to the nearest 0.01 unit.

8.6 Gently raise and wash the pH electrode with a stream of RO water.

9. Calculations

No calculations are needed. Report the pH of the water sample to the nearest 0.1 pH unit.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

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Ground and Surface Water Analyses (4l)
Electrical Conductivity and Salts (4l2)
Conductivity Bridge and Cup (4l2a)
Electrical Conductivity (4l2a1)

1. Introduction to Surface Water Electrical Conductivity

USDA–NRCS projects requiring collection of water samples are usually completed in conjunction with pedon sampling or for specific research projects. Choice of the water-sampling site depends not only on the purpose of the investigation but also on local conditions, depth, and frequency of sampling (Velthorst, 1996).

The amount and composition of water samples vary strongly with small changes in location. Some water analyses, e.g., electrical conductivity, total C, and inorganic C, need to be performed promptly because optimal preservation of the sample is not possible (Velthorst, 1996).

2. Scope and Field of Application

A primary source of salts in water is chemical weathering of the minerals in soils and rocks. This weathering includes dissolution, hydrolysis, carbonation, acidification, and oxidation-reduction in a soil (National Research Council, 1993). All of these reactions contribute to an increase in the dissolved mineral load in the soil solution and in waters. The measurement of electrical conductivity (EC) and total dissolved salts (TDS) is therefore important to the understanding of soil hydrology and translocation of salts.

3. Principle

The electrical conductivity of the water sample is measured using a conductivity meter.

3.1 Interferences

Reverse osmosis water is used to zero and flush the conductivity cell. The extract temperature is assumed to be 25 °C. If the temperature deviates significantly, a correction may be required.

Provide airtight storage of KCl solution and samples to prevent soil release of alkali-earth cations. Exposure to air can cause gains and losses of water and dissolved gases, significantly affecting EC readings.

4. Apparatus

4.1 Syringe filters, 25-mm, 0.45-µm pore size

4.2 Tubes, 50-mL, with caps

4.3 Conductivity meter and conductivity cell

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Potassium chloride solution, 0.010 N

Components: Potassium chloride (KCl) (CAS# 7447-40-7), RODI water

- To a 1-L volumetric flask, add the following in order:
  - 750 mL of RODI water
  - 0.7456 g of KCl (dried overnight in an oven at 110 °C)
  - Fill to volume with RODI water.
- Invert to mix.
- Conductivity of KCl solution at 25 °C is 1.412 mmhos cm^{-1}.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

7. Sample Preparation

Surface water samples are collected from a study site. If sample pH is not to be analyzed immediately after collection, store samples at 4 °C. Analyze samples within 72 hours.

8. Procedure

8.1 Water sample is filtered into a 50-mL tube and capped.

8.2 Standardize the conductivity meter using RO water (blank) and 0.010 *N* KCl (1.41 mmhos cm^{-1}).

8.3 Read conductance of water sample directly from the meter.

8.4 Record conductance to 0.01 mmhos cm^{-1}.

9. Calculations

9.1 Use the following relationship to estimate the total soluble cation or anion concentration (meq L^{-1}) in the water.

EC (mmhos cm^{-1}) x 10 = Cation or Anion (meq L^{-1})

9.2 Report the pH of the water sample to the nearest 0.1 pH unit.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

National Research Council. 1993. Soil and water quality. An agenda for agriculture. Natl. Acad. Press, Washington, DC.

Ground and Surface Water Analyses (4l)
Electrical Conductivity and Salts (4l2)
Ion Chromatograph (4l2c)
Conductivity Detector (4l2c1)
Self-Regeneration Suppressor (4l2c1a)
Bromide, Chloride, Fluoride, Nitrate, Nitrite, Phosphate, and Sulfate (4l2c1a1-7)

1. Introduction to Ground Water Ion Chromatograph Analyses

USDA–NRCS projects requiring collection of water samples are usually completed in conjunction with pedon sampling or for specific research projects. Choice of the water-sampling site depends not only on the purpose of the investigation but also on local conditions, depth, and frequency of sampling (Velthorst, 1996). The amount and composition of water samples vary strongly with small changes in location.

2. Scope and Field of Application

Nutrients (nitrogen and phosphorus), sediments, pesticides, salts, or trace elements in ground water and surface water affect soil and water quality (National Research Council, 1993). This procedure is developed for the analysis of ground or surface water.

Sample filtration using a 0.45-µm membrane separates dissolved from suspended material. The sample is then split into two subsamples: one is acidified to pH 2 for cation analyses (e.g., Al, Fe, Mn) and the other is used for anion analyses.

3. Principle

The water sample is filtered and is diluted according to its electrical conductivity (EC_S). The diluted sample is injected into the ion chromatograph, and the anions are separated. A conductivity detector is used to measure the anion species and content. Standard anion concentrations are used to calibrate the system. The water anions Br^-, Cl^-, F^-, NO_3^-, NO_2^-, PO_4^{3-}, and SO_4^{2-} are reported in mmol (−) L^{-1} (meq L^{-1}.)

3.1 Interferences

Some water samples contain suspended solids and require filtering. Organic anions that have low molecular weight will co-elute with inorganic anions from the column.

4. Apparatus

4.1 Syringe filters, 25-mm, 0.45-µm pore size

4.2 Tubes, 50-mL, with caps

4.3 Ion chromatograph, double-column, conductivity detection with associated guard column, analytical column, self-regeneration suppressor, autosampler, and software

4.4 Digital diluter/dispenser, with syringes, 10,000-µL and 1,000-µL, gas tight

4.5 Poly-vials with caps, 5-mL

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.2 Helium gas. De-gas RODI water used in eluent generation for at least 15 minutes.

5.3 **Primary stock standards solutions,** high purity, commercially made:

1,000 mg/L Cl^-, Chloride Standard
1,000 mg/L F^-, Fluoride Standard
1,000 mg/L NO_3^-, Nitrate Standard
1,000 mg/L NO_2^-, Nitrite Standard
1,000 mg/L SO_4^{2-}, Sulfate Standard
1,000 mg/L PO_4^{3-}, Phosphate Standard
1,000 mg/L CH_3COO^-, Acetate Standard
1,000 mg/L Na^+, Sodium Standard
1,000 mg/L NH_4^+, Ammonium Standard
1,000 mg/L K^+, Potassium Standard
1,000 mg/L Mg_2^+, Magnesium Standard
1,000 mg/L Ca_2^+, Calcium Standard

5.4 **Anion and cation calibration standards**

Components: Primary stock standards, 1,000 mg L^{-1}; RODI water

- Refer to table 4I2c–1 and table 4I2c–2 for anion mixing instructions and concentrations.
- Refer to table 4I2c–3 and table 4I2c–4 for cation mixing instructions and concentrations.
- Prepare fresh weekly.

5.4.1 Anion 5

- To a 500-mL glass volumetric flask, add the following in order:
  - 250 mL of RODI water
  - 1 mL of Fluoride Standard
  - 10 mL of Acetate Standard
  - 40 mL of Chloride Standard
  - 10 mL of Nitrite Standard
  - 40 mL of Nitrate Standard
  - 40 mL of Sulfate Standard

- 40 mL of Phosphate Standard
- Fill to volume with RODI water.

- Invert to mix.

5.4.2 Anion 4

- To a 500-mL glass volumetric flask, add the following in order:
  - 250 mL of RODI water
  - 0.5 mL of Fluoride Standard
  - 5 mL of Acetate Standard
  - 20 mL of Chloride Standard
  - 5 mL of Nitrite Standard
  - 20 mL of Nitrate Standard
  - 20 mL of Sulfate Standard
  - 20 mL of Phosphate Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.4.3 Anion 3

- To a 500-mL glass volumetric flask, add the following in order:
  - 250 mL of RODI water
  - 0.25 mL of Fluoride Standard
  - 2.5 mL of Acetate Standard
  - 10 mL of Chloride Standard
  - 2.5 mL of Nitrite Standard
  - 10 mL of Nitrate Standard
  - 10 mL of Sulfate Standard
  - 10 mL of Phosphate Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.4.4 Anion 2

- To a 500-mL glass volumetric flask, add the following in order:
  - 250 mL of RODI water
  - 50 mL of Anion 4 standard solution
  - Fill to volume with RODI water.
- Invert to mix.

5.4.5 Anion 1

- To a 500-mL glass volumetric flask, add the following in order:
  - 250 mL of RODI water
  - 25 mL of Anion 4 standard solution
  - Fill to volume with RODI water.
- Invert to mix.

5.4.6 Anion CVS

- To a 500-mL glass volumetric flask, add the following in order:
  - 250 mL of RODI water
  - 0.1 mL of Fluoride Standard
  - 1 mL of Acetate Standard
  - 5 mL of Chloride Standard
  - 1 mL of Nitrite Standard
  - 4 mL of Nitrate Standard
  - 4 mL of Sulfate Standard
  - 4 mL of Phosphate Standard
  - Fill to volume with RODI water.
- Invert to mix.

Table 4I2c–1.—Preparation of Anion Calibration Standards and Calibration Verification Standard. (Prepare in 500-mL volumetric flasks.)

Calibration Std.	Fluoride	Acetate	Chloride	Nitrite	Nitrate	Sulfate	Phosphate	RODI Water
	(mL)	*(mL)*	*(mL)*	*(mL)*	*(mL)*	*(mL)*	*(mL)*	
Anion 5	1	10	40	10	40	40	40	Fill to 500 mL with RODI water
Anion 4	0.5	5	20	5	20	20	20	
Anion 3	0.25	2.5	10	2.5	10	10	10	
Anion 2	Add 50 mL of Anion 4 standard to 500-mL flask							
Anion 1	Add 25 mL of Anion 4 standard to 500-mL flask							
Anion CVS	0.1	1	4	1	4	4	4	

Table 4I2c–2.—Concentrations of Anion Calibration Standards and Calibration Verification Solution.

Calibration Std.	Fluoride	Acetate	Chloride	Nitrite	Nitrate	Sulfate	Phosphate
	(ppm)	*(ppm)*	*(ppm)*	*(ppm)*	*(ppm)*	*(ppm)*	*(ppm)*
Anion 5	2	20	80	20	80	80	80
Anion 4	1	10	40	10	40	40	40
Anion 3	0.5	5	20	5	20	20	20
Anion 2	0.1	1	4	1	4	4	4
Anion 1	0.05	0.5	2	0.5	2	2	2
Anion CVS	0.2	2	8	2	8	8	8

5.4.7 Cation 4

- To a 500-mL glass volumetric flask, add the following in order:
  - 250 mL of RODI water
  - 15 mL of Sodium Standard
  - 5 mL of Ammonium Standard
  - 2.5 mL of Potassium Standard
  - 5 mL of Magnesium Standard
  - 15 mL of Calcium Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.4.8 Cation 3

- To a 500-mL glass volumetric flask, add the following in order:
  - 250 mL of RODI water
  - 7.5 mL of Sodium Standard
  - 2.5 mL of Ammonium Standard
  - 1.25 mL of Potassium Standard
  - 2.5 mL of Magnesium Standard
  - 7.5 mL of Calcium Standard
  - Fill to volume with RODI water.
- Invert to mix.

5.4.9 Cation 2

- To a 500-mL glass volumetric flask, add the following in order:
  - 250 mL of RODI water
  - 50 mL of Cation 4 standard solution
  - Fill to volume with RODI water.
- Invert to mix.

5.4.10 Cation 1

- To a 500-mL glass volumetric flask, add the following in order:
  - 250 mL of RODI water
  - 25 mL of Cation 4 standard solution
  - Fill to volume with RODI water.
- Invert to mix.

5.4.11 Cation CVS

- To a 500-mL glass volumetric flask, add the following in order:
  - 250 mL of RODI water
  - 3 mL of Sodium Standard
  - 1 mL of Ammonium Standard

- 0.5 mL of Potassium Standard
- 1.0 mL of Magnesium Standard
- 3.0 mL mL of Calcium Standard
- Fill to volume with RODI water.

- Invert to mix.

Table 4l2c–3.—Preparation of Cation Calibration Standards and Calibration Verification Standard. (Prepare in 500-mL volumetric flasks.)

Calibration Std.	Sodium	Ammonium	Potassium	Magnesium	Calcium	RODI Water
	(mL)	*(mL)*	*(mL)*	*(mL)*	*(mL)*	
Cation 4	15	5	2.5	5	15	Fill to 500 mL with RODI water
Cation 3	7.5	2.5	1.25	2.5	7.5	
Cation 2	Add 50 mL of Cation 4 standard to 500-mL flask					
Cation 1	Add 25 mL of Cation 4 standard to 500-mL flask					
Cation CVS	3	1	0.5	1	3	

Table 4l2c–4.—Concentrations of Cation Calibration Standards and Calibration Verification Standard.

Calibration Std.	Sodium	Ammonium	Potassium	Magnesium	Calcium
	(ppm)	*(ppm)*	*(ppm)*	*(ppm)*	*(ppm)*
Cation 4	30	10	5	10	30
Cation 3	15	5	2.5	5	15
Cation 2	3	1	0.5	1	3
Cation 1	1.5	0.5	0.25	0.5	1.5
Cation CVS	6	2	1	2	6

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

7. Sample Preparation

Surface water samples are collected from study site. If sample pH is not to be analyzed immediately after collection, store samples at 4 °C. Analyze samples within 72 hours.

8. Procedure

8.1 Estimate the total soluble anion concentration (meq L^{-1}).

8.1.1 Anion concentration (meq L^{-1}) = $(EC_S \times 10) - (HCO_3^- + CO_3^{2-})$

- Multiply the EC_S (from method 4F2b1) by 10.

8.2 Subtract the CO_3^{2-} and HCO_3^- concentrations (from method 4F2c1c1a1-2) from the total anion concentration. Use the following CO_3^{2-} and HCO_3^- equations.

8.2.1 Determine carbonate:

CO_3^{2-} (mmol (−) L^{-1}) = $[2 \times T_{8.25} \times N] / V$

8.2.2 Determine bicarbonate

HCO_3^- (mmol (−) L^{-1}) = $[(T_{4.60} - T_{8.25} - B) \times N] / V$

$T_{8.25}$ = Titer for $CO_3^{2-} \rightarrow HCO_3^-$ (mL)

$T_{4.60}$ = Titer for $HCO_3^- \rightarrow H_2CO_3$ (mL)

N = Normality of H_2SO_4 (mmol(+)/mL)

B = Average titer of blank solution (mL)

V = Volume of saturation extract titrated (L)

2 = Multiplier to calculate CO_3^{2-} (mmol (−) L^{-1}) from $T_{8.25}$

8.2.3 The remainder is the approximate concentration (meq L^{-1}) of anions to be separated by ion chromatography.

8.3 Dilute the saturation extract with the RODI water as follows:

EC_S	Dilution Factor
(dS cm^{-1})	
0.00 to 0.9	3
0.9 to 1.1	5
1.1 to 1.6	10
1.6 to 2.5	20
2.5 to 4.1	50
4.1 to 7.10	100
7.1 to 13.3	200
13.3 to 27.6	400
27.6 to 56.5	800
56.5 to 138.5	1,500
138.5 to 250	6,000

8.4 Set-up and operation of ion chromatograph (IC).—Refer to the manufacturer's manual for the set-up and operation of the chromatograph. An example of instrument parameters, ranges, and typical settings specific to a system follows.

Example Anion Parameters

Anion Parameters	Range and/or Typical Setting
Calibration model	Peak Area
Detector	Conductivity
Column type	Ionpac AS20
Gradient program	Gradient
Column program	Hold 13 mmol KOH, 9 min/linear increase to 55 mmol KOH, 9-16 min/hold 55 mmol KOH, 16-20 min
Pump flow setting	0.9 mL/min
Pump pressure	≈2,700 psi
Injection volume	25 µL
Column temperature	30 ºC
Suppressor current	112 mA

Example Cation Parameters

Cation Parameters	Range and/or Typical Setting
Calibration model	Peak Area
Detector	Conductivity
Column type	Ionpac CS12A
Gradient program	Isocratic
Column program	20 mmol Methane sulfonic Acid
Pump flow setting	0.9 mL/min
Pump pressure	≈2,700 psi
Injection volume	25 µL
Column temperature	30 ºC
Suppressor current	53 mA

8.5 IC Calibration and Analysis

8.5.1 Calibrate the chromatograph and analyze samples according to the instrument method. Analyze a CVS for both anions and cations every 12 samples. If the CVS is outside the accepted range (+/- 10%), recalibrate and re-analyze from the last passing CVS.

8.5.2 If samples are outside the calibration range for one or more analytes, further dilution of the sample extract is required. Dilute sample extracts with RODI water and re-analyze.

8.5.3 Perform one quality control using Anion CVS and Cation CVS for every 12 samples. If reading is not within the accepted range (+/- 10%), recalibrate and re-analyze from the last CVS that is within range.

8.5.4 Record analyte readings to 0.01 mg L^{-1}.

9. Calculations

9.1 Concentrations are converted from mg L^{-1} to meq L^{-1}:

Analyte Concentration in Soil (meq L^{-1}) = (A x B) / C

A = Analyte (Br^-, Cl^-, F^-, NO_3^-, NO_2^-, PO_4^{3-}, and SO_4^{2-}) concentration in extract (mg L^{-1})

B = Dilution ratio, if needed

C = Equivalent weight

Equivalent Weight	
Analyte	**mg mmol L^{-1}**
F^-	19.00
CH_3COO^-	59.04
Cl^-	35.45
NO_2^-	46.01
NO_3^-	62.00
SO_4^{2-}	48.03
PO_4^{3-}	31.66
Na^+	22.99
NH_4^+	18.04
K^+	39.10
Mg^{2+}	12.20
Ca^{2+}	20.04

9.2 Report the water extraction anions (Br^-, Cl^-, F^-, NO_3^-, NO_2^-, PO_4^{3-}, SO_4^{2-}) to the nearest 0.1 meq L^{-1} (mmol (−) L^{-1}).

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist for final review.

10.6 Compare individual results to method detection limits (MDL) and practical quantitation limits (PQL) before reporting analysis results.

10.6.1 Report numerical values for results that are above the PQL.

10.6.2 Report “trace” for results that are between the MDL and PQL.

10.6.3 Report “non-detect” for results that are below the MDL.

MDL and PQL in Reporting Units

Analyte	MDL	PQL
	(mg kg^{-1} of oven-dried soil)	*(mg kg^{-1} of oven-dried soil)*

11. References

National Research Council. 1993. Soil and water quality. An agenda for agriculture. Natl. Acad. Press, Washington, DC.

Ground and Surface Water Analyses (4l)
Electrical Conductivity and Salts (4l2)
Automatic Titrator (4l2d)
Combination pH-Reference Electrode (4l2d1)
Acid Titration, H_2SO_4 (4l2d1a)
Carbonate and Bicarbonate (4l2d1a1-2)

1. Introduction to Surface Water Carbonate and Bicarbonate Analyses

Nutrients (nitrogen and phosphorus), sediments, pesticides, salts, or trace elements in ground water and surface water affect soil and water quality (National Research Council, 1993). This procedure is developed for the analysis of ground or surface water.

2. Scope and Field of Application

Carbonate and bicarbonate anions are among the dissolved materials found in surface water and can be used to evaluate the environmental impact of agricultural land on natural water resources. Studies at the KSSL reported a correlation between water-extractable elements for soils and their concentration in runoff from agricultural watersheds (Elrashidi et al., 2005a, 2005b).

3. Principle

The water sample is filtered, and an aliquot of the soil extract is titrated on an automatic titrator to pH 8.25 (CO_3^{2-}) and pH 4.60 (HCO_3^-) end points. The carbonate and bicarbonate are calculated from the titers, aliquot volume, blank titer, and acid normality. Carbonate and bicarbonate are reported in meq L^{-1} (mmol (−) L^{-1}).

3.1 Interferences

Clean the electrode by rinsing with distilled water and patting it dry with tissue. Wiping the electrode dry with a cloth, laboratory tissue, or similar material may cause electrode polarization.

Slow electrode response time may cause over shooting of the end point. A combination of slowing the burette speed and increasing the time delay may help. Cleaning the electrode with detergent may decrease the response time. If all else fails, changing the electrode generally solves the problem.

Blanks may not titrate properly because some sources of reverse osmosis (RO) water have a low pH.

4. Apparatus

4.1 Syringe filters, 25-mm, 0.45-µm pore size

4.2 Tubes, 50-mL, with caps

4.3 Automatic titrator, with control unit, sample changer, dispenser, and software

4.4 Combination pH-reference electrode

4.5 Pipettes, electronic digital, 2,500-µL and 10-mL, with tips, 2,500-µL and 10-mL

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Helium gas

5.3 Concentrated sulfuric acid (H_2SO_4) (CAS# 7664-93-9), 36 *N,* trace pure grade

5.4 Sulfuric acid solution, 0.0240 *N* standardized

Components: Sulfuric acid (H_2SO_4), RODI water (degassed ≈15 min)

- To a 5-L polyethylene carboy, add the following in order:
  - 4 L of RODI water, degassed
  - 2.67 mL of concentrated H_2SO_4
- Swirl to mix.
- Refer to section 4A for standardization of acids.
- Re-standardize the acid at regular intervals.

5.5 pH buffers, pH 4.00, 7.00, and 9.18

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids.

Follow the manufacturer's safety precautions when using the automatic titrator.

7. Sample Preparation

Surface water samples are collected from the study site. If sample pH is not to be analyzed immediately after collection, store samples at 4 °C. Analyze samples within 72 hours.

8. Procedure

8.1 Water sample is filtered into a 50-mL tube and capped. If extracts are not to be analyzed immediately after collection, then store samples at 4 °C. Analyze samples within 72 h.

8.2 Pipette 3 mL of the water sample into a 250-mL titration beaker.

8.3 Add 72 mL of RO water into a titration beaker. Final volume is 75 mL for blanks and samples. Run 8 to 12 blanks of RO water with each sample batch.

8.4 Calibrate automatic titrator with pH 9.18, 7.00 and 4.00 buffers. Set-up the automatic titrator to set end point titration mode. The "Set" pH parameters are listed as follows:

Parameter	Value
Ep_1	pH 8.25
Dyn change pH	1.5 units
Drift	0.4 mV s^{-1}
Time delay	10 s
Ep_2	pH 4.60
Dyn change pH	1.5 units
Drift	0.4 mV s^{-1}
Temp	25 °C
Stop volume	35 mL

8.5 Place the 250-mL titration beakers in the sample changer. Start titration.

8.6 Record titer and other titration parameters.

9. Calculations

9.1 Determine carbonate

$$CO_3^{2-}(\text{mmol}\ (-)\ L^{-1}) = [2 \times T_{8.25} \times N] / V$$

9.2 Determine bicarbonate

$$HCO_3^{-}\ (\text{mmol}\ (-)\ L^{-1}) = [(T_{4.60} - T_{8.25} - B) \times N] / V$$

$T_{8.25}$ = Titer for $CO_3^{2-} \rightarrow HCO_3^{-}$ (mL)

$T_{4.60}$ = Titer for $HCO_3^{-} \rightarrow H_2CO_3$ (mL)

N = Normality of H_2SO_4 (mmol(+)/mL)

B = Average titer of blank solution (mL)

V = Volume of saturation extract titrated (L)

2 = Multiplier to calculate CO_3^{2-} (mmol (−) L^{-1}) from $T_{8.25}$

9.3 Report saturation extract CO_3^{2-} and HCO_3^{-} concentrations to the nearest 0.1 mmol (−) L^{-1}.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

National Research Council. 1993. Soil and water quality. An agenda for agriculture. Natl. Acad. Press, Washington, DC.

Ground and Surface Water Analyses (4l)

Total Analysis (4l3)

Inductively Coupled Plasma Mass Spectrophotometer (4l3b)

Aluminum, Arsenic, Barium, Boron, Cadmium, Calcium, Chromium, Cobalt, Copper, Iron, Lead, Magnesium, Manganese, Molybdenum, Nickel, Phosphorus, Potassium, Selenium, Silicon, Sodium, Strontium, Vanadium, and Zinc (4l3b1-22)

1. Introduction to Surface Water ICP–MS Analyses

Nutrients (such as nitrogen and phosphorus), sediments, pesticides, salts, or trace elements in ground water and surface water affect soil and water quality (National Research Council, 1993). Elements may enter ground and surface waters through natural activities (e.g., mineral weathering and translocation through the soil or landscape) or human activities (e.g., pesticides, fertilizers, mining, smelting, and manufacturing). The relative reactivity or bioavailability of these elements in the environment is governed by a variety of chemical factors, such as pH, redox potential, organic material, and oxides (Pierzynski and Schwab, 1993; Gambrell, 1994; Keller and Vedy, 1994). This procedure is developed for the analysis of the elemental content of ground or surface water.

2. Scope and Field of Application

This method determines water-dissolved elements in surface or ground water samples. Environmental water sources may contain available forms of essential plant macro- and micro-nutrients (N, P, C, S, K, Ca, Mg, Fe, Mn, Cu, Zn, B, and Mo) and water-soluble forms of trace-elements and heavy toxic metals (Al, As, Se, Ba, Cd, Co, Cr, Ni, Pb, Sr, and Si).

This method can be implemented in water quality studies to determine the amount of soil elements that can be transported by runoff water from agriculture land to surface and ground waters (streams, rivers, lakes).

Environmental water samples are collected, centrifuged, and filtered. The concentration of Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Se, Si, Sr, V, and Zn are determined using an inductively coupled plasma mass spectrometer (ICP–MS). Element concentrations are reported as mg/L.

3. Principle

Environmental water samples are collected from surface or ground water sources. The samples are centrifuged or filtered to remove suspended material prior to ICP–MS analysis. Calibration standards plus a blank are prepared for elemental analysis. The concentration of all or selected elements (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Se, Sr, Si, V, and Zn) are determined by inductively coupled plasma mass spectrophotometer (ICP–MS). Data from this procedure are reported as mg/L.

3.1 Interferences

Element-specific interferences are corrected or minimized by using internal standards, collision/reaction cell technology, and careful selection of specific masses for data reporting.

