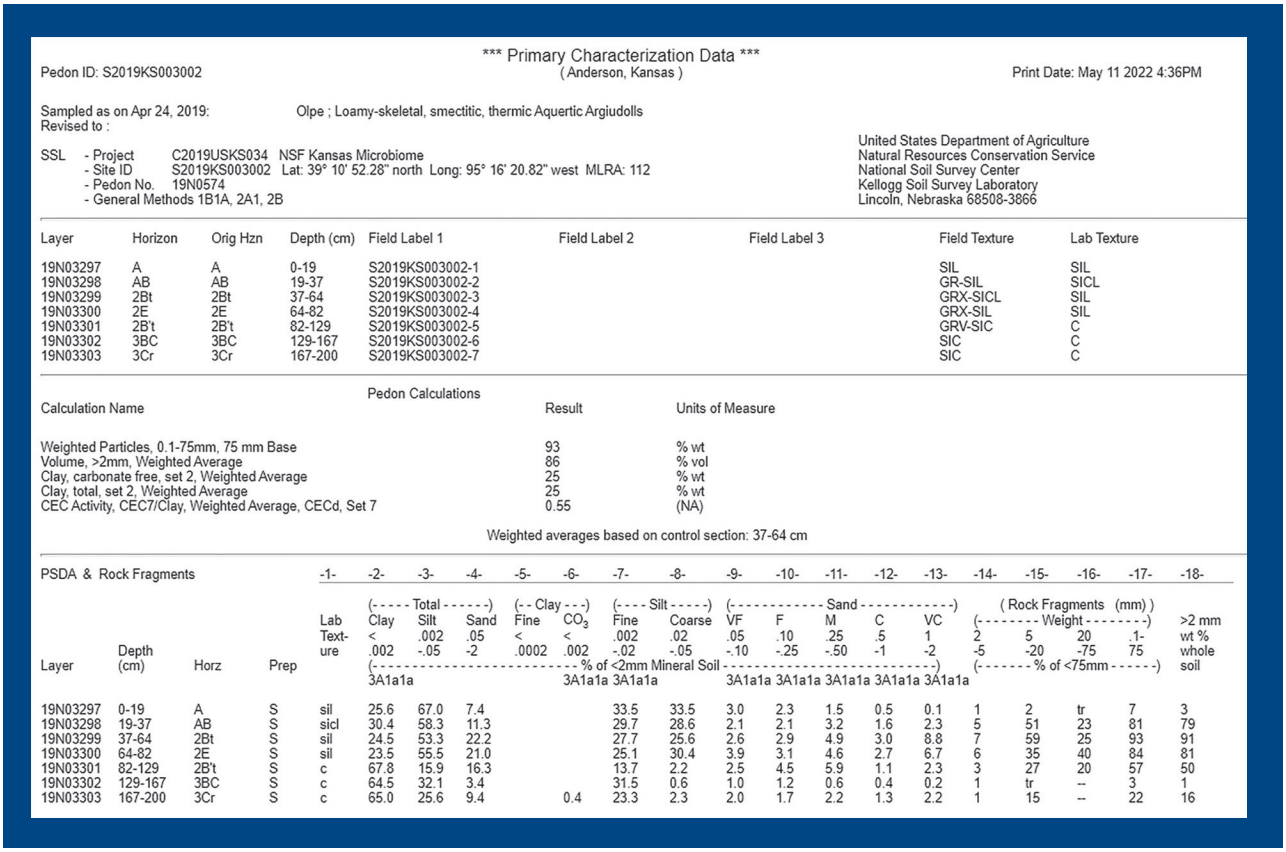
USDA Natural Resources Conservation Service
U.S. DEPARTMENT OF AGRICULTURE

Kellogg Soil Survey Laboratory Methods Manual

Soil Survey Investigations Report No. 42, Version 6.0

Part 2: Obsolete Methods



*** Primary Characterization Data ***
(Anderson, Kansas)

Pedon ID: S2019KS003002 — Print Date: May 11 2022 4:36PM

Sampled as on Apr 24, 2019: Olpe ; Loamy-skeletal, smectitic, thermic Aquertic Argiudolls
Revised to :

SSL - Project C2019USKS034 NSF Kansas Microbiome
- Site ID S2019KS003002 Lat: 39° 10' 52.28" north Long: 95° 16' 20.82" west MLRA: 112
- Pedon No. 19N0574
- General Methods 1B1A, 2A1, 2B

United States Department of Agriculture
Natural Resources Conservation Service
National Soil Survey Center
Kellogg Soil Survey Laboratory
Lincoln, Nebraska 68508-3866