4. Apparatus

4.1 Pipettes, electronic digital, 1-mL and 10-mL

4.2 Volumetric flasks, 1-L and 500-mL, class A glass

4.3 Centrifuge tubes, 50-mL, disposable

4.4 Disposable sample tubes, 15-mL, trace-metal grade polymer

4.5 Centrifuge

4.6 Funnel rack and funnels

4.7 #42 alpha cellulose filter paper

4.8 Inductively coupled plasma mass spectrophotometer (ICP–MS)

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.2 Concentrated nitric acid (HNO_3) (CAS # 7697-37-2), 16 *N,* trace pure grade

5.3 Concentrated hydrochloric acid (HCl) (CAS# 7647-01-0), 12 *N,* trace pure grade

5.4 Compressed argon (minimum purity 99.99%)

5.5 Compressed hydrogen (minimum purity 99.999%)

5.6 Compressed helium (minimum purity 99.999%)

5.7 **Trace metals in drinking water (TMDW) stock**, commercially prepared certified reference material (CRM) containing:

2 µg/L Ag
10 µg/L Sb, Cd, and Se
20 µg/L Be, Cr, and Cu
25 µg/L Co
30 µg/L V
40 µg/L Pb and Mn
50 µg/L Ba,
60 µg/L Ni
70 µg/L Zn
80 µg/L As
100 µg/L Fe and Mo
120 µg/L Al

250 µg/L Sr

9,000 µg/L Mg

5.8 Water extractable elements, commercially prepared stock solution containing:

1,000 mg/L Ca, K, Mg, and Na

150 mg/L P and Sr

100 mg/L Al, Ba, Fe, and Mn

50 mg/L Cu, V, and Zn

10 mg/L Co, Cr, Ni, and Pb

5 mg/L As and Cd

1 mg/L Mo

5.9 High purity concentrated primary standards; individual high purity elemental, standards, commercially prepared individual solutions containing:

1,000 mg/L Au, Gold Standard

1,000 mg/L B, Boron Standard

1,000 mg/L Be, Beryllium Standard

1,000 mg/L Cr, Chromium Standard

1,000 mg/L, Phosphorus Standard

1,000 mg/L Se, Selenium Standard

1,000 mg/L Si, Silicon Standard

1,000 mg/L Li^6, $Lithium^6$ Standard

1,000 mg/L Sc, Scandium Standard

1,000 mg/L Ge, Germanium Standard

1,000 mg/L Y, Yttrium Standard

1,000 mg/L Tb, Terbium Standard

1,000 mg/L In, Indium Standard

1,000 mg/L Bi, Bismuth Standard

1,000 mg/L Sr, Strontium Standard

1,000 mg/L Ce, Cerium Standard

1,000 mg/L Fe, Iron Standard

1,000 mg/L Mg, Magnesium Standard

1,000 mg/L Pb, Lead Standard

1,000 mg/L U, Uranium Standard

5.10 Rinse solution for ICP–MS sample introduction

Components: Nitric acid (HNO_3); hydrochloric acid (HCl); 1,000 mg/mL Au, Gold Primary Standard; RODI water

- To a 2-L polypropylene jug, add the following in order:
  - 500 mL of RODI water

- 2 mL of 1,000 mg/L Au standard
- 63 mL of HNO_3
- 45 mL of HCl
- Fill to volume with RODI water.

- Mix thoroughly.

5.11 ICP–MS tuning solutions

Components: Nitric acid (HNO_3), RODI water, 1,000 µg/L primary standards, nitric acid (HNO_3), RODI water

5.11.1 Tuning stock solution; 1 mg/L tune solution

- To a 1-L glass volumetric flask, add the following in order:
  - Approximately 500 mL of RODI water
  - 1.0 mL of 1,000 mg/L Be, Beryllium Standard
  - 1.0 mL of 1,000 mg/L Ce, Cerium Standard
  - 1.0 mL of 1,000 mg/L Fe, Iron Standard
  - 1.0 mL of 1,000 mg/L In, Indium Standard
  - 1.0 mL of 1,000 mg/L Li^6, $Lithium^6$ Standard
  - 1.0 mL of 1,000 mg/L Mg, Magnesium Standard
  - 1.0 mL of 1,000 mg/L Pb, Lead Standard
  - 1.0 mL of 1,000 mg/L I, Indium Standard
  - 1.0 mL of 1,000 mg/L U, Uranium Standard
  - Fill to volume with RODI water.
- Mix thoroughly.

5.11.2 Daily tuning solution

- To a 1-L glass volumetric flask, add the following in order:
  - Approximately 500 mL of RODI water
  - 18 mL of concentrated HNO_3
  - 1 mL of tuning stock solution
  - Fill to volume with RODI water.
- Mix thoroughly.

5.11.3 Monthly tuning solution (dual detector)

- To a 1-L glass volumetric flask, add the following in order:
  - Approximately 500 mL of RODI water
  - 18 mL of HNO_3
  - 6 mL of HCl
  - 0.2 mL each of 1,000 mg/L: Al, Ba, Ce, Co, Cu, In, Li^6, Mg, Mn, Ni, Pb, Tb, U; and Zn
  - Fill to volume with RODI water.
- Mix thoroughly.

5.12 Calibration verification (CVS) and internal standard (IS) solutions

Components: Nitric acid (HNO_3), RODI water, 1,000 µg/L primary standards, nitric acid (HNO_3), hydrochloric acid (HCl), RODI water

5.12.1 Internal standard solution

- To a 2-L glass volumetric flask, add the following in order:
  - Approximately 500 mL of RODI water
  - 18 mL of HNO_3
  - 6 mL of HCl
  - 0.250 mL of 1,000 mg/L Au, Gold Standard
  - 1 mL each of 1,000 mg/L Li^6, Sc, Ge, Y, In, Tb, and Bi
  - Fill to volume with RODI water.
- Mix thoroughly.

5.12.2 Silicon, phosphorus, strontium CVS (SiPSr)

- To a 1-L glass volumetric flask, add the following in order:
  - Approximately 500 mL of RODI water
  - 0.50 mL of 1,000 mg/L Si, Silicon Standard
  - 0.50 mL of 1,000 mg/L P, Phosphorus Standard
  - 0.50 mL of 1,000 mg/L Sr, Strontium Standard
  - Fill to volume with RODI water.
- Mix thoroughly.

5.12.3 TMDW CVS, 1:10 dilution

- To a 50-mL centrifuge tube, add the following in order:
  - 27 mL of RODI water
  - 3 mL of stock TMDW
- Mix thoroughly.

5.13 Water extractable elements calibration solutions

Components: Water extractable elements stock solution (commercially prepared), RODI water

- Refer to tables 4I3b–1 through 4I3b–6 for mixing instructions.
- Standards are matrix matched.
- Refer to table 4I3b–7 for standard concentrations.

5.13.1 Mixed elements solution WS-3 (high)

- To a 500-mL glass volumetric flask, add the following in order:
  - 300 mL of RODI water
  - 0.5 mL of Water Extractable solution

- Fill to volume with RODI water.
- Mix thoroughly.

5.13.2 Mixed elements solution WS-2 (medium)

- To a 500-mL glass volumetric flask, add the following in order:
  - 300 mL of RODI water
  - 50 mL of WS-3
  - Fill to volume with RODI water.
- Mix thoroughly.

5.13.3 Mixed elements solution WS-1 (low)

- To a 500-mL glass volumetric flask, add the following in order:
  - 300 mL of RODI water
  - 50 mL of WS-2
  - Fill to volume with RODI water.
- Mix thoroughly.

Table 4I3b–1.—Water Extractable Elements: Preparation of ICP–MS Mixed Elements Solutions WS-3, WS-2, and WS-1. (Prepare in 500-mL volumetric flasks.)

Component	WS-3 (High)	WS-2 (Medium)	WS-1 (Low)
Water extractable elements stock	1.0 mL	--	--
WS-3	--	50 mL	--
WS-2	--	--	50 mL
RODI water	250 mL of RODI water initially. Fill to volume with RODI water.		

5.14 Elemental phosphorus calibration and verification standards

Components: 1,000 mg/L P, Phosphorus Standard; RODI water

5.14.1 Phosphorus standard solution WS-5 (high)

- To a 1-L glass volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 1 mL of 1,000 mg/mL P, Phosphorus Standard
  - Fill to volume with RODI water.
- Mix thoroughly.
- Refer to table 4I3b–7 for concentrations.

5.14.2 Phosphorus standard solution WS-4 (low)

- To a 1-L glass volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 100 mL of WS-5 solution
  - Fill to volume with RODI water.
  - Mix thoroughly.
  - Refer to table 4I3b–7 for concentrations.

Table 4I3b–2.—Water Extractable Elements: Preparation of ICP–MS Phosphorus Calibration Solutions WS-5 and WS-4. (Prepare in 1-L volumetric flasks.)

Component	WS-5 (High)	WS-4 (Low)
1,000 mg/mL P, Phosphorus Standard	1 mL	--
WS-5 solution	--	100 mL
RODI water	500 mL of RODI water initially. Fill to volume with RODI water.	

5.15 Elemental boron calibration and verification standards

Components: 1,000 mg/L B, Boron Standard; RODI water

5.15.1 Boron standard solution WS-7 (high)

- To a 1-L glass volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 1 mL of 1,000 mg/mL B, Boron Standard
  - Fill to volume with RODI water.
- Mix thoroughly.
- Refer to table 4I3b–7 for concentrations.

5.15.2 Boron standard solution WS-6 (low)

- To a 1-L glass volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 100 mL of WS-7 solution
  - Fill to volume with RODI water.
- Mix thoroughly.
- Refer to table 4I3b–7 for concentrations.

Table 4I3b–3.—Water Extractable Elements: Preparation of ICP–MS Boron Calibration Solutions WS-7 and WS-6. (Prepare in 1-L volumetric flasks.)

Component	WS-7 (High)	WS-6 (Low)
1,000 mg/mL B, Boron Standard	1.0 mL	--
WS-7 solution	--	100 mL
RODI water	500 mL of RODI water initially. Fill to volume with RODI water.	

5.16 Elemental silicon calibration and verification standard WS-8

Components: 1,000 mg/mL Si, Silicon Standard; RODI water

- To a 1-L glass volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 1 mL of 1,000 mg/L Si, Silicon Standard
  - Fill to volume with RODI water.
- Mix thoroughly.
- Refer to table 4I3b–7 for concentrations.

Table 4I3b–4.—Water Extractable Elements: Preparation of ICP–MS Silicon Calibration Solution WS-8. (Prepare in 1-L volumetric flask.)

Component	WS-8
1,000 mg/mL Si, Silicon Standard	1.0 mL
RODI water	500 mL of RODI water initially. Fill to volume with RODI water.

5.17 Selenium stock (2 ppm)

Components: 1,000 mg/L Se, Selenium Standard; RODI water

- To a 500-mL glass volumetric flask, add the following in order:
  - 250 mL of RODI water
  - 1 mL of 1,000 mg/L Se, Selenium Standard
  - Fill to volume with RODI water.
- Mix thoroughly.
- Refer to table 4I3b–7 for concentrations.

5.17.1 Selenium standard solution WS-10 (high)

- To a 500-mL glass volumetric flask, add the following in order:
  - 250 mL of RODI water
  - 2.5 mL of Selenium stock solution
  - Fill to volume with RODI water.
- Mix thoroughly.
- Refer to table 4I3b–7 for concentrations.

5.17.2 Selenium standard solution WS-9 (low)

- To a 1-L glass volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 0.250 mL of Selenium stock solution
  - Fill to volume with RODI water.
- Mix thoroughly.
- Refer to table 4I3b–7 for concentrations.

Table 4I3b–5.—Water Extractable Elements: Preparation of ICP–MS Selenium Stock Solution and Calibration Solutions WS-10 and WS-9. (Prepare in 500-mL volumetric flasks.)

Component	Se Stock Solution	WS-10 (High)	WS-9 (Low)
1,000 mg/mL Se, Selenium Standard	0.5 mL	--	--
Se stock solution	--	2.5 mL	0.25
RODI water	250 mL of RODI water initially. Fill to volume with RODI water.		

5.18 Chromium stock (2 ppm)

Components: 1,000 mg/L Cr, Chromium Standard; RODI water

- To a 500-mL glass volumetric flask, add the following in order:
  - 250 mL of RODI water
  - 1 mL of 1,000 mg/mL Cr, Chromium Standard
  - Fill to volume with RODI water.
- Mix thoroughly.
- Refer to table 4I3b–7 for concentrations.

5.18.1 Chromium standard solution WS12 (high)

- To a 500-mL glass volumetric flask, add the following in order:
  - 250 mL of RODI water

- 2.5 mL of Chromium stock solution
- Fill to volume with RODI water.

- Mix thoroughly.
- Refer to table 4I3b–7 for concentrations.

5.18.2 Chromium standard solution WS11(low)

- To a 1-L glass volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 0.250 mL of Chromium stock solution
  - Fill to volume with RODI water.
- Mix thoroughly.
- Refer to table 4I3b–7 for concentrations.

Table 4I3b–6.—Water Extractable Elements: Preparation of ICP–MS Chromium Calibration Solutions WS-12 and WS-11. (Prepare in 500-mL volumetric flasks.)

Component	Cr Stock Solution	WS-12 (High)	WS-11 (Low)
1,000 mg/mL Cr, Chromium Standard	1.0 mL	--	--
Cr stock solution	--	2.5 mL	0.25
RODI water	250 mL of RODI water initially. Fill to volume with RODI water.		

5.19 Stock daily tuning solution; 1,000 mg/L tune solution

Components: 1,000 mg/L Primary Standards, RODI water

1,000 mg/L Be, Beryllium Standard
1,000 mg/L Li^6, $Lithium^6$ Standard
1,000 mg/L Ce, Cerium Standard
1,000 mg/L Fe, Iron Standard
1,000 mg/L Mg, Magnesium Standard
1,000 mg/L Pb, Lead Standard
1,000 mg/L In, Indium Standard
1,000 mg/L U, Uranium Standard

- To a 1-L glass volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 1 mL each of 1,000 mg/L: Be, Ce, Fe, In, Li, Mg, Pb, and U
  - Fill to volume with RODI water.

- Mix thoroughly.
- Refer to table 4I3b–7 for concentrations.

5.20 Daily tuning solution; 1 mg/L

Components: Stock tuning solution, nitric acid (HNO_3), RODI water

- To a 1-L volumetric polypropylene volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 18 mL of concentrated nitric acid (HNO_3)
  - 1 mL of stock tuning solution
  - Fill to volume with RODI water.
- Mix thoroughly.

5.21 Monthly tuning solution (dual detector)

Components: Nitric acid (HNO_3); 1,000 µg/L primary standards: Al, Ba, Ce, Co, Cu, In, Li, Mg, Mn, Ni, Pb, Tb, U, and Zn; RODI water

- To a 1-L glass volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 18 mL of nitric acid (HNO_3)
  - 0.2 mL each of 1,000 µg/mL: Al, Ba, Ce, Co, Cu, In, Li, Mg, Mn, Ni, Pb, Tb, U, and Zn
  - Fill to volume with RODI water.
- Mix thoroughly.

5.22 Nitric acid rinse solution, 2%

Components: Nitric acid (HNO_3); hydrochloric acid (HCl); Gold Standard, 1,000 mg/mL Au; RODI water

- To a 2-L glass volumetric flask, add the following in order:
  - 500 mL of RODI water
  - 2 mL of 1,000 mg/L Au
  - 63 mL of HNO_3
  - 45 mL of HCl
  - Fill to volume with RODI water.
- Mix thoroughly.

Table 4I3b–7.—Element Concentration for Each Calibration Standard in µg/L.

Element	Blank	WS1	WS2	WS3	WS4	WS5	WS6	WS7	WS8	WS9	WS10	WS11	WS12
Al	0	1	10	100	--	--	--	--	--	--	--	--	--
As	0	0.05	0.5	5	--	--	--	--	--	--	--	--	--
Ba	0	1	10	100	--	--	--	--	--	--	--	--	--
Cd	0	0.05	0.5	5	--	--	--	--	--	--	--	--	--
Ca	0	10	100	1,000	--	--	--	--	--	--	--	--	--
Co	0	0.1	1	10	--	--	--	--	--	--	--	--	--
Cu	0	0.5	5	50	--	--	--	--	--	--	--	--	--
Fe	0	1	10	100	--	--	--	--	--	--	--	--	--
K	0	10	100	1,000	--	--	--	--	--	--	--	--	--
Pb	0	0.1	1	10	--	--	--	--	--	--	--	--	--
Mg	0	10	100	1,000	--	--	--	--	--	--	--	--	--
Mn	0	1	10	100	--	--	--	--	--	--	--	--	--
Mo	0	0.01	0.1	1	--	--	--	--	--	--	--	--	--
Na	0	10	100	1,000	--	--	--	--	--	--	--	--	--
Ni	0	0.1	1	10	--	--	--	--	--	--	--	--	--
Sr	0	0.15	1.5	150	--	--	--	--	--	--	--	--	--
V	0	0.5	5	50	--	--	--	--	--	--	--	--	--
Zn	0	0.5	5	50	--	--	--	--	--	--	--	--	--
P	0	---	--	---	100	1,000	--	--	--	--	--	--	--
B	0	---	--	---	--	--	100	1,000	--	--	--	--	--
Si	0	---	--	--	--	--	--	--	1,000	--	--	--	--
Se	0	---	--	--	--	--	--	--	--	1	10	--	--
Cr	0	--	--	--	--	--	--	--	--	--	--	1	10

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids. Dispense concentrated acids in fume hood.

Dewars of liquefied argon should be maintained in an upright position following standard KSSL laboratory safety procedures.

Follow the manufacturer's safety precautions when using the ICP–MS.

7. Sample Preparation

Surface or ground water samples are filtered and analyzed within 72 hours of collection.

8. Procedure

8.1 ICP–MS Calibration Standards, Set-up, and Operations

8.1.1 Internal standard is added via peristaltic pump using 0.25 mm ID pump tubing. Sample is added using 0.38 mm tubing. Internal standard is mixed with the samples via mixing T/block prior to entering the nebulizer. Perform instrument checks (tune for sensitivity, torch alignment, nebulizer gas flow, gas cell performance, and STD performance) per instrument instruction manual. Check instrument gas pressures to ensure pressures are correct and gas is of adequate supply.

8.1.2 Establish detection limits using the blank standard solution. The instrumental detection limits are calculated using 3 times the standard deviation of 10 readings of the blank. These values establish the lower detection limits for each element. Analyzed values lower than the detection limits are reported as "ND" or non-detected.

9. Calculations

9.1 Calculate mg L^{-1} of each element in solution.

Analyte concentration in solution = A x C

A = Sample extract reading (µg L^{-1})

C = Dilution, if performed

9.2 Data are reported to the nearest 0.01 mg L^{-1}.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist for final review.

10.6 Compare individual results to method detection limits (MDL) and practical quantitation limits (PQL) before reporting analysis results.

10.6.1 Report numerical values for results that are above the PQL.

10.6.2 Report “trace” for results that are between the MDL and PQL.

10.6.3 Report “non-detect” for results that are below the MDL.

MDL and PQL in Reporting Units

Analyte	MDL	PQL
	(mg kg^{-1} of oven-dried soil)	*(mg kg^{-1} of oven-dried soil)*

11. References

National Research Council. 1993. Soil and water quality. An agenda for agriculture. Natl. Acad. Press, Washington, DC.

U.S. Environmental Protection Agency (USEPA). 1996. Environmental indicators of water quality in the United States. United States Environmental Protection Agency, U.S. Govt. Print. Office, Washington

ANALYSIS OF ORGANIC SOILS OR MATERIALS (5)

Mineral Content (5A)

1. Introduction to Mineral Content

Mineral content is determined through the process of loss on ignition (LOI) and consists of the plant ash and soil particles that remain after removal of organic matter. The determination of organic matter by loss on ignition is a taxonomic criterion for organic soil materials (Soil Survey Staff, 2014).

2. Scope and Field of Application

The percentage of organic matter lost on ignition can be used to define organic soils in place of the Walkley-Black method for organic carbon (6A1c, method obsolete). Organic C data by Walkley-Black are generally considered invalid if organic C >8%. Mineral Content and Rubbed Fiber (current method 5C) analyses are frequently both performed for a more thorough understanding of organic matter in the sample.

3. Principle

Dry the moist, field-state, whole-soil sample to a constant weight at 110 °C in moisture can. Cool and weigh. Place sample in a cold muffle furnace and raise the temperature to 400 °C. Heat sample overnight (16 h), cool, and weigh. The ratio of the weights (400 °C/110 °C) times 100 is the mineral content by percentage.

3.1 Interferences

The sample must be placed in a cold muffle furnace to prevent rapid combustion and sample splattering.

4. Apparatus

4.1 Metal weighing tins

4.2 Oven, 110 °C

4.3 Muffle furnace, 400 °C

4.4 Electronic Balance, ±0.01-g sensitivity

5. Chemicals

None.

6. Health and Safety

Personal Protective Equipment (PPE).—Safety glasses and/or face shield and lab coat or apron, should be used. Use heat resistant gloves and tongs when

working with hot samples and equipment. Thoroughly wash hands after handling samples.

Muffle furnace should be vented to general lab exhaust, or exhaust should be piped to ventilated fume hood.

7. Sample Preparation

A moist, field-state, whole-soil sample is used for this test. The sample should be stored in the refrigerator until time for analysis.

8. Procedure

8.1 Place a 10 to 15 g sample in a tared weighing tin.

8.2 Dry sample at 110 °C overnight.

8.3 Remove sample from oven, cap, and cool in a desiccator.

8.4 When cool, record weight to nearest 0.01 g.

8.5 Place sample and weighing tin in a cold muffle furnace. Raise temperature to 400 °C. Heat overnight (16 h).

8.6 Remove sample from oven, cap, and cool in a desiccator.

8.7 When cool, record sample weight to nearest 0.01 g.

9. Calculations

9.1 Mineral Content (%) = (RW / ODW) x 100

RW = Residue weight after ignition

ODW = Oven-dry soil weight

9.2 Organic Content (%) = 100 − Mineral Content (%)

9.3 Report mineral content to the nearest whole percent.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Soil Survey Staff. 2014. Keys to soil taxonomy. 12th ed. USDA–NRCS.

Pyrophosphate Color (5B)

1. Introduction to Pyrophosphate Color

Decomposed organic materials are soluble in sodium pyrophosphate. The combination of organic matter and sodium pyrophosphate form a solution color that correlates with the decomposition state of the organic materials. Dark colors are associated with sapric materials and light colors with fibric materials (Soil Survey Staff, 2006).

2. Scope and Field of Application

This test can be performed in field offices using whole soil and repeated in the lab. Benefits of using this test in the field office include having O horizons at field state conditions in which samples do not need to be stored or rehydrated prior to testing.

3. Principle

Organic material is combined with sodium pyrophosphate. After standing, the color is evaluated by moistening a chromatographic strip in the solution and comparing the color with standard Munsell color charts. The specific volume of moist material depends on how the sample is packed during sample preparation. The packing of the material should be standardized in order to obtain comparable results by different soil scientists (Soil Survey Staff, 2014).

3.1 Interferences

Moist field-state sample is used for this test to make results as comparable as possible to testing performed in field offices.

4. Apparatus

4.1 Polycons, hinged, 30-mL

4.2 Chromatographic paper

4.3 Munsell color book. The 10YR and 7.5YR pages are used most often.

4.4 Half-syringe, 6-mL. Cut the plastic syringe longitudinally to form a half-cylinder measuring device.

4.5 Scissors

4.6 Paper towel

4.7 Tweezers

4.8 Metal spatula

4.9 5-mL pipette

5. Chemicals

5.1 Sodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$) (CAS# 13472-36-1)

5.2 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

7. Sample Preparation

7.1 Pyrophosphate samples are representative, field-state, and whole-soil and should be kept in the refrigerator until testing. If the soil is dry at the time of testing, add water and let stand to saturate.

7.2 Place approximately 20 cc of a representative sample on a paper towel in a linear mound. Roll the towel around the sample to absorb excess water if necessary. Remove the sample and place on a fresh paper towel (fig. 5B–1). The sample should be firm but saturated with water.

7.3 Use scissors to cut sample into 5- to 10-mm long segments.

7.4 Randomly select a cut sample segment. Using a metal spatula, pack the cut sample into the half-syringe prepared in step 5.4. Fill to the 5-mL mark (or 2.5 mL [2.5 cm^3] volume) with the moist sample. If sample is limited, place the unused portion back in the bulk container for future analysis (fig. 5B–2).

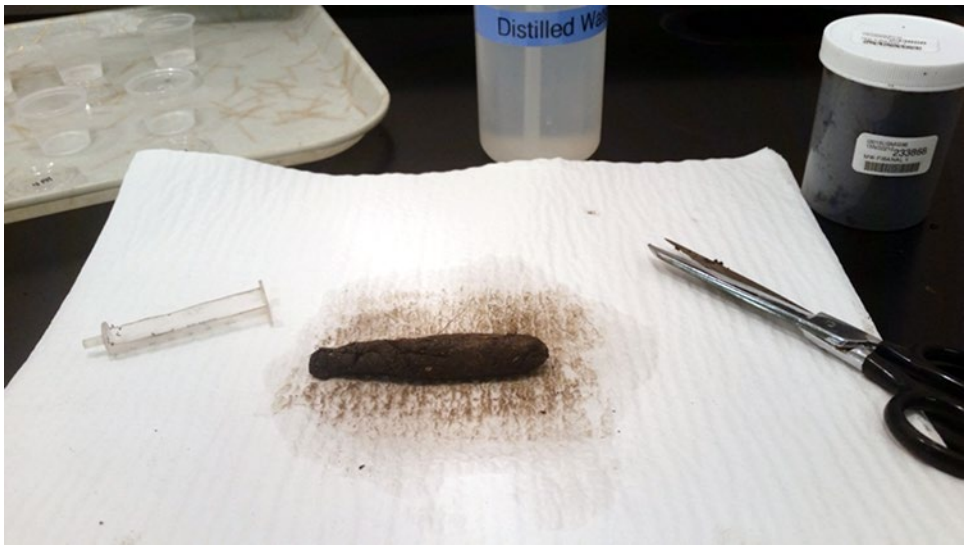

Figure 5B–1.—Sample preparation. Sample fibers are cut into 0.5- to 1.0-cm long segments.

Figure 5B–2.—Sample preparation. Sample segments are packed in syringe.

8. Procedure

8.1 In a 30-mL polycon container, dissolve 1 g (heaping ⅛ tsp) of sodium pyrophosphate in 4 mL of water. Allow to equilibrate for 5 minutes.

8.2 Transfer soil material from the syringe into the polycon. Mix thoroughly using a wooden stirrer or metal spatula. Cover and let stand overnight.

8.3 Mix soil sample in pyrophosphate again next morning.

8.4 Use tweezers to insert a strip of chromatographic paper vertically into the sample to a 1-cm depth. Let stand until the paper strip has wicked sample fluid 2 cm above the slurry height. Allow to stand approximately 5 minutes (fig. 5B–3).

8.5 Remove the chromatographic paper from the sample slurry. Place the paper strip on a piece of blotting paper and press gently with tweezers to make even contact.

8.6 Remove paper strip with tweezers and compare color of the strip to Munsell color charts.

9. Calculations

Report color using Munsell color notation. No calculations are required.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

Figure 5B–3.—Day 2 of test, chromatographic paper strips wicking solution.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Soil Survey Staff. 2014. Keys to soil taxonomy. 12th ed. USDA–NRCS.

Fiber Volume (5C)

1. Introduction to Fiber Volume

Water-dispersed fiber volume characterizes the physical decomposition state of organic matter, which is used in soil taxonomy to define sapric, hemic, and fibric organic materials (Soil Survey Staff, 2014).

2. Scope and Field of Application

This test can be performed in field offices using whole soil and repeated in the lab. As defined in soil taxonomy, organic materials that are >2 cm in cross section and that are too firm to be readily crushed between thumb and fingers are excluded from fiber. Sapric material passes through a 100-mesh sieve (0.15-mm openings) while fibers are retained on the sieve.

3. Principle

The sample is prepared to a standard 5-cc syringe volume. The unrubbed fiber procedure involves a series of steps designed to disperse sapric material by increasingly vigorous treatments. Depending on the level of decomposition, all three steps may not be necessary. The rubbed fiber content is determined by rubbing the sample between the thumb and fingers. Following each treatment, the percentage estimate of sapric material remaining is visually determined under a stereoscope. The percentage of unrubbed fiber after the last treatment and rubbed fiber are reported.

3.1 Interferences

Moist, field-state sample is used for this test to make results as comparable as possible to testing performed in field offices.

The specific volume of moist material is dependent on how the sample is packed in the sample syringe. The packing of the material should be standardized in order to obtain comparable results by different soil scientists (Soil Survey Staff, 2014).

4. Apparatus

4.1 Half-syringe, 6-mL. Cut plastic syringe longitudinally to form a half-cylinder measuring device.

4.2 Sieve, 100-mesh, 7.6-cm diameter

4.3 Eggbeater

4.4 Electric mixer

4.5 Scissors

4.6 Paper towel

4.7 Metal spatula

4.8 Stereoscope or hand lens (fig. 5C–1)

Figure 5C–1.—Stereoscope for examining sample.

5. Chemicals

Reverse osmosis (RO) water, ASTM Type III grade of reagent water

6. Health and Safety

Personal Protective Equipment (PPE).—As appropriate, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents or samples.

7. Sample Preparation

7.1 A subsample of field-state, whole soil is placed in a refrigerator until time for analysis. If the soil dried during storage, add water gradually; dry organic material can be hydrophobic. Allow to stand until saturated.

7.2 Place approximately 20 cc of a representative sample on a paper towel in a linear mound. Roll the towel around the sample to absorb excess water if necessary. Remove the sample and place on a fresh paper towel. The sample should be firm but saturated with water. See figure 5C–2.

7.3 Use scissors to cut sample into segments with a length of 0.5 to 1.0 cm.

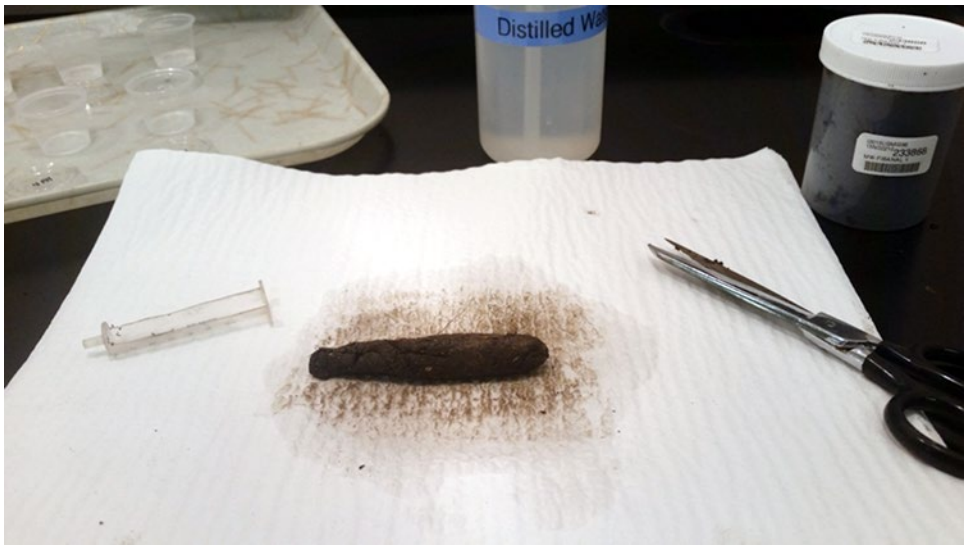

Figure 5C–2.—Sample preparation. Sample fibers are cut into 0.5- to 1.0-cm long segments.

7.4 Randomly select a cut-sample segment. Using a metal spatula, pack the cut sample into the half-syringe prepared in step 4.1. Fill to the 5-mL mark (or 2.5-mL [2.5-cm^3] volume) with the moist sample. See figure 5C–3. If sample is limited, place the unused portion back in the bulk container for future analysis.

Figure 5C–3.—Sample preparation. Sample segments are packed in syringe.

8. Procedure

The unrubbed fiber procedure involves a series of three increasingly vigorous treatments designed to disperse sapric material. All three steps may not be necessary. Following each treatment, the percentage of sapric material remaining is visually estimated under a microscope or hand lens (fig 5C–4).

8.1 Unrubbed Fiber: Part 1

8.1.1 Use a metal spatula to pack a half-syringe that is adjusted to the 5-mL mark or 2.5-mL (2.5-cm^3) volume with the moist, prepared sample.

8.1.2 Transfer all the soil material to a 100-mesh sieve and wash under a stream of tap water that is adjusted to deliver 200 to 300 mL in 5 seconds (medium stream). Wash sample until the water passing through the sieve appears clean. A white plastic container can be placed under the sieve to catch water from sieve to verify water clarity.

8.1.3 With the sample in the sieve, examine the sample under a stereoscope or hand lens to determine if sample is free of sapric material.

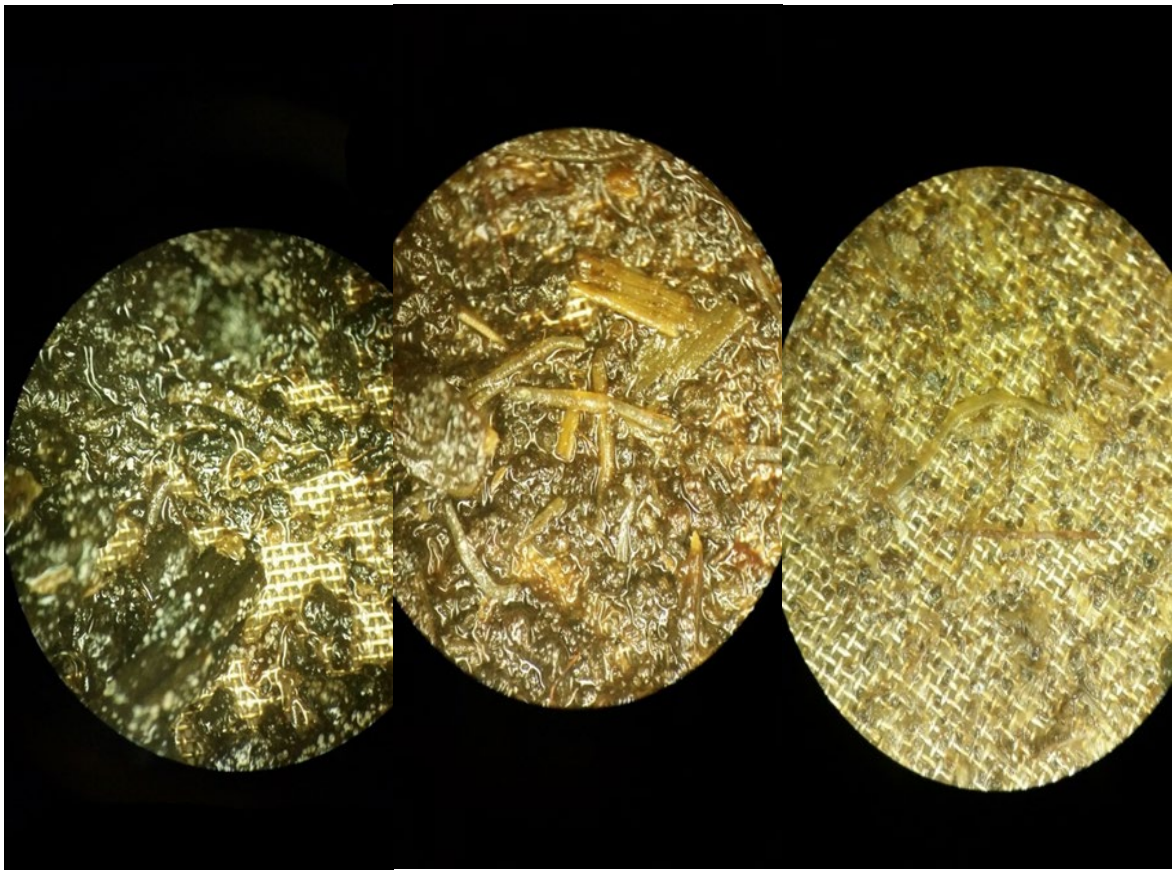

Figure 5C–4.—Different stages of rubbed fiber least aggressive (left) to most aggressive treatment (right), as seen through stereoscope.

8.1.4 If sample is:

- >10% sapric material, proceed to step 8.2
- <10% sapric material, wash the residue to one side of the screen and blot from underneath with absorbent tissue to withdraw excess water

8.1.5 Repack the sample into a half-syringe and blot again with absorbent tissue. The moisture content should be approximately that of the original sample in step 8.1.1.

8.1.6 Measure the volume by reading the value on the syringe scale. Record as a percentage of the initial 2.5-mL (2.5-cm^3) volume. Proceed to step 8.4 for rubbed fiber analysis.

8.2 Unrubbed Fiber: Part 2

8.2.1 Transfer the sample from the 100-mesh sieve to a 500-mL plastic container and fill about half full with water.

8.2.2 Stir vigorously with an eggbeater for 1 minute.

8.2.3 Carefully pour the suspended sample through the 100-mesh sieve; be careful not to lose material during the transfer.

8.2.4 Repeat steps 8.1.2 and 8.1.3. If sample is:

- >10% sapric material, proceed to step 8.3
- <10% sapric material, wash the residue to one side of the screen and blot from underneath with absorbent tissue to withdraw excess water.

8.2.5 Repack the residue into a half-syringe and blot again with absorbent tissue. The moisture content should be approximately that of the original sample.

8.2.6 Measure the volume by reading the value on the syringe scale. Record as a percentage of the initial 2.5-mL (2.5-cm^3) volume. Proceed to step 8.4 for rubbed fiber analysis.

8.3 Unrubbed Fiber: Part 3

8.3.1 Transfer sample from the sieve to an electric mixer container (malt mixer or blender) and fill to about two-thirds with water.

8.3.2 Mix for 1 minute.

8.3.3 Carefully pour the suspended sample through the 100-mesh sieve. Wash the residue to one side of the screen and blot from underneath with absorbent tissue to extract excess water.

8.3.4 Record the kind of fiber observed. Typical fibers are herbaceous, woody, and diatomaceous.

8.3.5 Repack the residue into a half-syringe and blot again with absorbent tissue. The moisture content should be approximately that of the original sample. Measure the volume by reading the value on the syringe scale. Record as a percentage of the initial 2.5-mL (2.5-cm^3) volume.

8.3.6 Proceed with step 8.4, the rubbed fiber determination.

8.4 Rubbed Fiber

8.4.1 Transfer the sample from the syringe to the 100-mesh sieve.

8.4.2 Rub sample between thumb and fingers under a stream of tap water, adjusted to deliver 150 to 200 mL in 5 s, until water passing through the sieve is clean. Clean rubbed fibers should roll between the thumb and fingers rather than slide or smear.

8.4.3 Repack the residue into a half-syringe and blot again with absorbent tissue. The moisture content should be approximately that of the original sample. Measure the volume by reading the value on the syringe scale. Record as a percentage of the initial 2.5-mL (2.5-cm^3) volume.

9. Calculations

9.1 Fiber volume (%) = Reading on half-syringe (mL) x 20

Fiber volume = Rubbed + unrubbed fiber

9.2 Categories used to estimate the remaining sapric contents are:

- Clean (<1% sapric)
- Nearly clean (1 to 10% sapric)
- Some sapric (10 to 30% sapric)
- Sapric (>30% sapric)

9.3 Record the percentage of unrubbed fiber after the final treatment.

9.4 Report the final unrubbed fiber and the rubbed fiber to the nearest whole percent and report fiber type.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist

11. References

Soil Survey Staff. 2014. Keys to soil taxonomy. 12th ed. USDA–NRCS.

Melanic Index (5D)

1. Introduction to Melanic Index

Melanic and fulvic Andisols have a high content of humus. The organic matter thought to result from large amounts of gramineous vegetation can be distinguished from organic matter formed under forest vegetation by the melanic index (Soil Survey Staff, 2014).

2. Scope and Field of Application

The soil color of melanic Andisols reflects their pedogenic processes. Typically, melanic Andisols are formed under grassland ecosystems and have humus dominated by A-type humic acid (highest degree of humification). Fulvic Andisols are formed under forest ecosystems and have humus characterized by a high ratio of fulvic acid to humic acid and a low degree of humification (P or B-type humic acid) (Honna et al., 1988).

3. Principle

A 0.5-g soil sample is mechanically shaken for 1 hour in 25 mL of 0.5% NaOH solution. One drop of mineral flocculant solution is added to sample, which is then centrifuged for 10 minutes. Either 1 or 0.5 mL of extract (<10% or >10% organic C, respectively) is pipetted into a test tube, followed by the addition of 20 mL of 0.1% NaOH solution and thorough mixing. Absorbance of the solution is read using a spectrophotometer at 450 and 520 nm within 3 hours of extraction. Melanic Index is calculated by dividing the absorbance at 450 nm by the absorbance at 520 nm.

3.1 Interferences

There are no known interferences.

4. Apparatus

4.1 Electronic balance, ±1.0-mg sensitivity

4.2 Mechanical reciprocating shaker, 200 oscillations min^{-1}, 1½-in strokes

4.3 Centrifuge tubes, 50-mL, polypropylene

4.4 Centrifuge capable of 4,000 rpm

4.5 Pipettes, electronic digital, 1,000-µL and 10-mL, with tips

4.6 Dispenser, 30-mL

4.7 Cuvettes, plastic, 4.5-mL, 1-cm light path

4.8 Spectrophotometer, UV-visible

4.9 Condiment cup, plastic, 6-oz

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.2 Sodium hydroxide (NaOH) (CAS# 1310-73-2)

5.3 Sodium hydroxide solutions, 0.5% and 0.1%

Components: Sodium hydroxide (NaOH), RODI water

- To a 1-L glass volumetric flask, add the following to create a 0.5% solution:
  - 5 grams of sodium hydroxide
  - 900 mL of RODI water
    - Invert to mix.
  - Dilute to 1 L with RODI water.
- To a 1-L glass volumetric flask, add the following to create a 0.1% solution:
  - 1 gram sodium hydroxide
  - 1 L of RODI water
- Invert to mix.

5.4 Mineral flocculant, weak solution in RODI water. (The KSSL can be contacted for more information.)

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. Subsamples are further processed via planetary ball mill to 80 mesh; either size fraction is appropriate for this test. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Weigh 0.5 g of <2-mm or fine-grind, air-dry soil to the nearest 1.0 mg into a 50-mL centrifuge tube. If sample is moist, weigh enough soil to achieve ≈0.5 of air-dry soil.

8.2 Dispense 25 mL of 0.5% NaOH solution into the tube.

8.3 Transfer the sample to the shaker. Shake for 1 h at 200 oscillations min^{-1} at room temperature.

8.4 Remove the sample from the shaker. Add one drop of mineral flocculant solution and centrifuge at 4,000 rpm for 10 minutes.

8.5 If sample contains <10% organic carbon, pipette 1 mL of extract to condiment cup.

8.6 If sample contains >10% organic carbon, pipette 0.5 mL of extract to condiment.

8.7 Add 20 mL of 0.1% NaOH solution and swirl.

8.8 Transfer to a 4.5-mL cuvette.

8.9 Autozero the spectrophotometer with the 0.5 % NaOH solution.

8.10 Set the spectrophotometer at 450 nm and autozero. Read absorbance.

8.11 Set the spectrophotometer at 520 nm and autozero. Read absorbance.

9. Calculations

9.1 Calculate melanic index:

$$\text{Melanic Index} = \text{Absorbance at 450 nm} / \text{Absorbance at 520 nm}$$

9.2 Report melanic index.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

Honna, T., S. Yamamoto, and K. Matsui. 1988. A simple procedure to determine melanic index that is useful for differentiating melanic from fulvic Andisols. Pedologist 32:69–78.

Soil Survey Staff. 2014. Keys to soil taxonomy. 12th ed. USDA–NRCS.

Ratios and Estimates Related to Organic Matter (5E)

The KSSL Primary Characterization Data Sheets include several ratios and estimates associated with organic matter, using either estimated or measured C values. For more detailed information on these ratios, their calculations, and their applications, refer to the SSIR No. 45, “Soil Survey Laboratory Information Manual” (Soil Survey Staff, 2011). Additional information on these ratios and estimates can also be obtained from the KSSL upon request.

References

Soil Survey Staff. 2011. Soil survey laboratory information manual. Version 2.0. USDA–NRCS. Soil Survey Investigations Report No. 45. U.S. Govt. Print. Office, Washington, DC.

INTRODUCTION TO SOIL BIOLOGICAL AND PLANT ANALYSIS (6)

Soil is an ecosystem that contains a broad spectrum of biological components representing many physiological types (Germida, 1993). The soil biota is critical to soil quality, affecting nutrient cycling, soil stability and erosion, water quality and quantity, and plant health (USDA–NRCS, 2004). Many components of this biota (e.g., fungi, bacteria, earthworms, protozoa, arthropods, and nematodes) and their relationship to soil health are discussed in the "Soil Biology Primer" (Tugel and Lewandowski, 2001). Also refer to Reeder et al. (2001) for information on root biomass and microbial biomass.

The KSSL performs several biological analyses, including, but not limited to, 0.02 *M* $KMnO_4$ extraction, oxidizable (POx C) or reactive carbon; particulate organic matter and mineral (HYPER-POM); and β-glucosidase assay.

References

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Soil Analyses (6A)

0.02 *M* $KMnO_4$ Extraction (6A2)

UV-Visible Spectrophotometer, Dual Beam (6A2a)

Permanganate Oxidizable (POx C) or Reactive Carbon (6A2a1)

Air-Dry, <2 mm (6A2a1a1)

1. Introduction to Oxidizable Permanganate and Reactive Carbon

This method, commonly called Weil Carbon (Weil et al., 2003), is designed to be a quick and easy field test for assessment of reactive soil organic carbon. Following the principle of bleaching chemistry, potassium permanganate ($KMnO_4$) is used to oxidize organic matter in soil. The oxidized organic matter is considered to be associated with the reactive carbon pool (Blair et al., 1995).

2. Scope and Field of Application

To estimate the amount of carbon oxidized, the method relies on the assumption that 1 mole of MnO_4^- is consumed (reduced from Mn^{+7} to Mn^{+2}) in the oxidation of 0.75 mole (9,000 mg) of C (Blair et al., 1995). The bleaching of the pink $KMnO_4$ color (reduction in absorbance) is proportional to the amount of POx C in soil; i.e., the $KMnO_4$ color loss (the lowering of the absorbance reading) is proportional to the amount of POx C in the soil (Weil et al., 2003).

A reactive soil carbon index can be expressed as the quotient of reactive carbon to soil organic carbon (Blair et al., 2001). The stability of this index over time is considered to be a useful measure of soil quality (Islam and Weil, 1997).

3. Principle

A 2.5-g soil sample is oxidized with 0.02 *M* potassium permanganate diluted with reverse osmosis water. Sample is vortexed and allowed to stand undisturbed for 10 minutes. A small aliquot of the supernatant is diluted with reverse osmosis water, and the absorbance of the solution is read at 550 nm using a spectrophotometer. Reactive carbon is reported in units of milligram POx C per kilogram oven-dry soil (mg reactive carbon kg^{-1}).

3.1 Interferences

Chemical oxidation methods for the determination of labile soil carbon have a number of limitations. Different soil samples may have variable amounts of readily oxidizable fractions, making standardization of any method difficult. Results are influenced by the amount of C in the sample, the concentration of MnO_4^-, and the contact time (Blair et al., 1995).

4. Apparatus

4.1 Centrifuge tubes, 50-mL, disposable, polyethylene, with screw tops

4.2 Pipette tips, 1-mL and 10-mL

4.3 Electronic balance ±0.01-g sensitivity
4.4 Stopwatch, timer, or a watch with a second hand
4.5 Pipette and tips, electronic digital, 10-mL and 1-mL
4.6 Volumetric flasks, 50-mL, 100-mL, 250-mL, and 2-L, with stoppers
4.7 Spectrophotometer, UV-visible
4.8 Cuvettes, plastic, 4.5-mL, 1-cm light path
4.9 Vortexer, mini

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water
5.2 Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) (CAS# 10035-04-8)
5.3 Potassium hydroxide (KOH) (CAS# 1310-58-3)
5.4 Potassium permanganate ($KMnO_4$) (CAS# 7722-64-7)
5.5 Calcium chloride solution, 0.1 M

Components: Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$), RODI water

- To a 2-L polyethylene volumetric flask, add the following in order:
  - 1 L of RODI water
  - 29.40 g calcium chloride
  - Fill to volume with RODI water.
- Store in a polyethylene bottle.

5.6 Potassium hydroxide solution, 0.1 M

Components: Potassium hydroxide (KOH), RODI water

- To a 100-mL polyethylene volumetric flask, add the following in order:
  - 50 mL of RODI water
  - 0.561 g of potassium hydroxide
  - Fill to volume with RODI water.
- Invert to mix.

5.7 Stock potassium permanganate solution, 0.2 *M* (Reagent A)

Components: Potassium permanganate ($KMnO_4$), 0.1 *M* calcium chloride solution, 0.1 *M* potassium hydroxide solution

- To a 250-mL glass volumetric flask, add the following in order:
  - 100 mL of calcium chloride solution
  - 7.90 g of potassium permanganate crystals
  - Fill to volume with calcium chloride solution.
- Adjust solution pH to 7.2 with1 or 2 drops potassium hydroxide solution.

- Solution is stable for approximately 3 days.

5.8 Working potassium permanganate solution, 0.02 *M* (Reagent A1)

Components: Reagent A, RODI water

- To a 2-L glass volumetric flask, add the following in order:
  - 200 mL of Reagent A
  - Fill to volume with RODI water.
- Invert to mix.
- Prepare fresh daily.

5.9 Standard $KMnO_4$ working solutions (Standards B1–B4)

Components: Reagent A1, RODI water

- Refer to table 6A2a–1 for dilutions.
- Refer to table 6A2a–2 for concentrations.
- Invert to mix thoroughly.
- Allow to equilibrate to room temperature before use.
- Store in a refrigerator.
- Prepare fresh weekly.

Table 6A2a–1.—Preparation of Standards B1–B4, $KMnO_4$ Working Solutions. (Prepare in 50-mL volumetric flasks.)

Standard	Reagent A1	RODI Water
	(mL)	
B1	10	RODI water to volume
B2	5	
B3	2.5	
B4	1.25	

Table 6A2a–2.—Concentrations of Standards B1–B4, $KMnO_4$ Working Solutions.

Standard	Final Concentration
	(Molarity)
B1	0.04
B2	0.02
B3	0.01
B4	0.005

5.10 Standard $KMnO_4$ calibration solutions (Standards B5–B8)

Components: Standards B1–B4, RODI water

- Refer to table 6A2a–3 for dilutions.
- Refer to table 6A2a–4 for concentrations.
- Invert to mix thoroughly.
- Allow to equilibrate to room temperature before use.
- Store in a refrigerator.
- Prepare fresh weekly.

Table 6A2a–3.—Preparation of Standards B5–B8, $KMnO_4$ Calibration and Verification Solutions. (Prepare in 50-mL volumetric flasks.)

Standard	Standards B1–B4	RODI water
	(mL)	
B5	0.5 mL of B1	RODI water to volume
B6	0.5 mL of B2	
B7	0.5 mL of B3	
B8	0.5 mL of B4	

Table 6A2a–4.—Concentrations of Standards B5–B8, $KMnO_4$ Calibration and Verification Solutions.

Standard	Final Concentration
	(Molarity)
B5	0.0004
B6	0.0002
B7	0.0001
B8	0.00005

5.11 Calibration blank

Components: 0.1 *M* $CaCl_2$ solution, RODI water

- To a 50-mL glass volumetric flask, add the following in order:
  - 5 mL of 0.1 *M* $CaCl_2$ solution
  - 45 mL of RODI water
- Invert to mix.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids. Dispense concentrated acids and bases in fume hood.

Review the safety data sheets (SDS) for potassium permanganate ($KMnO_4$) before beginning test. Potassium permanganate is a strong oxidizer; contact with other material may cause fire. In case of fire, soak with water. In case of spill, sweep up and remove. Flush spill area with water.

Avoid contact with eyes, skin, and clothing. Inhalation of $KMnO_4$ dust may severely damage respiratory passages, lungs, or both. Contact with skin or eyes may cause severe irritation or burns.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Weigh 2.5 g of <2-mm (sieved), air-dry soil to the nearest mg and add to centrifuge tube. Add 20 mL of Reagent A1.

8.2 Vortex each sample and allow 10 min for soil to settle. Do not disturb during settling period.

8.3 After 10 min, centrifuge for 10 min at 2,000 rpm.

8.4 Add 49.5 mL of RODI water to a clean, labeled centrifuge tube. Transfer 0.5 mL of sample liquid into the tube and mix.

8.5 Transfer sample extracts and standards B5–B8 to cuvettes.

8.6 Set the spectrophotometer to read at 550 nm. Autozero with calibration blank.

8.7 Calibrate the instrument by using standards B5–B8. Rejection criteria for calibration is R^2 <0.99.

8.8 Run samples using calibration curve. Sample concentration is calculated from the regression equation. Record results to the nearest 0.01 unit for the sample extract and each calibration solution.

9. Calculations

9.1 $KMnO_4$ C (mg kg^{-1}) = [0.02 – (100 x A)] x 9,000 x 0.02 x 1,000 x ADOD / smp_wt

0.02 mol L^{-1} = Initial solution concentration

A = Absorbance analyte reading (mol L^{-1})

9,000 = mg C (0.75 mole) oxidized by 1 mole MnO_4, changing from Mn^{7+} to Mn^{2+}

0.02 = Volume of $KMnO_4$ solution reacted

Smp_wt= Sample weight of soil used

ADOD = Air-dry/oven-dry ratio

9.2 For MnO_4^- concentration >0.000012 *M* and <0.000175, report "AC = X", where X = the standard calculation.

9.3 For MnO_4^- concentration >0.000175 M, report "AC not detected".

9.4 For MnO_4^- concentration <0.000012 M, report "AC > X" where X = standard calculation.

9.5 Report reactive C (mg kg^{-1}) as oxidizable C, potassium permanganate (POx C).

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

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Soil Analyses (6A)

Particulate Organic Matter and C-Mineral (6A4)

Total Analysis (6A4a)

Dry Combustion (6A4a1)

Thermal Conductivity Detector (6A4a1a)

Carbon, Nitrogen, Sulfur (6A4a1a1-3)

Air-Dry (6A4a1a1-3a)

≥53 µm, Particulate Organic Matter (6A4a1a1-3a1)

<53 µm, C-Mineral, Calculated (6A4a1a1-3a3)

1. Introduction to Particulate Organic Matter Determination

Particulate organic matter (POM) is soil organic matter (SOM) associated with a physical fraction of soil, operationally defined at >53 µm in diameter (Elliott and Cambardella, 1991; Cambardella and Elliott 1992; Follett and Pruessner, 1997). Although “light” fraction organic matter (LF) (Strickland and Sollins, 1987; Hassink, 1995) is often confused with POM, LF and POM are not the same. Particulate organic matter is a size-defined fraction, whereas LF is defined by density.

2. Scope and Field of Application

The POM soil fraction is similar to various sieved and physical fractions, such as resistant plant material (Jenkinson and Rayner, 1977), sand-size organic matter (Tiessen and Stewart, 1983), and size fractions (Gregorich et al., 1988). Some researchers consider POM to be a relatively labile component of SOM, whereas others have described it as slowly decomposable, or stabilized, SOM (Cambardella and Elliott, 1992).

The quantity of POM measured in soils is sensitive to management practices. Under tillage, the POM fraction becomes depleted (Jenkinson and Rayner, 1977; Cambardella and Elliott, 1992). Reductions of more than 50% have been found in long-term (20-year) tillage plots. Measurable reductions are believed to occur in the range of 1 to 5 years (Cambardella and Elliott, 1992). When paired sampling is done between tillage practices or by repeated sampling of the same plots through time, the impact of the management upon POM becomes more apparent (Marriot and Wander, 2006).

POM can be used in SOM modeling to estimate the dynamics of SOM using soil carbon (C) and a tenable soil quality indicator. Models incorporate at least two SOM components based on susceptibility to degradation—slow and rapid. Physical fractions, such as POM, have been found to be more useful than chemical fractions (e.g., fulvic and humic acids) in modeling applications (Hassink, 1995). A minimum data set for modeling soil organic carbon proposed by Gregorich (1994) includes POM as one of the primary parameters. Examples of models that incorporate these parameters can be found in Jenkinson and Rayner

(1977) and in tests of the CENTURY Soil Organic Model (Parton et al., 1994; Metherell et al., 1993; Montavalli et al., 1994).

3. Principle

The Hyper POM (HPOM) procedure is primarily the physical separation of <2-mm sieved soil into the ≥53-µm fraction and the <53-µm fraction (Cambardella and Elliot, 1992; Follett and Pruessner, 1997). HPOM-C and HPOM-N are measured directly by dry combustion analysis of the ≥53-µm fraction, whereas mineralizable carbon (MIN-C) and mineralizable nitrogen (MIN-N) (<53-µm fraction) are calculated by subtracting the HPOM-C and HPOM-N values from the direct measurement by combustion of total C and N of the <2-mm soil (method 4H2a1-3).

3.1 Interferences

Highly organic samples tend to clump or ball up during shaking. To break up these clumps, tubes are vortexed a few times during the 15 h shaking.

4. Apparatus

4.1 Pressure regulator for water, with stop cock attached to tubing

4.2 Centrifuge tube, 50-mL

4.3 Sieve, 270-mesh, 53-µm

4.4 Mechanical reciprocating shaker, 200 oscillations min^{-1}, 1½-in strokes

4.5 Evaporating crucibles

4.6 Oven, 110 °C

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

5.2 Sodium hexametaphosphate solution, 0.5%

Components: Sodium hexametaphosphate $(NaPO_3)_6$ (CAS# 68915-31-1), RODI water

- To a 5-L polyethylene carboy, add the following in order:
  - 4 L of RODI water
  - 20 g of sodium hexametaphosphate
- Swirl to mix.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or

apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Weigh 10 g of <2-mm (sieved), air-dry soil to the nearest mg into a 50-mL centrifuge tube. Add 30 mL of 0.5% sodium hexametaphosphate solution to the tube. Highly organic samples may require more solution.

8.2 Stopper sample tightly and shake for 15 h (overnight) at 200 oscillations min^{-1} at room temperature (≈20–25 °C).

8.3 Sieve slurry through a 53-µm sieve to retain the ≥53-µm fraction. Rinse the material retained on the sieve with RODI water until no further fine material comes through and the water that passes the sieve is clear.

8.4 Transfer the ≥53-µm fraction into a preweighed evaporating crucible. Rinse the sieve, including sides, into the crucible with a small amount of RODI water.

8.5 Dry the ≥53-µm fraction in an oven at 110 °C for 15 h or until sample is fully dry.

8.6 Cool to room temperature and record the weight of crucible plus ≥53-µm fraction to the nearest 0.1 mg.

8.7 Transfer the entire oven-dried ≥53-µm fraction into a labeled scintillation vial.

8.8 Determine total C and N for the ≥53-µm fraction, analyzing fine-ground (≈180-µm) sample. Refer to method 4H2a1-3 Dry Combustion: Total Carbon, Nitrogen, and Sulfur analysis for <53-µm fraction.

9. Calculations

9.1 $HPOM\text{-}C = (C{\geq}53\text{-}\mu m / AD/OD) \times (Wt_1 / Wt_2) \times AD/OD$

9.2 $HPOM\text{-}N = (N{\geq}53\text{-}\mu m / AD/OD) \times (Wt_1 / Wt_2) \times AD/OD$

HPOM-C = POM-Carbon in oven-dry, <2-mm fraction (%)

HPOM-N = POM-Nitrogen in oven-dry, <2-mm fraction (%)

C≥53-µm = Carbon in oven-dry, ≥53-µm fraction (%) (method 4H1a1-3)

N≥53-µm = Nitrogen in oven-dry, ≥53-µm fraction (%) (method 4H1a1-3)

Wt_1 = Weight of oven-dry, ≥ 53-µm fraction (g)

Wt_2 = Weight of air-dry, <2-mm fraction (g)

AD/OD = Air dry/oven dry ratio (method 3D1)

9.3 MIN-C = C_T − POM-C

9.4 MIN-N = N_T − POM-N

MIN-C = MIN-Carbon in oven-dry, <2-mm fraction (%)

MIN-N = MIN-Nitrogen in oven-dry, <2-mm fraction (%)

C_T = Total Carbon in oven-dry, <2-mm fraction (%) (method 4H2a1-3)

N_T = Total Nitrogen in oven-dry, <2-mm fraction (%) (method 4H2a1-3)

9.5 Report HPOM-C, MIN-C, HPOM-N, and MIN-N as percent of <2-mm soil.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

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Soil Analyses (6A)
Soil Enzymes (6A5)
p-Nitrophenol (6A5a)
ß-Glucosidase (6A5a1)
Air-Dry, <2 mm (6A5a1a1)
Field-Moist, <2 mm (6A5a1a2)

1. Introduction to Beta-Glucosidase

Soil enzymes are important to the biochemical functions of organic matter decomposition and serve as catalysts in reactions necessary for the life processes of organic wastes, organic matter formation, and nutrient cycling (Das and Varma, 2011). These enzymes include amylase, arylsulphatases, ß-glucosidase, cellulose, chitinase, dehydrogenase, phosphatase, protease, and urease released from plants, animals, organic compounds, microorganisms, and soils. ß-glucosidase is a common and predominant enzyme in soils (Eivazi and Tabatabai, 1988; Tabatabai, 1994). Enzyme assays, such as ß-glucosidase, reflect potential activity; they do not represent true in situ activity levels and should be viewed as an index.

2. Scope and Field of Application

Glucosidase is involved in the hydrolysis and biodegradation of various ß-glucosides present in plant debris decomposing in the ecosystem. The final product is glucose, which is an important C energy source for microbes in the soil (Esen, 1993). ß-glucosidase enzyme is sensitive to changes in pH and soil management practices. As such, it has proved to be a useful indicator of soil quality (Acosta-Martinez and Tabatabai, 2000; Madejon et al., 2001; Das and Varma, 2011).

3. Principle

The ß-glucosidase assay can be determined on both air-dry and field-moist samples; immediate analysis is not required for air-dry samples.

A 1 g sample is treated with a modified universal buffer and p-nitrophenyl-ß-D-glucopyranoside (PNG) and then incubated for 1 h at 37 ºC. After incubation, $CaCl_2$ and THAM (pH 12) are added. A 10-mL sample is then filtered and analyzed, and a calibration curve is prepared by plotting absorbance at 405 nm versus the amount of p-nitrophenol. Data are reported as mg p-nitrophenol per kg oven-dry soil per hour.

3.1 Interferences

ß-glucosidase activity declines with air-drying, but the ranking of soil treatments within a soil type or the ranking across different soil types stays the same (Bandick and Dick, 1999).

Samples must be read as soon as possible after filtration because p-nitrophenol is light sensitive.

4. Apparatus

4.1 Electronic balance, ±1.0-mg sensitivity
4.2 Volumetric flasks, acid washed, 50-mL, 100-mL, 1-L, 1.5-L
4.3 Plastic bottle, amber, 1,000-mL
4.4 Disposable plastic cups, 8-oz
4.5 Filter, 0.45-µm
4.6 Pipettes, electronic digital, 2,500-µL and 10-mL, with 2,500-µL and 10-mL tips
4.7 Syringe filters, 0.45-µm
4.8 Centrifuge tubes, 50-mL, polypropylene
4.9 Cuvettes, plastic, 4.5-mL, 1-cm light path
4.10 Centrifuge
4.11 Disposable pipettes
4.12 Incubator or water bath, 37 ºC
4.13 Spectrophotometer, UV-visible
4.14 Vortexer, mini
4.15 Syringes, 1-mL

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water
5.2 THAM: 2-amino-2(hydroxymethyl)-1-3-propanediol ($NH_2C(CH_2OH)_3$) (CAS# 77-86-1)
5.3 p-nitrophenyl-β-D-glucopyranoside (PNG) ($C_{12}H_{15}NO_8$) (CAS# 2492-87-7)
5.4 Hydrochloric acid (HCl) (CAS# 7647-01-0), concentrated, 12 *N*
5.5 Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) (CAS# 10035-04-8)
5.6 Maleic acid ($HO_2CCH=CHCO_2H$) (CAS# 110-16-7)
5.7 Sodium hydroxide (NaOH) (CAS# 1310-73-2)
5.8 Citric acid ($C_6H_8O_7$) (CAS # 77-92-9)
5.9 Boric acid (H_3BO_3) (CAS# 10043-35-3)
5.10 p-Nitrophenol ($C_6H_5NO_3$) (CAS# 100-02-7)
5.11 Hydrochloric acid solution, 0.1 M

Components: Hydrochloric acid (HCl), RODI water

- To a 1.5-L glass volumetric flask, add the following in order:
  - 1 L of RODI water

- 8.33 mL of 12 *N* HCl
- Fill to volume with RODI water.

- Invert to mix.

5.12 Sodium hydroxide solution, 1.0 M.

Components: Sodium hydroxide (NaOH), RODI water

- To a 1-L polyethylene volumetric flask, add the following in order:
  - 700 mL of RODI water
  - 40.00 g of sodium hydroxide
  - Fill to volume with RODI water once sodium hydroxide has dissolved.
- Invert to mix.

5.13 Sodium hydroxide solution, 0.5 M.

Components: Sodium hydroxide (NaOH), RODI water

- To a 1-L polyethylene volumetric flask, add the following in order:
  - 700 mL of RODI water
  - 20 g of sodium hydroxide
  - Fill to volume with RODI water once sodium hydroxide has dissolved.
- Invert to mix.

5.14 MUB stock solution: Modified universal buffer

Components: THAM: ($NH_2C(CH_2OH)_3$), maleic acid ($HO_2CCH=CHCO_2H$), citric acid ($C_6H_8O_7$), boric acid (H_3BO_3), 1.0 *M* sodium hydroxide solution, RODI water

- To a 1-L glass volumetric flask, add the following in order:
  - 488 mL of 1.0 *M* sodium hydroxide solution
  - 12.10 g of THAM
  - 11.60 g of maleic acid
  - 14.00 g of citric acid
  - 6.30 g of boric acid
  - Fill to volume with RODI water.
- Invert to mix.
- Store in refrigerator.

5.15 MUB 6.0: Working solution (pH 6.0)

Components: MUB stock solution, 0.1 *M* HCl solution, RODI water

- Place a magnetic stir bar in a 500-mL beaker, place on magnetic stirrer, and add the following in order:
  - 200 mL of MUB stock solution
  - Add 0.1 *M* HCl to the MUB stock solution until the pH reaches 6.0.

- Transfer acidified solution to 1-L glass volumetric flask.
    - Fill to volume with RODI water.

5.16 PNG solution: 0.05 *M*

Components: p-nitrophenyl-β-D-glucopyranoside (PNG) ($C_{12}H_{15}NO_8$), MUB 6.0 solution

- To a 100-mL polyethylene volumetric flask, add the following in order:
    - 80 mL of MUB 6.0
    - 1.506 g of PNG
    - Fill to volume with MUB 6.0.
- Invert to mix.
- Store in the refrigerator at 4 °C.
- Use within 5 days.

5.17 Calcium chloride solution, 0.5 *M*

Components: Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$), RODI water

- To a 1-L polyethylene volumetric flask, add the following in order:
    - 700 mL of RODI water
    - 73.5 g of calcium chloride
    - Fill to volume with RODI water after calcium chloride has dissolved.
- Invert to mix.

5.18 THAM 10 solution, 0.1 *M*

Components: THAM ($NH_2C(CH_2OH)_3$), RODI water

- To a 1-L polyethylene volumetric flask, add the following in order:
    - 800 mL of RODI water
    - 12.20 g of THAM
    - Fill to volume with RODI water after THAM has dissolved.
    - Invert to mix.
- Solution should be pH ≈10.

5.19 THAM 12 solution: 0.1 *M*

Components: THAM ($NH_2C(CH_2OH)_3$), 0.5 *M* sodium hydroxide solution, RODI water

- To a 1-L glass volumetric flask, add the following in order:
    - 800 mL of RODI water
    - 12.20 g of THAM
        - Swirl to dissolve THAM.
    - Adjust the pH to 12 with 0.5 *M* sodium hydroxide.
    - Fill to volume with RODI water.
    - Invert to mix.

5.20 p-Nitrophenol stock standard solution (Reagent A)

Components: p-Nitrophenol ($C_6H_5NO_3$), RODI water

- In a fume hood, to a 1-L glass volumetric flask, add the following in order:
  - 700 mL of RODI water
  - 1.0 g of p-nitrophenol
  - Fill to volume with RODI water after p-nitrophenol is dissolved.
  - Invert to mix.
- Store in amber bottle at 4 °C.
- Use within 30 days.

5.21 p-Nitrophenol working standard solution (Reagent A1)

Components: Reagent A, RODI water

- In a fume hood, to a 100-mL glass volumetric flask, add the following in order:
  - 1.0 mL of Reagent A
  - Fill to volume with RODI water.
- Invert to mix.
- Store in amber bottle at 4 °C.
- Use within 30 days.

5.22 Standard p-nitrophenol calibration and verification solutions (Standards A2–A6)

Components: Reagent A1, THAM 12 solution, 0.5 *M* calcium chloride solution, RODI water

- Refer to table 6A5a–1 for preparation instructions.
- Refer to table 6A5a–2 for concentrations.
- Bring to volume with RODI water.
- Cap and shake tubes to mix.

Table 6A5a–1.—Preparation of Standards A2–A6, Standard p-nitrophenol Calibration and Verification Solutions. (Prepare in 50-mL centrifuge tubes.)

Standard	Reagent A1	0.5 *M* $CaCl_2$	THAM 12	RODI Water
	(mL)	*(mL)*	*(mL)*	*(mL)*
A2	5	1	4	0
A3	4			1
A4	3			2
A5	2			3
A6	1			4
Blank	0			5

Table 6A5a–2.—Concentrations of Standards A2–A6, Standard p-nitrophenol Calibration and Verification Solutions.

Standard	Final Concentration
	(µg)
A2	50.0
A3	40.0
A4	30.0
A5	20.0
A6	10.0
Blank	0

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids.

Always work under the fume hood when handling the p-Nitrophenol solutions.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Weigh 1 g (±0.03 g) of <2-mm, air-dry soil into disposable centrifuge tubes. Label odd-numbered tubes “control” and even-numbered tubes “treatment.”

8.2 In a fume hood, add 4 mL of MUB 6.0 solution to all tubes (controls and treatments).

8.3 Add 1 mL of PNG solution to the “treatment” tubes only. Cap and vortex all tubes. Immediately start the 60 min timer. After starting timer, use vortexer to mix and place tubes in water bath.

8.4 Incubate all samples at 37 °C for 1 h.

8.5 Add 1 mL of 0.5 *M* calcium chloride solution and 4 mL of THAM 12 solution to all tubes and swirl.

8.6 Add 1 mL of PNG solution to "control" tubes and vortex. Remove caps and let samples settle 5 minutes before filtering.

8.7 Draw up sample into a 10-mL syringe and attach a 0.45-µm filter. Filter sample directly into cuvette. Samples must be read as soon as possible after filtration because p-nitrophenol is light sensitive. Cap the samples waiting to be read.

8.8 Prepare calibration curve plotting absorbance at 405 nm versus amount of p-nitrophenol.

8.9 Record amounts of p-nitrophenol. Read the samples in control/treatment pairs.

8.10 If readings exceed high standard, dilute with THAM 10 solution. Cap and swirl. Transfer to cuvettes and record the amount of p-nitrophenol.

9. Calculations

9.1 mg p-nitrophenol/kg oven-dry soil/h = $B \times [(D_T \times A_T / Wt_T) - (D_C \times A_C / Wt_C)] / T$

A_T = Amount of p-nitrophenol in treatment sample (µg)

A_C = Amount of p-nitrophenol in control sample (µg)

Wt_T = Weight of treatment sample (g)

Wt_C = Weight of control sample (g)

D_C = Dilution factor for control sample

D_T = Dilution factor for treatment sample

T = Incubation time (h)

B = Air-dry/oven-dry ratio (method 3D1) or field-moist/oven-dry ratio

Note: µg p-nitrophenol/g oven-dry soil/hour = mg p-nitrophenol/kg oven-dry soil/hour

9.2 Report ß-glucosidase activity as mg p-nitrophenol/kg oven-dry soil/h.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

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Ratios and Estimates Related to Biological Analyses (6D)

Estimates or calculated values associated with soil biological and plant analyses are described within the respective methods. Additional information on the reporting of these calculated values can be obtained from the KSSL upon request.

INSTRUMENTAL ANALYSES (7)

The physical and chemical properties of a soil are controlled to a very large degree by the soil minerals, especially by those minerals constituting the clay fraction (McBride, 1989; Whittig and Allardice, 1986). Positive identification of mineral species and quantitative estimation of their proportions in soils usually requires the application of several complementary qualitative and quantitative analyses (Whittig and Allardice, 1986). Some of the semiquantitative and quantitative procedures that have been performed by the KSSL include x-ray diffraction and thermogravimetric analysis (TGA). Indirect measures to infer mineral composition include linear extensibility, elemental analysis, and CEC to clay ratios.

Analysis by x-ray diffraction facilitates identification of crystalline mineral components of soil and semiquantitative estimates of relative amounts. It is commonly applied to the clay fraction in soils and to layer-silicate (phyllosilicates) minerals in particular. Identification is by d-spacings (spatial distance between repeating planes of atoms) characteristic of a mineral, according to Bragg's Law. Because layer-silicate structures are very similar, except in the direction perpendicular to the layers, several treatments (cation saturation and heating) are used to correctly identify these layered silicates. In x-ray analysis of soils or clay samples, mineral identification is challenging because of variations in chemical composition, degree of crystallization, amorphous minerals, and particle size. A more reliable and accurate estimation of mineral percentages is provided when x-ray diffraction analysis is used in conjunction with other methods, e.g., differential-thermal, surface-area, elemental analysis, and other species-specific chemical methods (Alexiades and Jackson, 1966; Karathanasis and Hajek, 1982).

Upon heating, many soil constituents undergo thermal reactions that serve as diagnostic properties for qualitative and quantitative identification of these substances (Tan et al., 1986; Karathanasis and Harris, 1994). Thermogravimetric analysis (TGA) is a technique for determining weight loss of a sample when it is heated at a constant rate. TGA is an outgrowth of dehydration curves that were used in early studies of various phyllosilicate clay minerals (Jackson, 1956). The TGA sample weight, however, is monitored continuously rather than measured at discrete intervals after periods of heating at a constant temperature (Wendlandt, 1986). TGA provides quantitative information about quantities of substances gained or lost by the solid phase during certain thermally driven reactions.

TGA has replaced DSC (differential scanning calorimetry—obsolete method 7A4a) at the KSSL, but they are complementary methods. Many of the same clay mineral reactions that are studied by DSC can also be studied by TGA. Examples include dehydroxylation, loss of surface adsorbed water, decomposition of carbonates, and oxidation. Some transformation reactions, e.g., melting or structural reorganization (quartz alpha-beta transition), cannot be measured by TGA because no weight loss is involved (Karathanasis and Harris, 1994).

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Instrumental Analyses (7A)
X-Ray Diffractometer (7A1)
Filter Peel on Glass (7A1b)
Mg Room Temperature, Mg Glycerol Solvated, K 300 °C, K 500 °C (7A1b1)

1. Introduction to Filter Peel Clay XRD

One of the most useful methods to identify crystalline mineral components of soil is x-ray diffraction analysis (Hughes et al., 1994; Kahle et al., 2002). Clay fractions of soils are composed of one or more phyllosilicate (layer-silicate minerals) together with primary minerals inherited directly from the parent material (Olson et al., 1999). Positive identification of mineral species and estimation of their proportions requires the application of several complementary qualitative and quantitative analyses (Whittig and Allardice, 1986; Amonette and Zelazny, 1994; Wilson, 1994; Moore and Reynolds, 1997). More complex quantification procedures include using standard additions, full pattern fitting, and determining mineral intensity factors (Kahle et al., 2002). At best, quantification can approach a precision of ±5% and an accuracy of ±10 to 20% (Moore and Reynolds, 1997).

2. Scope and Field of Application

Generally, no two minerals have exactly the same d-spacings in three dimensions and diffraction angles are distinctive for a particular mineral (Whittig and Allardice, 1986; Moore and Reynolds, 1997). Phyllosilicates have very similar structures, except in the direction perpendicular to the layers (c-dimension).

The KSSL determines mineral quantification on first order peak intensities; second order peaks are used to differentiate specific minerals that share similar peaks. Semiquantitative interpretations have been held consistent over time (1964 to the present) by adjusting instrumental parameters (e.g., scan speed) to maintain a constant peak intensity for in-house reference soil and clay standards thereby keeping interpretations consistent from sample to sample.

3. Principle

Soils are dispersed and separated into fractions. Zero-background sample holders are used for larger grained materials. Clay filter peels are placed on glass slides to dry and to preferentially orient clay minerals. Quantification of a mineral by x-ray diffraction requires consistency in terms of sample (slide) size relative to the incident x-ray beam, thickness and particle-size uniformity of sample, and beam-sample orientation (Moore and Reynolds, 1997).

Diffraction maxima (peaks) are produced from the interaction of x-rays with planes of elements that repeat at a constant distance (d-spacing) through the crystal structure. Copper radiation (CuKα) with a wavelength of 1.54 Å (0.154

nm) is used at the KSSL. Several treatments are used to alter this spacing and interpret the mineral suite present:

- Glycerol is added to expand smectites.
- Ionic saturation and/or heat treatments are used to collapse some 2:1 layer silicates.
- Heat treatments are also used to dehydroxylate kaolinite, gibbsite, and goethite, eliminating characteristic peaks.

Standard clay slide analyses include:

- Mg^{2+} (room temperature)
- Mg^{2+}-glycerol (room temperature)
- K^{+} (300 °C)
- K^{+} (500 °C)

Standard tables to convert θ or 2 θ angles to crystal d-spacings are published in the U.S. Geological Survey Circular 29 (Switzer et al., 1948) and in other publications (Brown, 1980). The soil clay minerals of greatest interest are phyllosilicates. Examples include kaolinite, mica (illite), smectite, vermiculite, hydroxy-interlayered vermiculite, hydroxy-interlayered smectite, and chlorite. X ray by this method is semiquantitative.

3.1 Interferences

Interstratified mixtures of phyllosilicates create challenges in identification due to differences in crystal size, purity, chemical composition, atomic unit cell positions, background or matrix interferences, and affect quantification (Moore and Reynolds, 1997; Kahle et al., 2002).

Pretreatments to remove impurities, such as organic matter, carbonates, and iron oxides, may result in degradation of certain mineral species (e.g., smectites) and loss of precision (Hughes et al., 1994). Do not use pretreatments other than ionic saturation and dispersion with sodium carbonate for separation and isolation of the clay fraction for this procedure.

The separation (centrifuge) procedure used to isolate the clay fraction from the other size fractions of the soil skews the <2-µm clay suspension toward the fine clay, but it minimizes the inclusion of fine silt in the fraction. Settling may favor larger-particle-sized clays, such as kaolinite. The placement of the x-ray generator and detector in the instrument may skew the results toward lower angle (higher d-spacing) minerals.

X-ray analysis should be performed within 4 hours of glycerol addition to expand smectites to 18 Å. If excess glycerol is applied to the slide, use a desiccator or gentle air flow from a benchtop fan to dry excess glycerol.

4. Apparatus

4.1 Dispenser for sodium carbonate solution

4.2 Centrifuge, capable of 750 rpm and holding 100-mL centrifuge tubes
4.3 Centrifuge tubes, plastic, 100-mL, on which 10-cm solution depth is marked
4.4 Rubber stoppers, no. 6, for centrifuge tubes
4.5 Wrist-action shaker, capable of holding 100-mL centrifuge tubes
4.6 Sieve, 80-mesh, copper
4.7 Spray bottle, plastic, 30-mL (1-oz), for a 1:7 glycerol:water mixture
4.8 Muffle furnace
4.9 X-ray diffractometer (XRD) that has an X-Y autosampler and copper radiation (CuKα) with a wavelength of 1.54 Å (0.154 nm)
4.10 XRD slides, glass, 25.4 x 25.4 mm
4.11 Clay slide XRD sample holders
4.12 Reference slides: quartz and clay from reference soil
4.13 Check-standard soil
4.14 Vortex mixer
4.15 Reusable heavy wall filter flask
4.16 Four filter holder vacuum manifolds, PVC, three-place. (The KSSL can be contacted for more information.)
4.17 Twelve 47-mm filter holders for flasks or manifolds, glass
4.18 Slide roller (fig. 7A1–1)
4.19 Vacuum chuck (fig. 7A1–1)
4.20 House vacuum
4.21 Water aspirator used as vacuum source with large vacuum rated Erlenmeyer flask as ballast for liquid reservoir (fig. 7A1–2)

Figure 7A1–1.—Vacuum chuck (top) and slide roller (bottom).

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water
5.2 Sodium carbonate (Na_2CO_3) (CAS# 497-19-8)
5.3 Potassium chloride (KCl) (CAS# 7447-40-7)
5.4 Magnesium chloride ($MgCl_2$) (CAS# 7786-30-3)
5.5 Glycerol ($HOCH_2)_2CHOH$) (CAS# 56-81-5)
5.6 Toluene ($C_6H_5CH_3$) (CAS# 108-88-3)
5.7 **Sodium carbonate solution, 0.25 *N***
Components: Sodium carbonate (Na_2CO_3), RO water

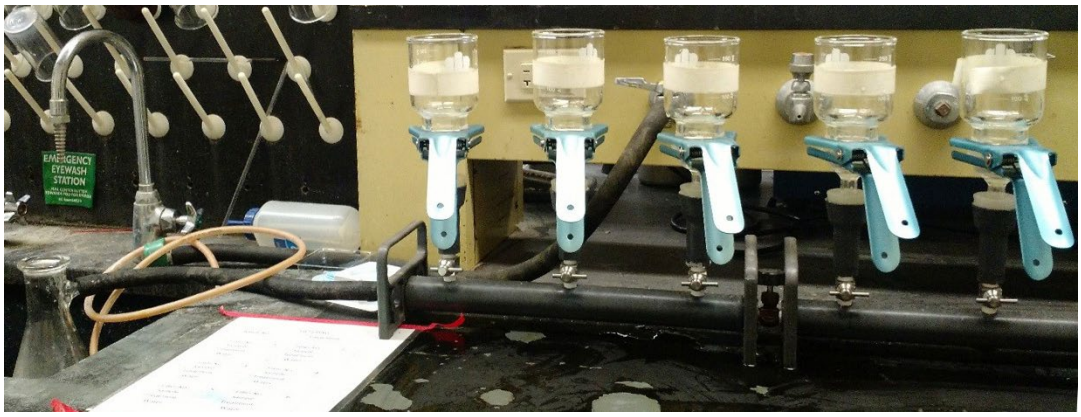

Figure 7A1–2.—Vacuum apparatus.

- To a 1-L polyethylene bottle, add the following in order:
  - 26.50 g of Na_2CO_3
  - 1 L of RO water
- For a greater quantity, to a 5-L polyethylene carboy, add the following in order:
  - 132.50 g of Na_2CO_3
  - 5 L of RO water
- Swirl to mix.

5.8 Potassium chloride solution, 1.0 *N*

Components: Potassium chloride (KCl), RO water

- To a 1-L polyethylene bottle, add the following in order:
  - 74.55 g of KCl
  - 1 L of RO water
- For a greater quantity, to a 10-L polyethylene carboy, add the following in order:
  - 670.96 g of KCl
  - 9 L of RO water
- Swirl to mix.

5.9 Magnesium chloride solution, 1.0 *N*

Components: Magnesium chloride ($MgCl_2$), RO water

- To a 1-L polyethylene bottle, add the following in order:
  - 47.61 g of $MgCl_2$
  - 1 L of RO water
- For a greater quantity, to a 10-L polyethylene carboy, add the following in order:
  - 428.49 g of $MgCl_2$

- 9 L of RO water
- Swirl to mix.

5.10 Glycerol:water mixture (1:7)

Components: Glycerol ($HOCH_2)_2CHOH$), toluene ($C_6H_5CH_3$), RO water

- To a 50-mL glass volumetric flask, add the following in order:
  - 28 mL of RO water
  - 4 mL of glycerol
  - 2 drops of toluene (or other preservative)
- Invert to mix.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Keep the lid closed when centrifuge is in operation. Ensure that all rotors and tubes are seated firmly in their proper location.

Use tongs and appropriate thermal protection when operating the muffle furnace.

The x-ray diffraction unit is a radiation-producing piece of equipment. Analysts must receive safety training before operating the equipment. Area radiation monitors must be used in the vicinity of the x-ray diffractometer.

7. Sample Preparation

7.1 Prepare two 100-mL plastic centrifuge tubes for each sample: Mg^{2+} and K^{+} filter treatments. Label each tube with a sample number and the treatment.

7.2 Use particle-size distribution data to weigh out enough soil to obtain 150 mg of clay. Place the clay into the 100-mL tube.

7.3 Fill tube to 9.5-cm height with sodium carbonate solution and add stopper.

7.4 Place the tubes on wrist-action shaker and shake for 2 h.

7.5 Remove stopper from tube and rinse stopper and sides of tube with enough sodium carbonate solution to bring the volume to the 10-cm mark. Vortex the clay suspension.

7.6 Centrifuge sample tubes at 750 rpm for 3.0 minutes. Make sure the pairs of tubes are balanced.

7.7 Label a 200-mL beaker with sample number and treatment. Decant 30 mL of liquid from centrifuge tube into beaker. Leave all sediment in the centrifuge tube.

7.8 Refill sample centrifuge tubes to the 10-cm mark with sodium carbonate

solution. Vortex the tubes. Repeat steps 7.5–7.8 three more times for a total of approximately 90 mL of decanted sample. Clay suspension in the beaker is used for x-ray diffraction and TGA analysis.

8. Procedure

8.1 Label glass slides with sample number and treatment.

8.2 Squirt a few drops of water on the base of the vacuum filter holder and then place the filter, being careful to center it. Clamp the funnel down over the base, do not displace the filter paper. Make sure vacuum is turned on and open valve below the base of the filter holder.

8.3 Pour half of the clay suspension on the filter and wait for the liquid to pull through the filter. Do not allow filter to dry. The required amount of time varies depending on clay type.

8.4 When the standing liquid in the center of the filter is pulled through, swirl remaining sample in the beaker to disperse the clay particles. Pour remainder of the sample into the funnel. Wash any settled clay from the bottom of the beaker into the funnel using a squirt bottle filled with RO water. Do not allow filter to dry.

8.5 When the center of the filter has no standing liquid, use a squirt bottle to cover the filter with approximately 3 mL of desired treatment solution ($MgCl_2$ or KCl).

8.6 When the filter begins drying once again, rinse the sides of the filter with approximately 3 mL or $^1/_{16}$-inch of RO water.

8.7 Wait until the filter begins drying and a color change is observed at the edge of the clay filter. Within 15 seconds, peel the filter from the base and turn the vacuum valve to the “off” position.

8.8 Place the glass slide (labeled-side down) on the vacuum chuck (fig. 7A1–1). Apply vacuum.

8.9 Place the filter (clay-side down) on the slide and then (using the roller; fig. 7A1–2) run across all four sides of the slide. Then roll across the top of the filter gently. Peel up the filter paper, leaving the clay film on the slide.

8.10 If extra clay is needed (such as for TGA analysis), roll the remaining clay onto an auxiliary slide.

8.11 Allow slides to dry in air for at least 4 h.

8.12 For each sample number on the bench sheet, there should be two slides. One slide is treated with $MgCl_2$, and the other is treated with KCl. Each slide is analyzed twice, so there are four treatments in total. Treatments are as follows:

- Mg^{2+}-room temperature
- Mg^{2+}-glycerol
- K^+-300 °C (heated 2 h)
- K^+-500 °C (heated 2 h)

8.13 Transfer the K^+ treated slides to a 300 °C muffle furnace for 2 hours. Analyze the Mg^{2+}-room temperature and K^+-300 °C slides at the same time.

8.14 After analyzing, transfer the K^+-300 °C slides to 500 °C muffle furnace for 2 h. Transfer the Mg^{2+}-room temperature slides to a paper lined tray and spray with glycerol solution, making sure to coat all slides evenly. Allow to stand no longer than 4 hours. Analyze the Mg^{2+}-glycerol and the K^+-500 °C slides at the same time. Complete x-ray analysis immediately after glycerol treatment and within the 4 hour time period. If not possible, spray additional glycerol prior to run.

8.15 For XRD analysis, place the slides in the sample holders and arrange in autosampler grid of the XRD.

8.16 XRD software parameters and scan range are established for each type of analysis. General equipment operating conditions are in table 7A1–1. Peak intensities and tube wear must be monitored over time and use of the machine. Compare patterns for quartz and a soil standard with previous runs to ensure peak intensity and positions have remained constant. Slit adjustments may be automatic or manual depending on model of machine. Refer to the XRD manual.

Table 7A1–1.—General XRD Operating Parameters.

Parameter	Setting
CuKα radiation, λ	1.54 Å (0.154 nm)
Scan range	2° to 35° 2θ
Generator settings	40 kV, 30 mA

Note: Generator settings (kV, mA) listed in table 7A1–1 are for reference. Real values are modified for tube wear to achieve specific peak count for a reference standard.

8.17 Preferential orientation of clay minerals enhances diffraction from the basal (00/) spacing and tends to minimize the number and intensity of peaks from diffraction by other hkl planes. With preferential orientation, second, third, and fourth order peaks may be recorded in addition to the basal first order peaks. Groups of associated peaks that differ by order of diffraction are as follows:

8.17.1 Smectite (Mg^{2+}-glycerol)

- 17 to 18 Å
- 8.5 to 9 Å (weak)

8.17.2 Chlorite, vermiculite, and smectite

- 14, 7, 4.7, and 3.5 Å
- 7, 4.7, and 3.5 Å, weak for smectite

- High Fe substitution in the chlorite structure results in a decrease in the peak intensity of even numbered orders (e.g., 14 and 4.7 Å) and increase in peak intensity of odd number orders (7 and 3.5 Å).

8.17.3 Mica

- 10, 5 (weak in biotites and moderate in muscovites), and 3.3 Å

8.17.4 Kaolinite

- 7 and 3.5 Å

8.18 Use the following x-ray diffraction criteria to identify minerals that may exhibit a change in angstrom size with hydration, heating, or treatments or that share d-spacing with other minerals. For a more complete list of d-spacings to confirm or identify a mineral, consult the "Mineral Powder Diffraction File–Data Book" (JCPDS, 1980).

8.18.1 Kaolinite and Halloysite

- Crystal structure missing at 500 °C
- Å (7.2 to 7.5 Å) with all other treatments:
  - Is there a 7 Å peak? Is it destroyed at 500 °C?
    - Interpretation: If so, the mineral is kaolinite or halloysite.
  - Is there a sharp peak at ≈7.1 Å (absent at 500 °C)?
    - Interpretation: If so, the mineral is kaolinite.
  - Is there a broad peak at 7.2 to 7.5 Å (absent at 500 °C)?
    - Interpretation: If so, the mineral is halloysite.

8.18.2 Mica (Illite)

- 10 Å with all treatments
- 10 Å with Mg^{2+}-saturation

8.18.3 Chlorite

- Crystal structure of Fe-chlorites destroyed at 650 to 700 °C
- 14 Å with all other treatments
- 14 Å peak when heated to 500 °C
- Generally, also has a strong 7 Å peak

8.18.4 Smectite

- 14 Å with Mg^{2+}-saturation
- 12 to 12.5 Å with K^{+}- or Na^{+}-saturation
- 17 to 18 Å with Mg^{2+}-glycerol solvation
- 10 Å with K^{+}-saturation and heating to 300 °C
  - Is there a 17 to 18 Å peak upon solvation?
    - Interpretation: If so, the mineral is smectite.

8.18.5 Vermiculite

- 14 Å with Mg^{2+}-saturation
- 14 Å with Mg^{2+}-glycerol solvation
- Nearly 10 Å with K^{+} saturation
- 10 Å when K^{+}-saturated and heated to 300 °C
    - Is there an enhanced 10 Å peak with K^{+}-saturation in comparison to Mg^{2+} saturation that cannot be attributed to smectite?
        - Interpretation: If so, the mineral is vermiculite.

8.18.6 Hydroxy-Interlayed Vermiculite or Smectite

- Failure to completely collapse to 10 Å of smectite or vermiculite when K^{+}-saturated and heated to 300 °C

8.18.7 Mixed Layer Vermiculite-Mica

- Randomly interstratified: Peak is between 10 and 14 Å with Mg^{2+}, does not expand with Mg^{2+}-glycerol, and collapses to 10 Å with K^{+}-saturation and heating to 300 °C.
- Regularly interstratified: A 24 Å peak (and higher orders) that shows no change with Mg^{2+}-glycerol treatment and K^{+} saturation and heating collapses vermiculite and produces a 10 Å peak.

8.18.8 Mixed Layer Smectite-Mica

- Randomly interstratified: Peak is between 10 and 14 Å with Mg^{2+}, expands to 14–16 Å with Mg^{2+}-glycerol, and collapses to 10 Å with K^{+}-saturation and heating to 300 °C.
- Regularly interstratified: A small 24 Å peak and large peak at 12 Å with Mg^{2+}-saturation; expands to 28 Å with Mg^{2+}-glycerol treatment. K^{+}-saturation and heating collapses smectite and then produces a 10 Å peak.

8.18.9 Mixed Layer Chlorite-Vermiculite

- Randomly Interstratified: Peak is at 14 Å with Mg^{2+} and Mg^{2+}-glycerol and collapses incompletely to between 10 and 14 Å with K^{+}-saturation and heating.
- Regularly interstratified: Peak is at 28 Å (and higher orders) with Mg-saturation and does not expand with Mg^{2+}-glycerol treatment. K^{+}-saturation and heating to 500 °C collapses vermiculite and a produces a 24 Å peak.

8.18.10 Mixed Layer Chlorite-Smectite

- Randomly interstratified: Peak is at 14 Å with Mg^{2+}-saturation, expands to higher spacings (≈16 Å) with Mg^{2+}-glycerol treatment, and peak collapses incompletely to between 10 and 14 Å with K^{+}-saturation and heating.

8.18.11 Gibbsite

- Peak is at 4.83 to 4.85 Å with Mg^{2+} and Mg^{2+} glycerol but is destroyed when heated to 300 °C.

8.18.12 Goethite

- Peak is at 4.16 to 4.18 Å with Mg^{2+} and Mg^{2+}-glycerol but is destroyed when heated to 300 °C.

8.18.13 Lepidocrocite

- Peak is at 6.2 to 6.4 Å with Mg^{2+} and Mg^{2+}-glycerol but is destroyed when heated to 300 °C.

8.18.14 Gypsum

- Peak is destroyed when heated to 300 °C.

8.18.15 Quartz

- Peaks are at 4.27 Å and 3.34 Å with all treatments (only 3.34 Å present in small percentages).

8.18.16 Potassium Feldspar

- Peak is at 3.24 Å with all treatments.

8.18.17 Plagioclase Feldspar

- Twin peaks are between 3.16 and 3.21 with all treatments.

8.18.18 Calcite

- Peak is at 3.035 Å with all treatments.

8.18.19 Dolomite

- Peak is at 2.88 to 2.89 Å with all treatments.

9. Calculations

9.1 X-ray diffraction produces graphed peaks that correspond to the 2θ angle on a goniometer and detects x-ray intensity from the detector. The crystal "d" spacings of minerals, i.e., the interval between repeating planes of atoms, can be calculated by Bragg's Law as follows:

$$n\lambda = 2\,d \sin\theta$$

n = Integer that denotes order of diffraction

λ = X-radiation wavelength (Angstroms, Å)

d = Crystal "d" spacing (Å)

θ = Angle of incidence

When n = 1, diffraction is of the first order.

9.2 Use the x-ray diffraction criteria, i.e., diagnostic basal 00/ spacings (Å), in table 7A1–2 for identification and ready reference of some common crystalline minerals as affected by differentiating sample treatments.

Table 7A1–2.—X-Ray Diffraction Parameters of Common Soil Minerals.

Mineral	Treatment						
	Na^+	Mg^{2+}	Mg^{2+} glycerol	K^+	K^+ 300 °C	K^+ 500 °C	K^+ 700 °C
	(00/ diffraction spacing in angstroms)						
Kaolinite	7	7	7	7	7	LD[1/]	LD
Halloysite	7B[2/]	7B	7B	7B	7B	LD	LD
Mica (Illite)	10	10	10	10	10	10	10
Chlorite	14*[3/]	14*	14*	14*	14*	14*	T[4/]
Vermiculite	14	14	14	10	10	10	10
Smectite	12.5	14	18	12.5	10	10	10
Gibbsite	4.85	4.85	4.85	4.85	LD	LD	LD
Goethite	4.18	4.18	4.18	4.18	LD	LD	LD
Lepidocrocite	6.24	6.24	6.24	6.24	LD	LD	LD
Interlayer	10-14	10-14	10-18	10-14	10-14	10-14	10-14
Quartz	3.34 and 4.27 for all treatments						
Calcite	3.035 for all treatments						
Dolomite	2.886 for all treatments						

[1/] LD=Lattice destroyed.
[2/] B=Broad peak is common.
[3/] *=Sometimes <14 Å.
[4/] T=Temperature of decomposition varies with chemical composition, particle-size, and heating conditions.

9.3 From the "Detected Peaks File" and graphics chart, identify the minerals present according to the registered "d" spacings. As a first approximation, use the following peak intensities, i.e., peak heights above background in counts per second, to assign each layer silicate mineral to one of the 5 semiquantitative classes.

Class	Peak Height above Background
	(counts sec^{-1})
5 (Very large)	>1,800
4 (Large)	1,120 to 1,800
3 (Medium)	360 to 1,120
2 (Small)	110 to 360
1 (Very small)	<110

9.4 Adjust class placement to reflect area under the curve if peak is broad relative to peak height or if thermal, elemental, or clay activity data or other evidence warrant class adjustment.

9.5 If there are no peaks and no evidence of crystalline components, place the sample in NX class (non-crystalline). If there are only 1 to 3 very small (class 1) peaks, also indicate NX to infer a major non-crystalline component. Indicate the exact counts of each identified peak in the LIMS database.

9.6 Report class of each mineral detected.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

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Instrumental Analyses (7A)
Thermogravimetric Analysis (7A2)
Thermal Analyzer (7A2a)

1. Introduction to Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is a technique for determining weight loss of a sample as it is being heated at a controlled rate. The weight changes are recorded as a function of temperature, i.e., a thermogravimetric curve, and provide quantitative information about substances under investigation. Examples include gibbsite, kaolinite, goethite, and 2:1 expandable minerals (smectite and vermiculite).

Recent work found good agreement between gypsum quantification using dissolution procedures and thermal analysis. The TGA procedure is especially useful for soils with a large percentage (>20%) of gypsum. Burt et al. (2001) had good agreement between total Mg analysis and TGA quantification (12.9% weight loss between 600–650°C) of serpentine minerals in ultramafic-derived soils in Oregon.

2. Scope and Field of Application

Thermal analysis defines a group of analyses that determine some physical parameter, e.g., energy, weight, or evolved substances, as a dynamic function of temperature (Tan et al., 1986; Karathanasis and Harris, 1994).

During TGA, the heating rate varies based on the rate of weight loss of the sample; once weight loss begins, the heating rate slows until reaction completes. Heating then resumes until weight loss is detected again. Some minerals, such as gibbsite and kaolinite, are quantified by calculating the weight loss at approximately 250 to 350°C and 450 to 550°C. The weight loss is due to dehydroxylation, i.e., loss of crystal lattice hydroxyl ions. In the absence of gibbsite, the quantification of goethite, which is an iron oxyhydroxide, can be based on the characteristic weight loss of 10.1 to 11.2% between 300 and 400°C (Karathanasis and Harris, 1994). Sample weight loss of 2:1 expandable minerals (smectite+vermiculite) is observed at <250°C from loss of adsorbed water (Karanthasis and Hajek, 1982a; Karanthasis and Hajek, 1982b; Tan et al., 1986). At this low temperature, adsorbed water is proportional to the specific surface area of the sample (Jackson, 1956; Mackenzie, 1970; Tan and Hajek, 1977; Karathanasis and Hajek, 1982b).

3. Principle

A 5- to 10-mg sample of clay or fine-earth (finely ground) soil is placed in a platinum sample pan. The pan is placed in the TGA balance. The instrument records the initial sample weight. The sample is then heated to 750°C–900°C in a flowing N_2 atmosphere. Heating rate varies based on the rate of weight loss.

Once weight loss begins, the heating rate slows until reaction completes. Heating then resumes until weight loss is detected again. The computer collects weight changes as a function of temperature and records a thermogravimetric curve.

3.1 Interferences

Samples that have a significant amount of organic matter should be pretreated with hydrogen peroxide (H_2O_2) (method 3A1a1). Organic matter may interfere with calculations because it loses weight by dehydrogenation and by oxidation to CO_2 between 300 and 900 °C (Tan et al., 1986).

Samples should be washed free of any soluble salts. Mineral salts that contain water of crystallization may also interfere.

In some cases, weight loss from gibbsite and goethite overlap and prevent quantitative interpretation. These samples can undergo iron removal by using method 4F1a1 to eliminate goethite.

Do not include large aggregates in the sample. They can cause thermal interferences; i.e., differential kinetics of gas diffusion through the sample and physical movement of sample in a reaction.

Due to the weathering, observed weight losses are going to be greater than theoretically predicted. Damaged clay structures hold more water than intact structures. This problem is particularly apparent with kaolinitic and illitic samples, which characteristically contain more “structural” water than ideal structural formulae would indicate (Rouston et al., 1972; Weaver and Pollard, 1973).

It is well established that various minerals lose the major portion of their crystal lattice water in different temperature ranges (Tan et al., 1986). The weight loss regions (WLR) of minerals, however, have overlaps that interfere in the identification and measurement of the minerals of interest.

- The WLR of goethite (250 to 400 °C) overlaps with the WLR of gibbsite (250 to 350 °C) (Mackenzie and Berggen, 1970).
- The WLR of illite (550 to 600 °C) overlaps with the high-end of the WLR of kaolinite (450 to 550 °C) (Mackenzie and Caillere, 1975).
- The WLR of hydroxy-Al interlayers in hydroxy-Al interlayered vermiculite (HIV) (400 to 450 °C) overlaps with the low-end of the WLR of kaolinite (450 to 550 °C), especially in the poorly crystalline kaolinites (Mackenzie and Caillere, 1975).

In TGA, there is a greater probability of measuring water losses in specific temperature regimes that are not specifically associated with dehydroxylation reactions of interest. The dehydroxylation of nontronites, which are iron-rich dioctahedral smectites (450 to 500 °C), may interfere with kaolinite identification and measurement (Mackenzie and Caillere, 1975).

4. Apparatus

4.1 Thermal analyzer, with associated software

4.2 N_2 gas, 99.99% purity

4.3 Two-stage gas regulator, 20-psi maximum outlet pressure
4.4 Forceps, flat-tipped
4.5 Weighing spatula
4.6 Desiccator, glass
4.7 Mortar and pestle
4.8 Sieve, 80-mesh
4.9 Razor blade
4.10 Kaolinite, standard, poorly crystalline sample KGa-2, Clay Minerals Society
4.11 Gibbsite, standard, Surinam Gibbsite, SSL, 67L022

5. Chemicals

5.1 Magnesium nitrate saturated solution

Components: Magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$) (CAS #13446-18-9), RO water

- This super saturated solution is intended to serve as a humidity control and is made qualitatively.
- To a petri dish or other small glass vessel, add the following in order:
  - ≈5 mL of RO water
  - Add a small amount of magnesium nitrate, swirl until dissolved.
  - Continue to add magnesium nitrate until crystals no longer dissolve.
- Place solution in a crucible and store in a desiccator.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium bicarbonate (CAS# 497-9-8) and water to neutralize and dilute spilled acids.

Secure high-pressure N_2 tanks and handle with care. When changing the tanks, protect valves with covers.

7. Sample Preparation

7.1 Refer to the method for Filter Peel on Glass (method 7A1b, steps 7.1 to 7.8) to prepare Mg-saturated clay film for analysis.
7.2 Scrape clay from auxiliary clay slide using a razor blade.
7.3 Lightly grind sample with pestle to make a homogeneous powder.

7.4 Sieve sample through an 80-mesh sieve. Equilibrate sample for 4 hours over a saturated magnesium nitrate solution (55% relative humidity) in a glass desiccator.

8. Procedure

8.1 Always use high quality purge gases with the TGA. Minimum purity of 99.9% is recommended.

8.2 Load empty pans into autosampler, making sure that they are lined up properly and that the bails are in line with each other.

8.3 Input batch information and run the tare procedure on the empty pans.

8.4 Remove autosampler tray from machine. Use spatula to place approximately 10 mg (estimated by volume) of sample into each pan. Load the pans back into the autosampler tray, making sure that they are seated correctly and that their bails are lined up with one another.

8.5 Run "Preweigh" procedure on filled pans.

8.6 Run samples. Gas pressures are instrument-specific.

8.7 Access universal analysis software. Display file and calculate weight loss in specific regions for selected minerals. Mark beginning and end of weight loss for sample.

9. Calculations

9.1 The thermogravimetric curve is displayed on the computer monitor. The ordinate (Y) is expressed as a relative weight percentage, i.e., the initial sample weight is 100.0%. Use the computer to calculate the total change in sample weight (ΔY), within the predetermined temperature range, as a sample weight percent.

9.2 % Kaolinite =

$$[(\Delta \text{ sample weight \% 450–550 °C}) / 14] \times 100$$

or

$$(\Delta \text{ sample weight \% 450–550 °C}) \times 7.14$$

Δ sample weight = total change in sample weight expressed as relative percent.

14 = percent weight of hydroxyl water lost from pure kaolinite during dihydroxylation

9.3 % Gibbsite = $[(\Delta \text{ sample weight \% 250–350 °C}) / 34.6] \times 100$

Δ sample weight = total change in sample weight expressed as relative percent of the 110 °C base weight.

34.6 = percent weight of hydroxyl water lost from pure gibbsite during dehydroxylation

9.3.1 If Fe oxides are removed prior to analysis to prevent the interference with gibbsite determination, the calculation is modified to account for weight loss due to deferration as follows:

% Gibbsite = {[Δ Sample weight % 250–350 °C x (Wt2 / Wt1)] / 34.6} x 100

- Wt1 = Weight before deferration
- Wt2 = Weight after deferration

9.4 The percent weights of hydroxyl water lost from kaolinite and gibbsite are derived from the following assumed dehydroxylation reactions.

9.4.1 Gibbsite: $2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$

9.4.2 Kaolinite: $Si_2Al_2O_5(OH)_4 \rightarrow 2SiO_2 + Al_2O_3 + 2H_2O$

9.4.2.1 Using kaolinite as an example, percent weight of hydroxyl water lost is calculated from the following formula weights.

- $Si_2Al_2O_5(OH)_4 = 258$ g mol^{-1}
- $2H_2O = 36$ g mol^{-1}
- Percent weight of hydroxyl water lost = (36 / 258) x 100 = 14%

9.5 TGA can be used to quantify serpentine minerals (Burt et al., 2001) based on an onset temperature of 600 to 650 °C (Karathanasis and Harris, 1994) and a weight loss from 600 to 900 °C (12.9%) based on the mineral structure $Mg_3Si_2O_5(OH)_4$.

9.5.1 % Serpentine minerals =

[(Δ sample weight % 600–900 °C) / 12.9] x 100

or

(Δ sample weight % 600–900 °C) x 7.75

9.6 Gypsum can be quantified based on a loss of 20.9% (Karathanasis and Harris, 1994) based on the weight loss in the region of 100 to 350 °C.

9.6.1 % Gypsum =

[(Δ sample weight % 100–350 °C) / 20.9] x 100

or

(Δ sample weight % 100–350 °C) x 4.78

9.7 Report percent gibbsite, kaolinite, gypsum, or antigorite to nearest whole number.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

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Instrumental Analysis (7A)

Surface Area (7A5)

N_2 Adsorption (7A5a)

Brunauer, Emmett, and Teller (BET) Theory (7A5a1)

Vacuum Degassing (7A5a1a)

Multi-point (7A5a1a1)

Air-Dry, <2 mm (7A5a1a1a1)

Single Point (7A5a1a2)

Air-Dry, <2-mm (7A5a1a2a1)

1. Introduction to Nitrogen Surface Adsorption and Clays

Soils vary widely in their relative surface area because of differences in mineralogical and organic composition and differences in particle-size distribution. Surface area influences such properties as physical adsorption of molecules and the heat loss or gain resulting from this adsorption; shrink-swell capacity; water retention and movement; cation exchange capacity; pesticide adsorption; and soil aggregation (Carter et al., 1986). In addition, many biological processes are closely related to specific surfaces.

Specific surface area (SSA) is an operationally defined concept, dependent upon the measurement technique and sample preparation (Pennell, 2002). Nitrogen adsorbed SSA testing is considered an indirect measurement.

2. Scope and Field of Application

Nitrogen adsorbed SSA is based on measurements of the adsorption or retention of probe molecules on a solid surface at monolayer coverage (Pennell, 2002). The current method used by the KSSL is N_2-BET(multi-point) sorption, using the theory of Brunauer, Emmett, and Teller. N_2 is a nonpolar gas and does not interact with, or have access to, interlayer crystallographic planes of expandable clay minerals. N_2 is therefore considered to provide a measure of external surface area. Polar molecules, such as ethylene glycol monoethyl ether (EGME), are known to penetrate the interlayer surfaces of expandable clay minerals and therefore have been used to provide a measure of total surface areas (internal+external surface area) (Pennell, 2002). Significant differences between these methods are most apparent in soils containing expandable clay minerals and soil organic matter (Chlou and Rutherford, 1993; Pennell et al.,1995; de Jong, 1999; Quirk and Murray, 1999).

In the past, the KSSL determined surface area by glycerol retention (obsolete method 7D1) or EGME retention (obsolete method 7D2).

3. Principle

A <2-mm, air-dry soil sample is ground to pass a 0.25-mm (60-mesh) sieve and is oven-dried (24 h, 110 °C). Enough soil (typically 0.5 to 1 g) is added to

a weighed sample cell to achieve 2- to 50-m^2 total surface area. Soil is cleaned of contaminants, e.g., water and oils, by vacuum degassing at 10 millitorr for a minimum of 3 h at 110 °C and then reweighed to obtain degassed sample weight. The sample is brought to a constant temperature by means of an external bath in liquid nitrogen (77 °K; -333 °C). Next, small amounts of gas (N_2), called the "absorbate," are admitted in steps to evacuate sample chamber. Gas molecules that stick to the surface of the solid (absorbent) are said to be adsorbed and tend to form a thin layer that covers the entire adsorbate surface. The number of molecules required to cover the adsorbent surface with a monolayer of adsorbed molecules, N_m, can be estimated based on the BET theory. Multiplying N_m by the cross-sectional area of an adsorbate molecule yields the sample's surface area. Specific surface area is reported in $m^2\ g^{-1}$.

3.1 Interferences

Organic material can coat or cover mineral surfaces, generally reducing SSA as determined by N_2-BET. Removal of organic matter prior to analysis typically increases these values.

Air-drying may result in the collapse and shrinkage of soil humic acid. Freeze-drying maintains an intricate structural network more characteristic of a natural state and may provide SSA values that are more representative of field conditions (Pennell, 2002).

4. Apparatus

4.1 Surface area analyzer, with vacuum degassing, and associated hardware

4.2 Vacuum pump, capable of achieving 50 millitorr required, 10 millitorr recommended

4.3 Dewar flask with insulated lid for liquid N_2

4.4 Oven, 110 °C

4.5 Sample cells, glass, with outside stem diameters of 6, 9, and 12 mm and internal diameters of 4, 7, and 10 mm

4.6 Glass filler rods, 6 x 268.5 mm and 6 x 131.5 mm

4.7 Mortar and pestle

5. Chemicals

5.1 Compressed Nitrogen (N_2), high purity, 99.9%

5.2 Liquid N_2 (77 °K)

5.3 Standard reference material, 31.16 $m^2\ g^{-1}$ SSA, with ±2.03 $m^2\ g^{-1}$ reproducibility

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate

rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents.

Wear protective gloves when handling heating mantle. Never insert fingers inside the pocket to determine if the mantle is heating up. Switch off the heating mantle when not in use. Refer to the manufacturer's manual for safe operation of the surface area analyzer.

Wear protective gloves when handling liquid nitrogen. Use in well-ventilated areas; high concentrations of nitrogen gas in an enclosed area can cause asphyxiation.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

8.1 Set N_2-regulator at 10 PSIG (70 kPa).

8.2 Refer to the manufacturer's manual for the routine operation, manifold calibration, and sample cell calibration.

8.3 The dosing manifold is factory calibrated. There is no need to repeat this calibration before every analysis. The operator should check this calibration periodically (e.g., once every month) or if changes to the system may have altered the manifold volume.

8.4 Perform a sample cell calibration for each combination of sample cell+filter rod+station and for each combination of adsorbate+coolant. Once completed, further calibration for that particular combination is not needed. For most users, all standard (bulbless) cells can be considered equivalent for each diameter; i.e., one cell+rod+station calibration suffices for all cells of the same diameter with the same rod in the same station.

8.5 Ensure Dewar flask is filled to the red line (approximately 1 in from top) with liquid N_2. Allow 5 min for liquid N_2 to equilibrate for best results. If the liquid N_2 is still boiling heavily, then the Dewar needs to be cleaned before filling with liquid N_2. If boiling continues after a dry clean Dewar is filled for 5 min, then replace the Dewar. Residual boiling requires the Dewar to be topped-off again. Ensure proper alignment of sample cells with Dewar mouth. Foam cap is not required for BET analysis. If, however, a long isotherm is required, then use the foam cap. Ensure that there is no condensed water visible in the stem of the sample cell.

8.6 Follow set-up instructions on the surface area analyzer (e.g., select cell for Stations, enter sample ID for Stations, enter dry degassed sample weight by measuring sample volume, etc.) until prompted to proceed with analysis. Analytical data include Multi Point BET (adsorption), slope, intercept, correlation coefficient, BET C, total surface area in cell (m^2), and specific

surface area ($m^2\ g^{-1}$). Set-up and analytical data are automatically recorded by computer and then printed.

8.7 Grind <2-mm, air-dry soil sample with a mortar and pestle to break up any aggregates.

8.8 Weigh sample cell to the nearest 0.1 mg. Weigh enough soil (typically 0.5 to 1.0 g) into sample cell to achieve 2- to 50-m^2 total area (sample size will vary depending on the SSA of the soil). Oven-dry at 110 °C for 24 h.

8.9 Remove sample cell with soil from oven and seal immediately. Allow to cool to touch.

8.10 Place the sample cell in the pouch of the heating mantle, set clamp in place, insert cell into fitting, tighten fitting, and loop elastic cords over hooks provided. Set the degas temperature at 110 °C for a minimum of 3 h.

8.11 Upon completion of degassing, switch the mantle off. Allow sample to cool. Unload degasser when ready to analyze sample.

8.12 Remove cell and reweigh to obtain dry, degassed soil sample weight to the nearest 0.1 mg.

8.13 Using the "Preset Analysis" option on surface area analyzer allows the user to preset and save the following: User ID, stations for analysis, setup files, cell numbers, sample ID numbers, and comments.

9. Calculations

9.1 The BET equation for determination of the surface area of solids:

$$1/\{W\,[(P_0/P) - 1)]\} = [1/(W_m - C)] + \{[(C - 1)/W_m C] \times (P/P_0)\}$$

W = weight of gas adsorbed at a relative pressure of P/P_0

W_m = weight of adsorbate constituting a monolayer of surface coverage

C = BET C constant, related to energy of adsorption in first adsorbed layer and indicative of the magnitude of absorbed/adsorbate interactions (typically, 50 to 250 for most solid surfaces).

- The BET equation requires a linear plot of $1/\{W\,[(P_0/P) - 1)]\}$ versus P/P_0 which for most solids, using nitrogen as adsorbate, is restricted to a limited region of the adsorption isotherm. Usually in the P/P_0 range of 0.05 to 0.35 (Quantachrome Corp., 2000).
- The standard multi-point BET procedure requires a minimum of three points in the appropriate relative pressure range. The weight of the monolayer of adsorbate W_m can then be obtained from the slope s and intercept i of the BET plot.

9.2 The weight of the monolayer ($W_m = 1/[s+i]$) can be obtained by combining two equations:

$$s = (C - 1)/W_m C$$

$$i = 1/W_m C$$

9.3 Calculate the total surface area (St) of the sample:

$$S_t = W_m \times N \times A_{cs} / M$$

N = Avogadro's number (6.023×10^{23})

M = Molecular weight of absorbate (28.02 g mol^{-1})

A_{cs} = Close-packed nitrogen monolayer at 77 °K, the cross-sectional area for nitrogen = 16.2 Angstroms^2

9.4 Calculate the specific surface area (S):

$$S = St / w$$

w = Degassed sample weight

9.5 Report specific surface area in $m^2\ g^{-1}$ to the nearest 0.01 unit.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

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Instrumental Analyses (7A)

Visible and Near-Infrared Diffuse Reflectance Spectroscopy (VNIR–DRS) (7A6)

Air-Dry, <2 mm (7A6a1)

1. Introduction to VNIR Analysis

Visible and Near-Infrared Diffuse Reflectance Spectroscopy (VNIR–DRS) is the measurement of diffuse reflected spectra of a sample after exposure to visible near-infrared radiation (350–2,500 nm) (McWhirt, 2012; Workman and Springsteen, 1998; Sparks, 1996). VNIR–DRS has been used in the evaluation and prediction of a wide range of soil properties, including exchangeable cations, cation exchange capacity, pH, organic carbon, free iron, particle-size separates, gravimetric water content, and relative kaolinite and smectite (Ben-Dor and Banin, 1995; Shepherd and Walsh, 2002; Islam et al., 2003; Brown et al., 2006). This analysis is nondestructive, noninvasive, and provides nearly instantaneous measurements.

2. Scope and Field of Application

The VNIR–DRS spectrometer contains a dispersive energy source that enables the intensity at different wavelengths to be detected and recorded (McWhirt, 2012; Workman and Springsteen, 1998). The resulting spectrum of DRS does not necessarily produce a directly proportional relationship between wavelength intensity and analyte concentration; therefore, corrections and statistical analysis must be used to interpret the resulting spectra and to build models (McWhirt, 2012). Refer to Workman and Springsteen (1998) for multivariate regression techniques often used for this statistical application.

3. Principle

An air-dry, <2-mm soil sample is placed in the sample holder and pressed at approximately 46 psi. The sample holder is placed onto a Muglight, and a scan is performed. The resulting VNIR pattern is stored for future data analysis.

3.1 Interferences

Calibration may be less accurate than other, more conventional chemistry. A large set of VNIR patterns is required to compare results to conventional methods.

Measurements outside the range of calibration samples are invalid, and small calibration sample sizes can lead to overconfidence.

Pure compounds can be positively identified only if a library of compounds is developed, preferably by using known standards.

Due to the IR signature of water, moist samples are typically not scanned by VNIR–DRS analysis.

The exposure time of material to intense light (heat) source, such as the Muglight used for analysis, affects the IR signature. Samples should not be allowed to remain subjected to the light source before analysis.

4. Apparatus

4.1 Visible and near-infrared diffuse reflectance spectrometer (VNIR–DRS) and sample holders (pucks)

4.2 Press, approximately 46-psi

4.3 Pancake air compressor, 3-gal, 100-psi, oil-less. Alternatively, canned air may be used, taking precautions to keep propellant from coating samples during use.

4.4 Microfiber cloth

4.5 Muglight

4.6 ASD White reference puck for calibration

5. Chemicals

5.1 RO water

5.2 Isopropyl alcohol wipes, 70%

5.3 QC standards (high and low), appropriate reference materials with data models

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Only trained personnel should use VNIR–DRS equipment. Follow the manufacturer's safety precautions when using the VNIR–DRS.

7. Sample Preparation

The field sample is air-dried at 30 to 35 °C, crushed, and sieved to <2 mm. The weight of air-dry soil remains relatively constant. Biological activity is low during storage.

8. Procedure

The following are suggestions regarding equipment set up, calibration, and maintenance. Always follow the manufacturer's instructions and recommendations.

8.1 Spectrometer preparation

- To minimize dust coatings, use a clean, dry microfiber cloth to clean the Muglight lens, inner and outer Muglight sample holder windows, ASD white reference window, and ASD wave cal puck window. If smudges remain, use a slightly dampened microfiber cloth or isopropyl alcohol wipe and then thoroughly dry with a clean, dry microfiber cloth.
- Check window on ASD white reference puck (#1) to ensure it is clean.
- Prepare spectrometer by warming Muglight for 3 h and spectrometer for 20 min after power is on. Muglight and spectrometer can be left on continuously during times of constant or intermittent usage.
- Run Wavelength Analyzer program daily before scanning samples.

8.2 Running reference and calibration puck scans

- For pucks that have ASD white reference on one side and ASD wave cal on the other, place the #1 side face down onto the Muglight first.
- ASD white reference, ASD wave cal puck, white reference, or soil samples should be scanned immediately upon loading onto Muglight. The exposure time of material to the intense light (heat) source affects the IR signature.

8.3 Perform daily QC sample check

- QC check sequence is only necessary once per QC project. It is conducted at the time that the QC project is initially set-up and the scans are made. All future accesses to QC project will have spectra settings in place.
- Check the window on Muglight white reference and the lens on the Muglight to ensure they are clean. Note: This white reference is not the same as the ASD white reference puck.
- Clean sample holder while working over a waste container or dust collector. Turn the sample holder upside down and gently tap with a wooden dowel or knife handle until the compacted soil falls out. Use compressed air from an oil-less air compressor or canned air to blow out remaining residue from inside of sample holder. Set output regulator on compressor to 25 psi.

8.4 Sample Analysis

8.4.1 Check the inner window of the Muglight sample holder to ensure it is clean. Heap air-dry, <2-mm sample into sample holder to slightly overflowing capacity.

8.4.2 Level the sample to the top of sample holder by striking off excess with a straight edge.

8.4.3 Pack the sample. Support the underside of the sample holder window (not the metal portion of the sample holder itself) with a

rubber stopper to prevent the window from being pushed out or broken. Properly align the piston so it does not catch as it presses into the well of the sample holder. Brush away any excess from top and sides of sample holder while the sample is being packed, preventing the soil from spilling onto the Muglight lens.

8.4.4 Pack sample with approximately 46 psi pressure using a press/penetrometer and holding for approximately 10 s. During compaction process, some soil particles may cling to the piston surface. Wipe face of piston before packing the next sample.

8.4.5 After the sample is packed, wipe the bottom of the sample holder free of extraneous soil. Place the sample holder on a clean towel.

8.4.6 Place loaded sample holder onto the Muglight immediately prior to performing the scan.

8.4.7 Scan air-dry samples using spectrometer software instructions, parameters, and methods.

8.4.8 Clean sample holder after scanning.

9. Calculations

No calculations are used. Spectral scans are saved as files for spectral interpretation, model building, and future corrections.

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

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Instrumental Analyses (7A)

Mid-Infrared Diffuse Reflectance Fourier Transform Spectroscopy (MIR–DRIFTS) (7A7)

Air-Dry, <2 mm (7A7a1)

1. Introduction to Mid-Infrared (MIR) Diffuse Reflectance Fourier Transform Spectroscopy (DRIFTS)

The MIR spectrum of a soil varies depending on the soil's composition and particularly on specific vibrational signatures for organic matter and mineral components, such as quartz, kaolinite, smectite, carbonates, gypsum, iron oxides, and aluminum oxides (CSIRO, 2013). Each of these soil constituents absorbs differing amounts of light in specific regions of the MIR spectrum. Quantitative information on mineralogy (Madejova, 2003) and organic matter composition (Margenot et al., 2015) can be extracted directly from the MIR spectra. MIR-DRIFTS, however, is more often used to estimate a wide range of chemical and physical properties closely associated with the soil bulk properties (e.g., total clay, organic carbon, moisture content at 1,500-kPa, CEC, and calcium carbonate equivalent).

2. Scope and Field of Application

MIR does not directly measure soil properties (CSIRO, 2013); instead, calibrations for estimating soil properties from MIR spectra are derived by modeling MIR spectra and conventionally measured property values. Using these calibrations, soil properties of unknown samples can be estimated from the MIR spectra of the samples. The advantages of MIR spectrometry are speed, safety, low cost, and the objectivity of the models. The models rely exclusively on MIR spectra of legacy samples and previously measured data from the samples. Further, multiple soil properties can be estimated from a single MIR spectrum (McCarty et al., 2002). The KSSL spectral library and appropriate statistical models have shown that reasonably accurate and precise estimates of a range of soil properties can be obtained (Comstock et al., 2019; Dangal et al., 2019; Ng et al., 2019; Nocita et al., 2014; Sanderman et al., 2020; Seybold et al., 2019; Shepherd, 2007, 2015; Terhoeven-Urselmans et al., 2010; Viscarra Rossel et al., 2008; Wijewardane et al., 2018).

3. Principle

A sample of <2-mm, air-dry soil is ground to 80 mesh (<177 µm). Ground samples are placed in the wells of a microplate, which is inserted into a microplate reader for MIR data collection. The resulting MIR spectra are stored for future analysis.

3.1 Interferences

The optical bench is not purged with an IR inactive gas, such as nitrogen. Thus, when background and sample scans are collected, changes to the amount of water and carbon dioxide gas in the air can apparently result in spurious spectral features in the final absorbance spectrum.

Use of canned air, which typically contains a fluorocarbon, in the general area of the spectrometer can result in strong absorption features unrelated to soil spectra. These features are due to gas diffusion into an unpurged optical bench.

Because of the small diameter (6 mm) of the microplate wells, the homogeneity and particle-size of the sample are important to examine when the spectral results are interpreted (Baldock and Hawke, 2010). Adequate sample grinding is indicated.

The main purpose of collecting MIR spectra is to estimate soil properties from models built on spectral and measured data. Although the topic of modeling is not covered in this method, the following comments are relevant.

- Calibration errors depend on not only the quality of the MIR spectra but also on the accuracy of the measured data to which the spectra are modeled. Even for a property that lends itself to being modeled (e.g., carbonates), poor quality measured data results in high model errors.
- Model performance on unknown samples depends on how well the soil variability was captured in the calibration. For optimal model performance and because of the great variability of soils, it is therefore important to capture the variability of the specific soils in the target area to which the calibration is intended to apply.
- MIR has difficulty predicting properties in the soil solution rather than in the soil matrix (e.g., extractable P, S, and N) because of the generally low concentration in the soil environment (Merry and Janik, 2013).

4. Apparatus

4.1 Spectrometer, Bruker Vertex-70 with HTS-XT reader extension for high-throughput scanning, computer, and software. Note: Due to the potential issue of calibration transfer among instruments, the manufacturer and model of an instrument are cited. This does not imply USDA endorsement, nor should one be inferred.

4.2 Microplates, 96-well sample plate, aluminum. The well bottoms are roughened surfaces of anodized aluminum for maximal diffuse reflectance (fig. 7A7–1).

4.3 Glass plate (fig. 7A7–1), used to cover used wells after filling them to minimize cross-contamination among samples during microplate preparation

4.4 Weight, used to hold glass in place during plate preparation (fig. 7A7–1)

4.5 Steel press rod (6.3 mm diameter) with slight bevel on end, used for compacting samples into microplate wells (fig. 7A7–2)

4.6 Coffee stir sticks, wooden, used for serving sample to microplates

4.7 Laboratory tissues

4.8 Cotton swabs

4.9 Vacuum cleaner, used to remove excess sample from around well (fig. 7A7–3)

4.10 Funnel for transferring liquid nitrogen into the detector

4.11 Dewar for storing liquid nitrogen

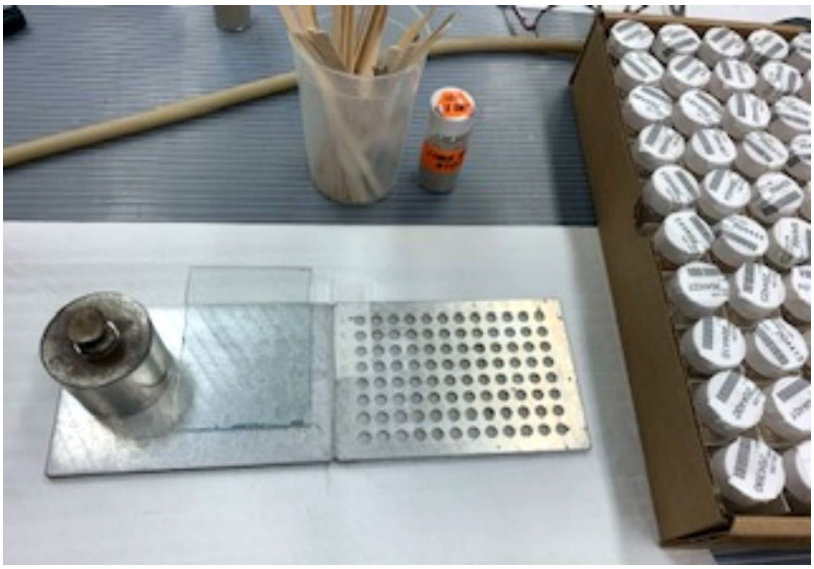

Figure 7A7–1.—A 96-well sample plate, protective glass, and weight to hold glass plate still.

Figure 7A7–2.—Steel press rod used for preparing microplate.

Figure 7A7–3.—Vacuum cleaner with small-end adaptor for removing excess sample from around filled wells on the microplate.

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type III grade reagent water

5.2 Dish soap

5.3 Liquid N_2 (77 °K)

5.4 Molecular sieves as desiccant

6. Health and Safety

Personal Protective Equipment (PPE).—During microplate preparation, wear disposable nitrile gloves, safety glasses, and lab coat or apron.

During spectrometer cooling, manage liquid nitrogen with care. Wear long-sleeved gloves designed to protect against cryogenic liquids. Also wear safety glasses and a lab coat or apron. Skin and eye contact with liquid nitrogen can cause severe cryogenic burns.

Use liquid nitrogen in well-ventilated areas. A high concentration of nitrogen gas in an enclosed area can cause asphyxiation.

Follow the manufacturer's safety precautions.

7. Sample Preparation

The field sample is thoroughly air-dried at 30 to 35 °C for 3 to 7 days and then passed through a 2-mm sieve. A 15 to 20 gram subsample of <2-mm material is ground to 80 mesh (<177 um) using planetary ball mill per method 1B1b.

8. Procedure

8.1 Microplate preparation

8.1.1 Position a clean microplate with well A1 at the upper left corner. Place another 96-well plate upside down to the left of and adjoining the plate being filled.

8.1.2 For each sample, four subsamples are scanned. Although a 96-well microplate could be used to collect spectra on 24 samples (four reps per sample), the reflectance from the anodized roughened aluminum surface of the bottom of well A1 is collected for a background, and wells B1, C1, and D1 are not used. See figure 7A7–1. Place a strip of clear tape over wells A1 through D1 to prevent contamination of cell A1.

8.1.3 Using a new wooden spatula (coffee stir stick), fill wells E1 through H1 with process control (reference) sample. The process-control sample should be well homogenized and available in sufficient quantity to scan with every batch of unknown samples. Add enough of the sample to fill the wells. Small spillage on the plate surface near the wells is expected. See figure 7A7–4.

8.1.4 Position the flat end of the press rod perpendicularly over each well, and very lightly press subsample into place. The surface of the sample should be flat. Sample height in the wells should be at least 1 mm and not exceed the height of the well. See figure 7A7–5.

8.1.5 Vacuum the excess soil from the top of the well plate using the micro-vacuum hose. The differential general density of the pressed soil

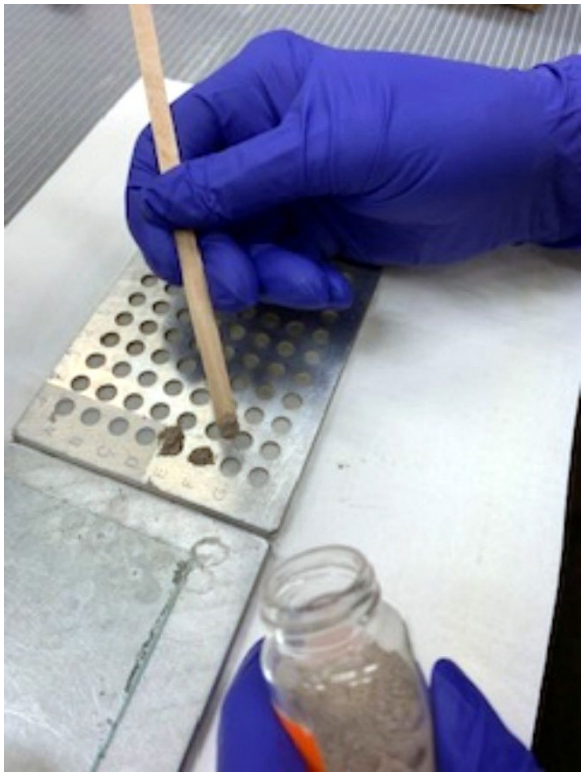

Figure 7A7–4.—Filling wells with sample.

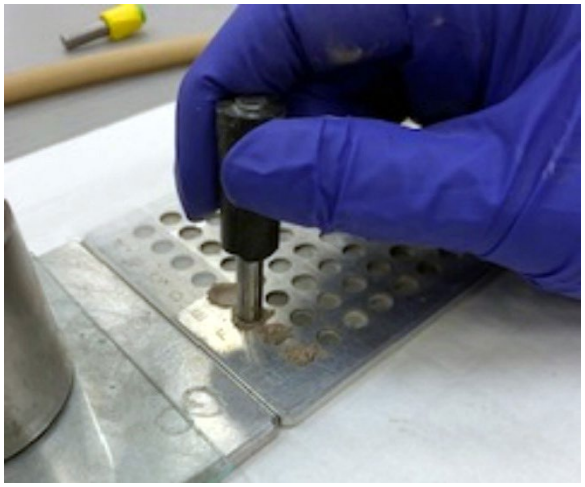

Figure 7A7–5.—Pressing samples into wells.

in the well and the loose soil outside of the well make is possible to collect the loose soil while leaving the pressed soil in place. If necessary, wipe the surface of the plate around the wells with a new cotton swab. Discard the wooden spatula. See figures 7A7–6 and 7A7–7.

Figure 7A7–6.—Vacuuming excess sample from around wells.

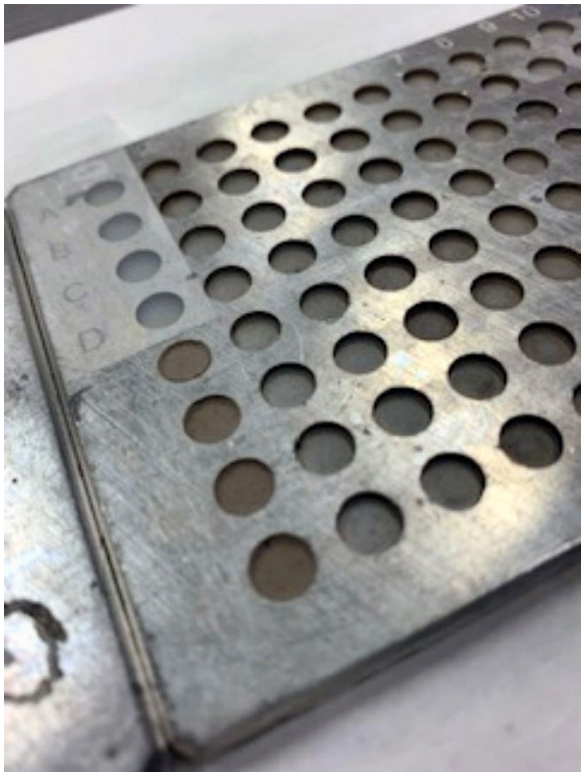

Figure 7A7–7.—Wells after excess sample is gone from around wells.

8.1.6 Position a glass plate on the microplate to cover the left column of the plate after it is filled. This protects the filled wells from cross-contamination by other samples. Place a weight on the glass to hold it in place. The glass should not touch the sample. See figure 7A7–8.

8.1.7 Thoroughly clean the flat end of the press rod with a new laboratory tissue.

8.1.8 Using a new wooden spatula, fill wells A2 through D2 with loose sample for the first unknown sample. Small spillage on the plate surface near the wells is expected. Repeat steps 8.1.4, 8.1.5, and 8.1.7.

8.1.9 Using a new wooden spatula, fill wells E2 through H2 with the next unknown sample. Then repeat steps 8.1.4, 8.1.5, and 8.1.7 again to load up the next unknown sample and complete the column. See figure 7A7–9.

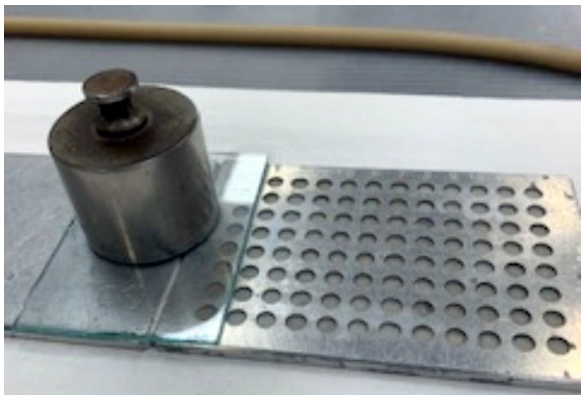

Figure 7A7–8.—Using a glass plate to protect filled wells against cross-contamination.

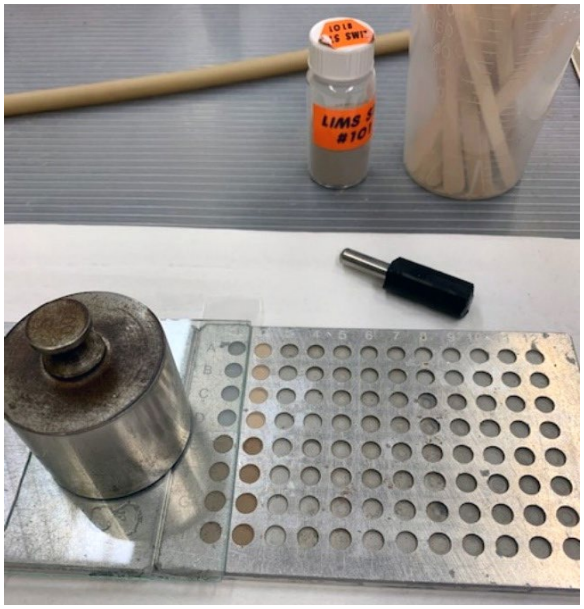

Figure 7A7–9.—Second column filled with sample.

8.1.10 Adjust the glass plate so it covers the leftmost two columns on the plate. See figure 7A7–10.

8.1.11 Fill the rest of the plate in a similar manner. Loading each column of wells with two samples in quadruplicate. Move the glass plate to cover all completed columns and thereby prevent cross-contamination.

Figure 7A7–10.—First two columns protected against cross-contamination with glass plate.

8.2 Instrument data collection

8.2.1 Do an instrument warm-up if instrument had been left off.

8.2.2 After cooling HTS-XT detector with liquid nitrogen for 30 minutes, conduct instrument performance qualification per manufacturer's instructions.

8.2.3 Data collection parameters that were set up in consultation with Bruker for Vertex-70 with HTS-XT are as follows:

8.2.3.1 Resolution: 4 cm^{-1}

8.2.3.2 Sample Scan: 32 scans

8.2.3.3 Background scan: 32 scans

8.2.3.4 Data range: 7,500–600 cm^{-1} (This is the current data collection range. The range used for modeling MIR spectra to measured properties is 4,000 to 600 cm^{-1})

8.2.3.4.1 Data blocks to save:

8.2.3.4.1.1 Absorbance

8.2.3.4.1.2 Single channel

8.2.3.4.1.3 Sample interferogram

8.2.3.4.1.4 Background

8.2.3.4.1.5 Background interferogram

8.2.3.5 Atmospheric compensation: OFF

8.2.3.6 Optic:

8.2.3.6.1 External synchronization: OFF

8.2.3.6.2 Source setting: MIR

8.2.3.6.3 Beamsplitter: KBr

8.2.3.6.4 Optical filter setting: OPEN

8.2.3.6.5 Aperture setting: 6 mm

8.2.3.6.6 Measurement channel: Right exit

8.2.3.6.7 Background measurement channel: Right exit

8.2.3.6.8 Detector setting: HTX Diffuse (microplate reader), which uses a MCT detector

8.2.3.6.9 Scanner velocity: 20 Hz

8.2.3.6.10 Sample signal gain: Automatic

8.2.3.6.11 Background signal gain: Automatic

8.2.3.6.12 Delay after device change: OFF

8.2.3.6.13 Delay before measurement: 5 seconds

8.2.3.6.14 Optical bench ready: OFF

8.2.3.7 Acquisition

8.2.3.7.1 Wanted high frequency limit: 8,000

8.2.3.7.2 Wanted low frequency limit: 0

8.2.3.7.3 High pass filter: OPEN

8.2.3.7.4 Low pass filter: 10 kHz

8.2.3.7.5 Acquisition mode: Double sided forward backward

8.2.3.7.6 Correlation mode: OFF

8.2.4 Proceed with batch set-up and spectral data collection as per software instructions. Consider the following.

8.2.4.1 Before loading the microplate into the HTS-XT accessory, remove protective clear tape covering positions A1 through D1 from the microplate.

8.2.4.2 As the optical bench is not purged, set the data collection program to take a background scan on position A1

right before every sample scan to help compensate for fluctuating concentrations of atmospheric gases.

8.2.5 After spectral data collection is complete, clean the aluminum plate with soapy water using a soft brush. Thoroughly rinse the plate with deionized water and let it dry on a clean laboratory wipe overnight. Once dry, place a piece of clear tape over wells A1 through D1 to protect the background position (A1) against dust. Never use compressed air to clean plates.

9. Calculations

Spectral interferograms are processed by Fourier transform to convert them to absorbance spectra which are then saved as a new Bruker opus file for each sample.

10. Quality Assurance/Quality Control

10.1 Send the process-control sample spectra through a model (or suite of models). Using a control chart with historical model estimates, check that estimates fall within the control limits of the chart. For example, the KSSL currently uses a carbonate-bearing process-control sample and sends the control sample spectra through a model that predicts carbonate content.

10.2 Do an initial visual inspection of spectra in groups of four replicates to ensure there are no obvious irregularities; e.g., signs of detector warming.

10.3 For each sample, compare the spectrum of the first subsample in a group of four with the second, third, and fourth spectra using OPUS “quick compare.” The quick comparison between spectra is performed by calculating the correlation coefficient. Reject and re-analyze samples if >99.6 % spectral similarity is not achieved, as this suggests cross-contamination from neighboring samples.

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Optical Analyses (7B)
Grain Studies (7B1)
Analysis and Interpretation (7B1a)

1. Introduction to Petrographic Grain Analysis and Interpretation

A petrographic microscope enables the researcher to distinguish specific minerals from other minerals that possess similar properties. This technique can be applied to individual minerals or used for aggregate identification.

The discussion of identification and significance of minerals, microcrystalline aggregates, and amorphous substances in optical studies of grain mounts was from material after John G. Cady (1965), with permission, and modified by Warren C. Lynn, research soil scientist, NRCS, Lincoln, Nebraska.

2. Scope and Field of Application

Optical analysis using plane and cross-polarized light reveals mineral properties that suggest mineral identity, parent material, weathering, and minerals formed in situ, such as carbonates and salts. In the finer soil separates, grain identification may be impossible because the grains may be too small or not in an orientation to permit measurement of some properties, e.g., optic angle (2V) or optic sign. The estimation of properties can be practiced by crushing, sieving, and mounting a set of known minerals and comparing these known standards to unknown samples.

3. Principle

A petrographic microscope is used to identify such characteristics as refractive index, relief, Becke-lines, birefringence, color, cleavage, extinction angles, and optical signs. These characteristics are used to distinguish mineral characteristics and are discussed in the procedure section of this method prior to the common minerals and their associated properties.

3.1 Interferences

Small grain size, clay films, or epoxy preparation could interfere with observed mineral properties.

4. Apparatus

Petrographic microscope

5. Chemicals

No chemicals are required. Refractive index oils and Alizarin red stain can be used for additional analysis under the guidance of a mineralogist.

6. Health and Safety

Personal Protective Equipment (PPE).—This method addresses observed characteristics of minerals. Wear protective gloves if using refractive index oils.

7. Sample Preparation

A natural fabric thin section or representative sample composed of individual grains can be used for mineral identification.

8. Procedure

8.1 Optical properties of minerals observed through polarizing microscope

8.1.1 Refractive index (R.I.) is the ratio of the speed of light in the medium (mineral) to the speed of light in a vacuum. It can be estimated by relief or can be accurately determined by using calibrated immersion liquids. When relief is used to estimate refractive index, the grain shape, color, and surface texture are considered. Estimation is aided by comparing an unknown to known minerals.

- Example: Thin platy grains may be estimated low, whereas colored grains and grains with rough, hackly surface texture may be estimated high.

8.1.2 Relief is an expression of the difference in refractive index between the grain and the mounting medium. The greater the difference, the greater the relief. The analogy is to topographic relief. When viewed through the microscope, grains with high relief are distinct, whereas grains with low relief tend to fade into the background.

- Example: The KSSL selects a mounting medium with an index of refraction close to quartz, which has low relief. Most other minerals are identified by comparison.

8.1.3 Becke line is a bright halo of light that forms near the contact of the grain and the mounting medium because of the difference in refractive index between the two. As the plane of focus is moved upward through the grain, the Becke line appears to move into the component with the higher refractive index.

- Example: When mounted in Petropoxy 154, the Becke line moves away from potassium feldspar (R.I. <1.54) but moves into mica (R.I. >1.54).

8.1.4 Birefringence is the difference between the highest and lowest refractive index of the mineral. Accounting for grain thickness and orientation, the birefringence is estimated by interference color. Interference color is observed when an anisotropic mineral is viewed between cross-polarized light. Several grains of the same

species must be observed because the grains may not all lie in positions that show the extremes of refractive index.

- Examples: Mica has a high birefringence. Mica shows a high interference color if viewed on edge in thin section but shows a low interference color when the platy mineral grain is perpendicular to the microscope axis. The low interference colors are due to the refractive indices of the two crystallographic directions in the plane are similar.
- Birefringence is extremely high (0.17 to 0.24) in carbonate minerals, intermediate (0.015 to 0.08) in most ferromagnesian minerals, low (0.008) in orthoclase feldspar, and very low (0.005) in apatite.

8.1.5 Color is used to discern among the heavy minerals. Pleochroism is the change in color or light absorption with stage rotation when the polarizer is inserted. Pleochroism is a good diagnostic characteristic for many colored minerals.

- Examples: Tourmaline, green beryl, and staurolite are examples of pleochroic minerals.

8.1.6 Shape, cleavage, and crystal form are unique characteristics for many minerals. Cleavage may be reflected in the external form of the grain or may appear as cracks within the grain. The cracks show as regularly repeated, straight parallel lines or as sets of lines that intersect at definite repeated angles. The crystal shape may be different from the shape of the cleavage fragment.

- Examples: Plagioclase feldspars, kyanite, and the pyroxenes have strong cleavage. Zircon and rutile usually appear in crystal forms.

8.1.7 Extinction angle(s) are observed under cross-polarized light and are important criteria for some groups of minerals. For extinction angles to be measured, the grain must show its cleavage or crystal form. These angles may be different along different crystallographic axes. Some minerals have sharp, quick total extinction, whereas other minerals have more gradual extinction. In some minerals that have high light dispersion, the interference color dims and changes at the extinction position.

- Examples: Biotite has a sparkled, multicolored, gradual extinction. Quartz fades to extinction and may reflect strain on the crystal.

8.1.8 Optic sign, optic angle, and sign of elongation are indicative, useful pieces of information but are often difficult to discern unless grains are large or in a favorable orientation. Determination of optic sign requires that the grains show dim, low-order interference colors or

show no extinction. Grains that have bright colors and sharp, quick extinction rarely provide usable interference figures.

- Examples: Quartz is unixaxial (+), calcite is uniaxial (-), olivine is biaxial (+), and orthoclase is biaxial (-).

8.2 Common Mineral Species

The following are predominant diagnostic characteristics of the most commonly occurring minerals and single-particle grains in the sand and silt fractions of soils. The refractive indices that are provided are the intermediate values.

8.2.1 Quartz (SiO_2)

- Refractive index of quartz (1.54) approximates that of the epoxy mounting medium.
- Becke line may be split into yellow and blue components.
- Interference colors are low order but are bright and warm.
- There is sharp extinction with a small angle of rotation, i.e., “blink extinction.”
- Crystal forms are sometimes observed and usually indicate derivation from limestone or other low-temperature secondary origin.
- Grain has irregular shapes.

8.2.2 Potassium feldspars ($KAlSi_3O_8$)

8.2.2.1 *Orthoclase*

- Refractive index (1.52) and birefringence are lower than that of quartz.
- May show cleavage.

8.2.2.2 *Microcline, ordered polymorph*

- Refractive index is 1.53.
- Becke line moves away from the grain with upward focus.
- A twinning intergrowth produces a plaid or grid effect between cross-polarized light. The effect is characteristic of microcline.

8.2.2.3 *Sanidine*

- Refractive index (1.52) and birefringence are the same as other potassium feldspars.
- Grains are usually clear, and twinning is not evident.
- The 2V angle is low (12°) and characteristic.
- The 2V angle is the acute angle between two optic axes, or more simply, the optical axial angle.

8.2.3 Plagioclase feldspars [$(Ca,Na)(Al,Si)AlSi_2O_8$]

- Refractive indices have a range based on the increased percent of calcium present. The refractive index of sodium end-member **albite** is 1.53. The refractive index of calcium end-member **anorthite** is 1.58. Some oligoclase feldspars have the same refractive index as quartz.
- Commonly shows a type of twinning (defined as albite twinning) that appears as multiple alternating dark and light bands in cross-polarized light.
- Cleavage is good in two directions parallel to (001) and (010), often producing lath-like or prismatic shapes.

8.2.4 Micas [$(K,Na)(Al, Li, Mg)_{2-3}(Al,Si)_{3-4}O_{10}(OH,F)$]

- Micas occur as platy grains that are commonly very thin.
- The plate view shows very low birefringence, whereas the edge view shows a very high birefringence.
- Plates are commonly equidimensional and may appear as hexagons or may have some 60° angles.

8.2.4.1 *Biotite* [$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$]

- Color is green to dark brown.
- Green grains may be confused with chlorite.
- Paler colors, a lowering of refractive index, and a distortion of the extinction and interference figure indicate weathering to hydrobiotite, kaolinite, or vermiculite.

8.2.4.2 *Muscovite* [$KAl_2(AlSi_3O_{10})(OH)_2$]

- Refractive index is moderate (1.59) in the plate view.
- Muscovite is colorless.
- Interference figure shows a characteristic 2V angle of 30° to 40°, which can be used as a standard for comparing 2V angles of other minerals.

8.2.5 Rutile (TiO_2)

- Refractive index is extremely high (2.6 to 2.9). Birefringence is also extremely high.
- Grains have prismatic shape.
- The interference colors typically are obscured by the brown, reddish-brown, or yellow colors of the mineral.
- Anatase and brookite are pseudomorphs. They typically occur as tabular or equidimensional grains that are difficult to distinguish in small grains.

8.2.6 Apatite [$Ca_5(PO_4)_3(F/Cl/OH)$]

- Refractive index is slightly less than 1.63. Birefringence is very low.
- Apatite is common in young soil materials.
- Crystal shapes are common, may appear as prisms, and are often bullet shaped. Rounding by solution produces ovoid forms.
- Apatite is easily dissolved by acids and may be lost in pretreatments.

8.2.7 Sillimanite and andalusite (Al_2SiO_5)

- Refractive index is ≈1.63.
- Minerals are fibrous to prismatic and have parallel extinction.
- Polymorph nesosilicates, signs of elongation are different. Andalusite is biaxial (-). Sillimanite is biaxial (+).
- Sillimanite is colorless, and andalusite commonly is pink.

8.2.8 Carbonates: Calcite ($CaCO_3$), dolomite [$Ca(Mg,Fe)CO_3$], and siderite ($FeCO_3$)

- Refractive index of calcite is 1.64–1.66.
- Refractive index of dolomite is 1.68.
- Refractive index of siderite is 1.87.
- Carbonates have rhombohedral cleavage forms.
- The extreme birefringence is always the identification clue. It is shown by bright colors between cross-polarized light and by a marked change in relief when the stage is rotated with one polarizer in place.
- The microcrystalline aggregates produce a twinkling effect when rotated between cross-polarized light.
- Calcite and dolomite may be differentiated by using a 1.5% solution of HCl plus alizarin red to stain thin sections. If applied for 1 minute and wiped off, calcite etches or stains red-pink but dolomite does not stain. X-ray diffraction may be used as another determination method.
- In soils, these minerals have other forms, e.g., scales and chips; cements in aggregates; and microcrystalline coatings or aggregates. These minerals also appear as fine-grained masses, often mixed with clays and other minerals

8.2.9 Gypsum ($CaSO_4 \cdot 2H_2O$)

- Refractive index is 1.52.
- Gypsum occurs in platy or prismatic, flat grains that have a brushed or “dirty” surface.

8.2.10 Opaque minerals: Magnetite (Fe_3O_4) and ilmenite (Fe_2+TiO_3)

- These minerals are difficult to identify, especially when grains are weathered.
- The best procedures are observations of color and luster by reflected light and aided by crystal form, if visible.
- Magnetic separations help to confirm the presence of magnetite and ilmenite.
- Many grains that appear opaque by plain light can appear translucent if viewed between strong cross-polarized light. Most grains that behave in this way are altered grains or aggregates and are not opaque minerals.

8.2.11 Amphiboles [$NaCa_2(Mg,Fe,Al)_5(Si,Al)_8O_{22}(OH)_2$]

- Refractive index of the group ranges from 1.61 to 1.73.
- Amphiboles are fibrous to platy or prismatic minerals.
- Typically, amphiboles have slightly inclined extinction. Occasionally, they have parallel extinction.
- Color and refractive index increase as the Fe content increases. Amphiboles have good cleavage at angles of ≈56° and 124°.

8.2.11.1 *Hornblende* is the most common member of the amphiboles.

- It is slightly pleochroic.
- It usually has a distinctive color that is close to olive-green.
- It has inclined extinction.
- It is often used as an indicator of weathering.

8.2.12 Pyroxenes: Enstatite ($MgSiO_3$), aegirine ($NaFeSi_2O_6$), and augite [$Ca(Fe,Mg)Si_2O_6$]

- Refractive indices (1.65 to 1.79) are higher than those for amphiboles.
- Pyroxenes are prismatic and have parallel extinction.
- Pyroxenes have unique and striking green-pink pleochroism.
- Augite and diopside have good cleavage at angles close to 90° and large extinction angles.
- Pyroxenes are typically shades of green with interference colors of reds and blues.

8.2.13 Olivine [$(Mg,Fe)SiO_4$]

- Refractive indices of the olivine group are approximately 1.63–1.73.

- Olivine is colorless to very pale green and usually irregular in shape (weak cleavage).
- Interference colors are vivid and warm.
- Olivine is easily weathered and may have cracks or seams filled with serpentine or goethite.
- Olivine is seldom identified in weathered soils but has been observed in volcanic soils from Hawaii.

8.2.14 Staurolite [$Fe_2Al_9O_6(SiO_4)_4(O,OH)_2$]

- The refractive index is ≈1.74.
- Pleochroic variations are yellow to pale brown and sometimes contains holes, i.e., the “Swiss cheese” effect.
- Grains may have a foggy or milky appearance, which may be caused by colloidal inclusions.

8.2.15 Epidote [$(Ca_2)(Al_2,Fe^{3+})(Si_3O_{12})(OH)$]

- High refractive index (1.72 to 1.76) is indicative. Epidote has strong birefringence.
- Pleochroism includes a distinct pistachio-green color.
- Typical interference colors are reds and yellows.
- Grains show an optic axis interference figure with a 2V angle that is nearly 90°.
- Epidote is a common heavy mineral, but the forms that occur in soils may be difficult to identify positively.
- Epidote is modified by weathering or metamorphism to colorless forms that have lower birefringence and refractive index.

8.2.16 Zoisite and clinozoisite pseudomorphs [$Ca_2Al_3Si_3O_{12}(OH)$]

- The refractive index is high (1.70 to 1.73), and grains are irregularly shaped or roughly platy.
- The appearance is commonly colorless, pale-green, or bluish-green.
- Anomalous interference colors (bright pale blue) and no complete extinction are shown. Zoisite has a distinctive deep blue interference color.
- Identification usually depends on determination of properties for many grains. Zoisite and clinozoisite pseudomorphs can be confused with several other minerals, e.g., kyanite and diopside.

8.2.17 Kyanite (Al_2SiO_5)

- Refractive index is 1.71.
- Extinction angles are large (30° extinction).

- Identification is easy because of large cleavage angles and platy, angular cleavage flakes.
- Kyanite is a common mineral but is seldom abundant.
- Colors include pale blue, grey, green, and colorless.

8.2.18 Garnet [$(Fe,Mg,Mn)Al_2Si_3O_{12}$]

- The refractive index is high (≥1.77).
- Garnet occurs in irregularly shaped, equidimensional grains that are isotropic.
- Garnet the size of fine sand and silt is commonly colorless. Pale pink or green colors are diagnostic in the larger grains.

8.2.19 Tourmaline [$Na(Mg,Fe)_3Al_6(BO_3)_3(Si_6O_{18})(OH)_4$]

- The refractive index is 1.62 to 1.66.
- The shape is prismatic.
- Strong pleochroism and parallel extinction are characteristic.
- Some tourmaline is almost opaque when at right angles to the vibration plate of the polarizer.

8.2.20 Zircon ($ZrSiO_4$)

- The refractive index is very high (>1.9).
- Zircon occurs as tetragonal prisms that have pyramidal ends.
- Zircon crystals and grains almost always appear clear and fresh.
- Extinction is parallel. Interference colors are bright and strong.
- Broken and rounded crystals are common.

8.2.21 Sphene (Titanite) ($CaTiSiO_5$)

- The refractive index is 1.84 to 2.00.
- Sphene has rounded or subrounded grains. In some forms, it resembles zircon, but the crystal forms have oblique extinction and the grains are commonly cloudy or rough-surfaced.
- Under crossed polarizers, color changes through ultra-blue instead of extinction because of high dispersion. Sphene is the only pale-colored or colorless high-index mineral that provides this effect.
- Sphene is amber colored in reflected light.

8.3 Examples of microcrystalline aggregates and amorphous substances

For purposes of soil genesis studies, aggregates in sand or silt fractions can provide important diagnostic information or indicators of provenance. Useful differentiating criteria for some of the commonly occurring aggregate types are discussed below.

8.3.1 Rock fragments include chips of shale, schist, and fine-gained igneous rocks, e.g., rhyolite.

- Identification depends on the recognition of structure, individual grains or components, and provenance or sources.
- Rock fragments are common in mountainous regions and are often hydrothermally altered in the western United States.

8.3.2 Clay aggregates may be present in a wide variety of forms.

- Silt and sand grains that are bound together into larger masses by a nearly isotropic brownish material usually indicate incomplete dispersion.
- Clay skins may resist dispersion and appear as fragments in grain mounts. Clay skins appear brown or red and translucent with wavy extinction bands. Check petrographic mineral properties to distinguish these fragments from weathered biotite.
- Clay aggregates may be mineral pseudomorphs. Kaolin pseudomorphs of feldspar are common. Montmorillonite clay aggregates can be weathered products of rock minerals. In this form, montmorillonite shows high birefringence and an extinction that is mottled or patchy on a small scale.
- Coarse kaolinite flakes, books, and vermicular aggregates resist dispersion and may be abundant in sand and silt. These particles may resemble muscovite but are cloudy. They show no definite extinction and have very low birefringence.
- Many cases of anomalously high cation exchange capacity (CEC) in sand and silt fractions are due to clay aggregates remaining in the sand and silt fractions.

8.3.3 Volcanic glass

- Volcanic glass is isotropic and has a low refractive index, ranging from 1.48 in the colorless siliceous glasses to as high as 1.56 in the green or brown basalt glass.
- Shapes vary but are regularly elongated shards, vesicular, and/or conchoidal. This glassy material may adhere to or envelop other minerals. Particles may contain small crystals of feldspar or forms of cristobalite (snowflakes).
- The colorless siliceous types (acidic, pumiceous) are more common in soils. Acidic glasses are more commonly part of “ash falls,” because the magma usually is gaseous. Basic glasses weather more quickly and are more commonly associated with volcanic flow rocks.

8.3.3.1 *Allophane*

- Allophane is in many soils that are derived from volcanic ash.
- Allophane can seldom be identified directly. Sand and silt appear cemented into aggregates by isotropic material with low refractive index, especially if volcanic ash shards are also present.

8.3.4 Opal

- This isotropic, hydrated mineral ranges from amorphous to opal-cristobalite. It occurs as a cementing material and in separate grains, some of which are of organic origin, i.e., plant opal, sponge spicules, and diatoms.
- The refractive index is very low (<1.45), which is lower than the value for volcanic ash.
- Identification may depend in part on form and occurrence. X-ray diffraction can aid in identifying opal.

8.3.5 Iron oxides

- Iron oxides may occur as separate grains or as coatings, cementing agents, and mixtures with other minerals.
- Iron oxides impart brown and red colors and raise the refractive index in the mixtures. Goethite is yellow to brown.
- Hematite has higher refractive index than goethite and is granular rather than prismatic. Large grains of hematite are nearly opaque. Red iron oxides have a higher refractive index and birefringence, possess a more organized crystal structure, and have prismatic or fibrous habit.
- Aggregates have parallel extinction. In oriented aggregates, the interference colors often have a greenish cast.

8.3.6 Gibbsite

- Refractive index is 1.56–1.58. The bright interference colors and aggregate extinction are diagnostic.
- Gibbsite commonly occurs as separate, pure, crystal aggregates, either alone or inside altered mineral grains.
- Colorless grains may appear to be well-crystallized single crystals, but a higher magnification in cross-polarized light shows patchy, banded extinction, indicating intergrown aggregates.

8.3.7 Chalcedony

- Chalcedony is a microcrystalline form of quartz formerly considered a distinct species. Chert is a massive form of chalcedony.

- The refractive index is slightly lower than that of quartz (1.54), and the birefringence is lower than that of gibbsite.
- Chalcedony exhibits aggregate structure with patchy extinction in cross-polarized light.
- Chalcedony occurs in nodules of limestone deposits, areas of infilling through ground water deposition, and as a replacement in calcareous fossils.

8.3.8 Glauconite

- Glauconite occurs in aggregates of small micaceous grains that have high birefringence.
- When fresh, glauconite is dark green and almost opaque. It weathers to brown and more translucent forms.
- Glauconite is difficult to identify on optical evidence alone. Knowledge of provenance or history is helpful in identification.

8.3.9 Titanium oxide

- Titanium oxide has an extremely high refractive index (2.6 to 2.9) and high birefringence similar to rutile.
- Aggregates have been tentatively identified in the heavy mineral separates of many soils.
- Yellow to gray colors are similar to those of anatase.
- The TiO_2 aggregates are granular and have a rough surface. This growth habit with the little spurs and projections suggests that TiO_2 aggregates may be secondary.

9. Calculations

No calculations are used. Report minerals observed, such qualities as grain rounding or weathering, and any structure or sorting in the thin section.

10. Quality Assurance/Quality Control

10.1 Assess plausibility of test sample data in context of expected soil profile trends.

10.2 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.3 Assign overall project data to soil data quality specialist.

11. References

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Optical Analyses (7B)
Grain Studies (7B1)
Separation by Heavy Liquids (7B1a1)

1. Introduction to Grain Separation with Heavy Liquids

The sand and silt fractions of most soils are dominated by quartz and feldspar minerals with a specific gravity of 2.57 to 2.76. The large numbers of "heavy" mineral grains (i.e., having specific gravity ≈2.9) that have a wide range of weatherability and diagnostic significance may be only a small percentage of the grains (Cady, 1965). These "heavy" minerals, however, provide information indicative of provenance, weathering intensity, and parent material uniformity (Cady et al., 1986).

2. Scope and Field of Application

This method is reserved for special studies involving the isolation of heavy minerals. A common approach is to concentrate these grains by specific-gravity separations in a heavy liquid. This method uses sodium polytungstate, which is a non-toxic alternative to historical fluids, such as bromoform and tetrabromoethane. Additional techniques that isolate and remove magnetic grains should be conducted prior to heavy-liquid separation. Retain these magnetic grains to be weighed with the final heavy mineral fraction.

3. Principle

Using RODI water, create a sodium polytungstate solution that has a specific gravity of 2.5 g/cm^3. The solution's specific gravity can be determined using a known, calibrated mineral standard or a specific-gravity balance. Fluid densities of 2.5 g/cm^3 and greater will concentrate volcanic glass, plant opal, or sponge spicules. The specific gravity of the solution can be adjusted to as high as 3.1 g/cm^3 based on the amount of water present in the solution.

Heavy minerals can be separated by the gravity method, which requires a separation time of nine hours and filtering time, or by the centrifuge method which requires a centrifuge capable of 1,000 rpm and, ideally, liquid nitrogen.

Diluted solution is recycled by driving off excess water from the solution using a low temperature oven, hot plate, or fume hood. The solution must not become super saturated, which would cause sodium polytungstate to fall out of suspension.

3.1 Interferences

Organic matter may prevent wetting and cause grains to clump or raft together.

Light coatings on the heavy grains may cause the heavy grains to float, and iron-oxide coatings may increase specific gravity.

Micas are difficult to separate because of their shape and because weathering (especially in biotite) significantly decreases the specific gravity. These differences in density in biotite may be used to concentrate weathered biotite in its various stages of alteration.

4. Apparatus

4.1 Centrifuge tubes, 50-mL, disposable, graduated
4.2 Centrifuge capable of 1,000 rpm
4.3 Combination magnetic stirrer and hot plate
4.4 Laboratory clamp stand
4.5 Separatory funnel with lower stopcock
4.6 Graduated cylinders, 25-mL, 40-mL, or 60-mL, depending on sample size
4.7 Squirt bottle for RODI water
4.8 Squirt bottle for sodium polytungstate solution
4.9 Parafilm *M* laboratory tape, watch glass, or both
4.10 Paper filter, coffee filter or alpha cellulose filter, 24-cm
4.11 Glass, long-stemmed funnel for 24-cm filters
4.12 Specific gravity balance or known, calibrated mineral standard
4.13 Ultrasonic bath
4.14 Electronic balance, ±1.0-mg sensitivity

5. Chemicals

5.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water
5.2 Liquid nitrogen
5.3 Sodium polytungstate solution, 70% mass solution

Components: Sodium polytungstate ($3Na_2WO_4 \cdot 9WO_3 \cdot H_2O$) (CAS# 12141-67-2), RODI water

Note: This heavy liquid is a mass solution, not volume.

- To a 100-mL glass flask, add a magnetic stir bar, and place on a magnetic hot plate. Add the following in order:
  - 30 grams of RODI water
  - 70 grams of sodium polytungstate
- Set heat on lowest setting. Use stir bar until polytungstate is dissolved. The solution will have 2.5 g/cm^3 specific gravity.
- Determine the specific gravity of the solution by using a known, calibrated mineral, or a specific-gravity balance.
  - Adding more RODI water will reduce the specific gravity of the solution.

  - Evaporating water from the solution will increase the specific gravity.
- Store in polypropylene container.
- To prevent evaporation and the separation of polytungstate from the solution, keep sodium polytungstate solution sealed.

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use sodium polytungstate in a well-ventilated area or fume hood. Avoid contact with skin.

7. Sample Preparation

Sand- and silt-size fractions of the sample are used in the heavy mineral separation process. For greatest accuracy, wash minerals of fine clay fraction in RODI water and allow sample to dry.

8. Procedure

8.1 Mineral separation by gravity method

8.1.1 Wash minerals of fine clay fraction in RODI water, allow to dry.

8.1.2 In a separation funnel, add a preweighed sample into sodium polytungstate solution. Gently stir the sample with a stirring rod to integrate grains into solution column and ensure proper wetting of grains.

8.1.3 Seal the funnel with parafilm, watch glass, or both and wait 3 hours for the heavy mineral grains to begin sinking in the solution. Stir sample and solution once every 3 h. The separation should be complete in about 9 h.

8.1.4 Filter sample using two flasks: one for undiluted solution and the other for diluted solution.

8.1.5 Unstop the separation funnel. Drain the polytungstate solution and heavy grain fraction into a funnel fitted with filter paper or coffee filter. Capture filtrate in flask marked for undiluted solution.

8.1.5.1 To increase the rate of filtration, a squirt bottle and small amounts of RODI water can be used to rinse solution from the grains and reduce viscosity of the solution. If RODI water is used, capture the filtrate in the flask marked for diluted solution. Additional steps are needed to recycle the diluted solution.

8.1.6 Use a separate filter and flask to capture lighter mineral washings and solution. Capture undiluted filtrate in flask marked for undiluted solution.

8.1.6.1 If filter becomes clogged, use a squirt bottle and a small amount of RODI water to dilute the solution through the filter to retain washings.

8.1.7 Once all of the sample has been filtered, rinse the sides of the separatory funnel with a small amount of RODI water and capture solution in the flask marked for diluted solution. Proceed to step 8.3 to recycle solution.

8.1.8 Rinse and dry heavy minerals to be weighed or examined via petrographic microscope or x-ray diffraction.

8.2 Separation by centrifuge

8.2.1 This method is most appropriate for fine-grained samples (<40 mesh). It is preferable to the gravity-settling method due to the speed of the procedure and the ability to overcome the viscosity at densities above 2.5 g/cm^3.

8.2.2 Add 5 to 10 grams of sample to a 50-mL disposable centrifuge tube.

8.2.3 Add 40 mL of sodium polytungstate solution and tighten centrifuge lids.

8.2.4 Place samples in an ultrasonic bath for 5 minutes to ensure the proper wetting of all the grains.

8.2.5 Centrifuge samples between 500 and 1,000 rpm. Duration depends on average grain size and sample amount. The finer the grain size, the longer the centrifuge time and the higher the speed required.

8.2.6 Once sample is centrifuged and heavy mineral separation has occurred, dip the lower portion of the centrifuge tube in liquid nitrogen, freezing the heavy mineral portion of the sample.

8.2.6.1 If liquid nitrogen isn't available, complete the following. After the sample has been centrifuged, use a pipette or syringe to remove the light mineral washings and excess solution from the centrifuge tube. Filter solution into the appropriate (diluted or undiluted) flask. Filter heavy minerals separately.

8.2.7 While lower portion of the tube is frozen, decant the light fraction mineral washings and sodium polytungstate through a filter and funnel. Rinse the sides of the tube with sodium polytungstate solution if light grains adhere to the sides of the tube. Use the appropriate (diluted or undiluted) flask to capture the polytungstate solution.

8.2.8 Add a small amount of RODI water to the frozen heavy mineral sample in centrifuge tube. Allow the sample to thaw.

8.2.9 Decant heavy minerals and solution into a filter and funnel. Rinse grains with RODI water to make sure they are free of polytungstate solution. Capture solution in the flask marked for diluted solution for recycling.

8.2.10 Rinse and dry heavy minerals to be weighed or examined via petrographic microscope or x-ray diffraction.

8.3 Recycling polytungstate solution

8.3.1 Set an oven at a low temperature (60 to 70°C). If using a hotplate, set at lowest setting.

8.3.2 If clays and smaller particles are suspended in polytungstate solution, re-filter the solution.

8.3.3 Place diluted sodium polytungstate solution in an open beaker capable of allowing air flow over the solution.

8.3.4 Allow water to evaporate from solution. Using a specific gravity balance or known mineral standard, calibrate the sodium polytungstate solution to the initial specific gravity desired.

8.3.4.1 Note: Do not allow solution to lose too much water and become super saturated. Sodium polytungstate will precipitate out of solution and become unusable.

9. Calculations

Weight % heavy minerals = beginning weight of sample – weight of heavy mineral fraction

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

11. References

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Optical Analysis (7B)
Grain Studies (7B1)
Grain Mounts, Epoxy (7B1a2)

1. Introduction to Epoxy Grain Mounts

Grain counts are used to identify and quantify minerals in the coarse silt and sand fractions of soils. The results are used to classify soil pedons in mineralogy families of soil taxonomy (Soil Survey Staff, 2014), to help determine substrate provenance of source materials, and to support or identify lithologic discontinuities. A mineralogical analysis of a sand or silt fraction may be qualitative or quantitative based on project goals. The KSSL performs a quantitative analysis counting coarse silt, very fine sand, and fine sand as independent size fractions.

2. Scope and Field of Application

This procedure works well to determine the mineralogy families for soil taxonomy (Soil Survey Staff, 2014). Analysis should be conducted while referencing method 7B1a (Optical Analysis and Interpretation). Depending on project focus, method 7B2a (Magnetic Separation) and method 7B1a1 (Mineral Separation by Heavy Liquids) can be used in conjunction with this method. Method 7B1a1 is applicable only if a large number of heavy minerals that have a specific gravity ≈2.9 are present.

Numerous resources exist for mineral identification procedures and reference data. Examples include:

- “Minerals in Thin Section” by Dexter Perkins, Kevin R. Henke. ISBN 0130109975
- “An Introduction to Rock Forming Minerals” by William Alexander Deer, Robert Andrew Howie, and J. Zussman. ISBN 0903056275
- “Optical Crystallography” by F. Donald Bloss. Mineralogical Society of America Monograph Series, No. 5. ISBN 0939950499

3. Principle

Sand and coarse silt fractions are separated by sieving. Following sample selection, the two most abundant particle-size fractions among the fine sand, very fine sand, and coarse silt are mounted in a thermo-setting epoxy cement that has a refractive index of 1.54. The grains are then identified and counted under a petrographic microscope. Data are reported as a list of minerals, and the estimated quantity of each mineral is given as a percentage of the grains counted in the designated fraction.

3.1 Interferences

Steel can attract magnetic minerals; use rubber, plastic, or glass utensils.

Thoroughly stir sample grains to ensure a representative subsample on the slide. If grains are coated with clay or if aggregates of finer material remain in the fraction that is counted, the results may be skewed.

Variations in the time or temperature of heating the epoxy may result in either matrix stress or variation in the refractive index of the epoxy.

4. Apparatus

4.1 Petrographic microscope slides, precleaned, 27 x 46 mm

4.2 Cover slips, glass, 25 x 25 mm

4.3 Oven, 110 °C

4.4 Hot plate

4.5 Micro-spatula

4.6 Dissecting needle

4.7 Plywood covered with countertop laminate (6 x 8 x 1.25 cm)

4.8 Timer

4.9 Polarizing petrographic microscope

4.10 Tally counter

4.11 Set of 76-mm (3-in) sieves that are square-weave phosphor bronze wire cloth, except the 300-mesh sieve, which is twilled weave. U.S. series and Tyler Screen Scale equivalent designations are as follows:

Sand Size	Opening	U.S. No.	Tyler Mesh Size
	(mm)		
Very coarse sand (VCS)	1.0	18	16
Coarse sand (CS)	0.5	35	32
Medium sand (MS)	0.25	60	60
Fine sand (FS)	0.105	140	150
Very fine sand (VFS)	0.047	300	300

5. Chemicals

5.1 Reverse osmosis (RO) water, ASTM Type III grade of reagent water

5.2 Petrographic kit including epoxy, resin, and curing agent. (The KSSL can be contacted for more information.)

5.3 **Sodium hexametaphosphate solution, 0.5%**

Components: Sodium hexametaphosphate $(NaPO_3)_6$) (CAS# 68915-31-1), RODI water

- To a 5-L polyethylene carboy, add the following in order:
  - 4 L of RO water
  - 20 g of sodium hexametaphosphate

- Swirl to mix.

5.4 Index immersion oils, used for special projects

6. Health and Safety

Personal Protective Equipment (PPE).—When preparing reagents or handling concentrated acids or bases, use disposable gloves with appropriate rating for chemical resistance; safety glasses, face shield, or both; and lab coat or apron. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations in the event of physical contact with reagent solutions.

Use caution when handling hot glass slides. Use heat resistant gloves as needed.

Heat the epoxy in a fume hood. Immediately wash or remove any epoxy that comes in contact with the skin.

Use gloves when handling immersion oils; read safety data sheets (SDS) before using.

7. Sample Preparation

During particle-size distribution analysis, material <20 µm in diameter is separated by settling and decanting and the sand and coarse silt fractions are separated by sieving.

8. Procedure

8.1 Review project objectives. Note any special instructions by soil scientists. Sample selection depends on the purpose of analysis.

8.2 If the particle-size sample or information is not available for a sand and coarse silt separate, perform the following grain-size separation:

8.2.1 Disperse the sample in sodium hexametaphosphate solution.

8.2.2 Pour the soil suspension into a 200-mL beaker that has a line marked 5 cm above the bottom.

8.2.3 Add RO water to the beaker up to the 5-cm mark.

8.2.4 Stir the suspension then allow to settle for 2.0 minutes (use a timer).

8.2.5 Decant and discard the suspension containing the clay and fine silt. Repeat until the supernatant is nearly clear.

8.2.6 Transfer the sediment to a drying dish and dry sample at 105–110 °C.

8.2.7 Sieve the dried sample to isolate the individual fractions.

8.3 Identify the one or two of the most abundant size fractions of the sample. This information can be found through PSDA data or the grain size separation. Size fractions are:

- Coarse silt (CoSi): Sample will have been stored in aluminum pans following PSDA.

- Very fine sand (VFS): Sample placed in gelatin capsules and stored in a labeled vial
- Fine sand (FS): Sample stored in gelatin capsules and stored in a labeled vial

8.4 Using beaker supplied by the manufacturer, mix a 1:10 ratio of epoxy resin to curing agent. Prepare epoxy at least 1 day prior to use and refrigerate until needed.

8.5 Turn on hot plate and allow it to equilibrate at 125 °C for ≈1 h.

8.6 Remove mixture from refrigerator at least 40 min prior to use. If the epoxy crystallizes, gently warm mixture until crystals dissolve.

8.7 Prepare 4 to 6 slides at a time:

8.7.1 Write sample ID and grain size designation on the edge of the slide.

8.7.2 Set sample vials or capsules next to the associated sample slides.

8.7.3 Use a small, rounded, glass or plastic rod to drop epoxy mixture on the upper middle of each slide. Use ½ drop epoxy for CoSi, one drop VFS, and 1½ drops for FS.

8.7.4 Use a micro-spatula to add the mixed grains to epoxy. Use larger amounts of sample for smaller size fractions.

8.7.5 Use a dissecting needle to slowly stir the grains into the epoxy. Avoid introduction of air bubbles. Air bubbles can be popped with the dissecting needle.

8.7.6 Line up the coverslip with the top edge of the thin section glass. Carefully place cover slip on the epoxy and sample.

8.7.7 Allow the epoxy to spread under the cover slip.

8.7.8 Gently press down on coverslip with dissecting needle to remove air bubbles. Use caution not to crack the coverslip or leave fingerprints.

8.8 Align samples slides in the center of the hot plate. Heat slides at 125 °C and set timer for 8 minutes. Epoxy will set and yield a refractive index of 1.540. Longer heating may distort epoxy optical index of 1.540.

8.9 After 8 min, remove slides from hotplate by sliding them onto the laminate block. Allow to cool. Begin next set of sample slide preparation, repeating steps 8.7 and 8.8.

8.10 Examine the grain mount under petrographic microscope:

- Epoxy medium should be isotropic.
- Anisotropic stress lines around grains under cross polarized light may interfere with observation of optical properties.
- Remake any unsatisfactory grain mounts.

8.11 Place grain mounts in a microscope-slide file box. Record project number and grain mount positions on interior of box lid. Record box number(s) in the LIMS sample disposition files.

8.12 Return the epoxy mixture to the refrigerator, which extends the shelf life of the mixture.

8.13 Seat the grain mount slide in the mechanical stage of the microscope. Assess grain assemblage for relative mineral abundances at low-power magnification (10X).

8.13.1 Identify the most abundant minerals. Be aware of common and rare or unique mineral assemblages. These mineral combinations provide clues to the minor species that may be expected.

8.14 To conduct a grain count, a 10X magnification is appropriate for FS and VFS. A 25X magnification is appropriate for CoSi.

8.14.1 Adjust the slide on the mechanical stage so the left border of cover slip is in view and near the lower left corner.

8.14.2 Starting in the upper right margin of the cover slip (as viewed from the oculars), scan the entirety of the slide, identifying all grains. Scan the slide by moving down vertically till you reach the end of the cover slip, then move left one field width at a time. Continue scanning until you reach the left margin of the cover slip.

8.14.3 Set counters to zero. Identify and tally each grain that touches the horizontal crosshair in each field of view until the right margin of cover slip is in view. Move right every time you reach the bottom or the top of the cover slip until the right margin of cover slip is in view or you have tallied 300 grains.

8.14.4 Note the observed minerals by a two-letter code, e.g., QZ for quartz. Refer to the list of mineral codes provided at the end of the mineralogy section (7).

8.14.5 List the most abundant grains and associated counter number in logbook. Mineral identification can be aided by characteristics listed in the method for Analysis and Interpretation (method 7B1a).

8.14.6 Repeat process until the end of the traverse in which 300 grains have been tallied. If there are only a few species, a counting of 300 grains provides a sample representation. As the number of species increases, the count should increase within limits of practicability. To count more than 1,000 grains is seldom necessary. A non-random distribution of grains is usually most pronounced near the edges of the cover slip. If the entire slide has been traversed and the total grain count is <300, reverse the direction of vertical translation and count traverses on odd-numbered settings, e.g., 81 or 79 mm.

8.15 If fractions are nearly equal in abundance, select the VFS fraction. It provides the widest range of information.

8.16 Different size fractions may be counted for different horizons within a single pedon. If it is appropriate to count the same size fraction for each horizon

within a pedon or project, such as for a study of soil lithology, this request must be specified by the project coordinator.

8.17 Counting isotropic grains only (e.g., volcanic glass) can be done more rapidly using the following microscope configurations:

8.17.1 Position the polarizer slightly off the extinction or "blackout" position.

8.17.2 With crossed Nicols and a gypsum plate, the outline of the grains is visible. The color of the grain is the same as the epoxy background.

8.17.3 Count the predominant fraction. If CoSi is not the predominant fraction in the sample, then count the CoSi fraction as well, resulting in two glass counts per slide.

8.17.4 When the count is complete, enter the raw data (project, sample number, fraction(s), minerals, and counts) into the KSSL LIMS data base.

8.17.5 Record raw grain-count data in a logbook. Most grain counts are made at 10X magnification for very fine or fine sand or 25X for coarse silt.

9. Calculations

9.1 Percentage of minerals (frequency per 100 grains):

$$\text{Mineral frequency (\%)} = (\text{Number of grains for a mineral} \times 100) / \text{Total number of grains counted}$$

- Calculations are conducted with software using grain-size fractions, mineral identification, and number of grains counted per mineral.

9.2 Report mineral contents to the nearest whole percentage of grains counted.

- These data are accurate number percentages for the size fraction analyzed but may need to be recomputed to convert to weight percentages (Harris and Zelazny, 1985).
- Grain counts can deviate significantly from weight percentage due to platy grains and density variations. These data are reported on the mineralogy data page of the primary characterization data set.
- For each grain size counted, the mineral type and amount are recorded. Refer to method 7C1 for more information on resistant minerals.

9.3 The KSSL does not count multiple fractions for a single sample, count combined fractions, or present the data as weighted averages. Fractions are reported as percent of <2-mm fraction for CoSi, VFS, or FS as determined by KSSL particle size distribution analysis (PSDA).

10. Quality Assurance/Quality Control

10.1 Consult KSSL LIMS for available accuracy, precision, and quality control charts.

10.2 Verify that batch control sample(s) and blank data are within acceptable limits.

10.3 Assess plausibility of test sample data in context of expected soil profile trends.

10.4 Assess plausibility of relationship of test sample data to other project laboratory analytical data and metadata.

10.5 Assign overall project data to soil data quality specialist.

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Ratios and Estimates Related to Optical Analysis (7C)

Total Resistant Minerals (7C1)

Method 7C1 is reported as the sum of the grain-count percentages. For more detailed information on total resistant minerals, refer to the Soil Survey Staff (2014, 2011). Also refer to the list of mineralogy codes for resistant and weatherable minerals.

References

Soil Survey Staff. 2011. Soil survey laboratory information manual. Version 2.0. USDA–NRCS. Soil Survey Investigations Report No. 45. U.S. Govt. Print. Office, Washington, DC.

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Mineral Codes and Glass Counts

Mineralogy Codes for Weatherable Minerals

Code	Mineral	Code	Mineral
AC	Actinolite	FD	Feldspar
AF	Arfvedsonite	FF	Foraminifera
AG	Antigorite	FG	Glass-Coated Feldspar
AH	Anthophyllite	FH	Anorthoclase
AI	Aegirine-Augite	FK	Potassium Feldspar
AL	Allophane	FL	Labradorite
AM	Amphibole	FM	Ferromagnesian Mineral
AO	Aragonite[1]	FN	Anorthite
AP	Apatite	FO	Oligoclase
AR	Weatherable Aggregates	FP	Plagioclase Feldspar
AU	Augite	FR	Orthoclase
AY	Anhydrite[1]	FS	Sanidine
BA	Barite	FT	Fluorapatite
BC	Biotite-Chlorite	FU	Fluorite[1]
BE	Boehmite	FZ	Feldspathoids
BG	Basic glass	GA	Glass Aggregates
BK	Brookite	GC	Glass-Coated Grain
BR	Brucite	GG	Galena
BT	Biotite	GL	Glauconite
BZ	Bronzite	GM	Glassy Materials
CA	Calcite[1]	GO	Glaucophane

Mineralogy Codes for Weatherable Minerals—Continued

Code	Mineral	Code	Mineral
CB	Carbonate Aggregates[1]	GY	Gypsum[1]
CC	Coal	HA	Halite[1]
CL	Chlorite	HB	Hydrobiotite
CM	Chlorite-Mica	HG	Glass-Coated Hornblende
CO	Collophane	HN	Hornblende
CY	Chrysotile	HY	Hypersthene
CZ	Clinozoisite	ID	Iddingsite
DL	Dolomite	IL	Illite (Hydromuscovite)
DP	Diopside	JO	Jarosite
DU	Dumortierite	KH	Halloysite
EN	Enstatite	LA	Lamprobolite
EP	Epidote	LC	Analcime[1]
FA	Andesine	LI	Leucite
FB	Albite	LO	Lepidomelane
FC	Microcline	LP	Lepidolite
LT	Lithiophorite	PU	Pyrolusite
MC	Montmorillonite-Chlorite	PY	Pyrophyllite
ME	Magnesite[1]	QC	Glass-Coated Quartz
MI	Mica	RB	Riebeckite (Blue Amphibole)
ML	Melilite	RO	Rhodochrosite
MM	Montmorillonite-Mica	SC	Scapolite
MR	Marcasite	SE	Sepiolite
MS	Muscovite	SG	Sphalerite
MT	Montmorillonite	SH	Schwertmannite
MV	Montmorillonite-Vermiculite	SI	Siderite
NA	Natron	SM	Smectite
NE	Nepheline	SR	Sericite
NJ	Natrojarosite	ST	Stilbite[1]
NX	Non-crystalline	SU	Sulphur
OG	Glass-Coated opaque	SZ	Serpentine
OT	Other	TA	Talc
OV	Olivine	TE	Tremolite
OW	Other Weatherable Minerals	TH	Thenardite[1]
PA	Palagonite	VC	Vermiculite-Chlorite
PD	Piemontite	VH	Vermiculite-Hydrobiotite

Mineralogy Codes for Weatherable Minerals—Continued

Code	Mineral	Code	Mineral
PG	Palygorskite	VI	Vivianite
PI	Pyrite	VM	Vermiculite-Mica
PJ	Plumbojarosite	VR	Vermiculite
PK	Pervoskite	WE	Weatherable Mineral
PL	Phlogopite	WV	Wavelite
PM	Pumice	ZE	Zeolite[1]
PR	Pyroxene	ZO	Zoisite
PT	Paragonite		

[1] Minerals not included as "weatherable minerals" as defined by "Keys to Soil Taxonomy" (Soil Survey Staff, 2014): "The intent is to include... only those weatherable minerals that are unstable in a humid climate compared to other minerals such as quartz and 1:1 lattice clays, but are more resistant to weathering than calcite." This group of minerals is not part of the calculation for percent resistant minerals used in the siliceous family mineralogy class or percent weatherable minerals used as criteria for oxic horizon but are included in the calculation of "total resistant minerals" on the Kellogg Soil Survey Laboratory (KSSL) mineralogy data sheet. Therefore, the value on the data sheet should be recalculated for strict use in "Soil Taxonomy" criteria if these minerals (e.g., calcite) are in the grain count of a selected horizon.

Mineralogy Codes for Resistant Minerals

Code	Mineral	Code	Mineral
AE	Anatase	MG	Magnetite
AN	Andalusite	MH	Maghemite
BY	Beryl	MZ	Monazite
CD	Chalcedony (Chert, Flint, Jasper, Onyx)	OP	Opaques
CE	Cobaltite	OR	Other Resistant Minerals
CH	Cliachite (Bauxite)	PN	Pollen
CN	Corundum	PO	Plant Opal
CR	Cristobalite	QC	Clay-Coated Quartz
CT	Cassiterite	QI	Iron-Coated Quartz
FE	Iron Oxides (Goethite, Magnetite, Hematite, Limonite)	QZ	Quartz
GD	Gold	RA	Resistant Aggregates

Mineralogy Codes for Resistant Minerals—Continued

Code	Mineral	Code	Mineral
GE	Goethite	RE	Resistant Minerals
GI	Gibbsite	RU	Rutile
GN	Garnet	SA	Siliceous Aggregates
HE	Hematite	SL	Sillimanite
HS	Hydroxy-Interlayered Smectite	SN	Spinel
HV	Hydroxy-Interlayered Vermiculite	SO	Staurolite
KS	Interstratified Kaolinite-Smectite	SP	Sphene
KK	Kaolinite	SS	Sponge Spicule
KY	Kyanite	TD	Tridymite
LE	Lepidocrocite	TM	Tourmaline
LM	Limonite	TP	Topaz
LU	Leucoxene	ZR	Zircon
MD	Resistant Mineraloids		

Codes for Glass Count Minerals and Mineraloids

Minerals on this list are identified during the "glass count" procedure by the KSSL during the quantification of particle size-separates in the sand-silt fraction. Minerals in the "OT" category are other weatherable or resistant minerals that would be quantified during a "full grain count."

Volcanic Glass Grains	Organic Origin Grains	Other Grains
BG=Basic Glass	DI=Diatoms	OT=Other
FG=Glass-Coated Feldspar	PO=Plant Opal	
GA=Glass Aggregates	SS=Sponge Spicule	
GC=Glass-Coated Grain		
GM=Glassy Materials		
GS=Glass		
HG=Glass-Coated Hornblende		
OG=Glass-Coated Opaque		
PA=Palagonite		
PM=Pumice		
QG=Glass-Coated Quartz		

Volcanic Glass Grains: Minerals and mineraloids in this column are all considered weatherable according to the KSSL and are defined in the "Keys to Soil Taxonomy," Twelfth Edition, 2014, as being "volcanic glass." The percentages of these minerals are summed as "volcanic glass" and used in the criteria for andic soil properties, subgroups with the "vitr(i)" formative element, families with "ashy" substitutes for particle-size class, and the glass mineralogy class in "Soil Taxonomy."

Organic Origin Grains: Mineraloids included in this list are regarded as resistant minerals according to the KSSL and included in the calculation of "total resistant minerals" as shown on the KSSL mineralogy data sheet.