Layer	Horizon	Orig Hzn	Depth (cm)	Field Label 1	Field Label 2	Field Label 3	Field Texture	Lab Texture
19N03297	A	A	0-19	S2019KS003002-1			SIL	SIL
19N03298	AB	AB	19-37	S2019KS003002-2			GR-SIL	SICL
19N03299	2Bt	2Bt	37-64	S2019KS003002-3			GRX-SICL	SIL
19N03300	2E	2E	64-82	S2019KS003002-4			GRX-SIL	SIL
19N03301	2B't	2B't	82-129	S2019KS003002-5			GRV-SIC	C
19N03302	3BC	3BC	129-167	S2019KS003002-6			SIC	C
19N03303	3Cr	3Cr	167-200	S2019KS003002-7			SIC	C

Pedon Calculations

Calculation Name	Result	Units of Measure
Weighted Particles, 0.1-75mm, 75 mm Base	93	% wt
Volume, >2mm, Weighted Average	86	% vol
Clay, carbonate free, set 2, Weighted Average	25	% wt
Clay, total, set 2, Weighted Average	25	% wt
CEC Activity, CEC7/Clay, Weighted Average, CECd, Set 7	0.55	(NA)

Weighted averages based on control section: 37-64 cm

PSDA & Rock Fragments

				-1-	-2-	-3-	-4-	-5-	-6-	-7-	-8-	-9-	-10-	-11-	-12-	-13-	-14-	-15-	-16-	-17-	-18-
					(----- Total -----)			(- Clay -)		(---- Silt -----)		(---------- Sand ----------)					(Rock Fragments (mm))				
				Lab	Clay	Silt	Sand	Fine	CO_3	Fine	Coarse	VF	F	M	C	VC	(-------- Weight --------)				>2 mm
				Text-	<	.002	.05	<	<	.002	.02	.05	.10	.25	.5	1	2	5	20	.1-	wt %
Layer	Depth (cm)	Horz	Prep	ure	.002	-.05	-2	.0002	.002	-.02	-.05	-.10	-.25	-.50	-1	-2	-5	-20	-75	75	whole soil
					(---------- % of <2mm Mineral Soil ----------)												(------- % of <75mm ------)				
					3A1a1a				3A1a1a	3A1a1a		3A1a1a	3A1a1a	3A1a1a	3A1a1a	3A1a1a					
19N03297	0-19	A	S	sil	25.6	67.0	7.4			33.5	33.5	3.0	2.3	1.5	0.5	0.1	1	2	tr	7	3
19N03298	19-37	AB	S	sicl	30.4	58.3	11.3			29.7	28.6	2.1	2.1	3.2	1.6	2.3	5	51	23	81	79
19N03299	37-64	2Bt	S	sil	24.5	53.3	22.2			27.7	25.6	2.6	2.9	4.9	3.0	8.8	7	59	25	93	91
19N03300	64-82	2E	S	sil	23.5	55.5	21.0			25.1	30.4	3.9	3.1	4.6	2.7	6.7	6	35	40	84	81
19N03301	82-129	2B't	S	c	67.8	15.9	16.3			13.7	2.2	2.5	4.5	5.9	1.1	2.3	3	27	20	57	50
19N03302	129-167	3BC	S	c	64.5	32.1	3.4			31.5	0.6	1.0	1.2	0.6	0.4	0.2	1	tr	--	3	1
19N03303	167-200	3Cr	S	c	65.0	25.6	9.4		0.4	23.3	2.3	2.0	1.7	2.2	1.3	2.2	1	15	--	22	16

Cover photo: Primary characterization data sheet for a soil in the Olpe series.

Citation:

Soil Survey Staff. 2022. Kellogg Soil Survey Laboratory methods manual. Soil Survey Investigations Report No. 42, Version 6.0. U.S. Department of Agriculture, Natural Resources Conservation Service.

Mention of names or commercial products in this document does not imply recommendation or endorsement by the U.S. Department of Agriculture.

KELLOGG SOIL SURVEY LABORATORY METHODS MANUAL

Soil Survey Investigations Report No. 42, Version 6.0

Part 2: Obsolete 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
Lincoln, Nebraska

Issued 2022

CONTENTS

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.

Scientists

Lyle T. Alexander, Steven L. Baird, Otto W. Baumer, Ellis C. Benham, C. Reese Berdanier Jr., Wade A. Blankenship, Benny R. Brasher, Laurence E. Brown, Rebecca Burt, John G. Cady, Frank J. Carlisle, James H. DeMent, Joe D. Dixon, Moustafa A. Elrashidi, Richard R. Ferguson, Klaus W. Flach, Carol D. Franks, Donald P. Franzmeier, Erling E. Gamble, Don W. Goss, Robert B. Grossman, Deborah S. Harms, George C. Holmgren, C. Steven Holzhey, Robert H. Jordan, R. Leo Juve, Frederick M. Kaisaki, John M. Kimble, Leo C. Klameth, Ellis G. Knox, Zamir Libohova, Susan E. Samson-Liebig, Warren C. Lynn, Maurice J. Mausbach, M. Dewayne Mays, Dean C. McMurty, Milton M. Meyer, John L. Millet, Curtis Monger, Steven E. Monteith, Reuben E. Nelson, W. Dennis Nettleton, Carolyn G. Olson, Ronald F. Paetzold, Roger B. Parsons, Richard L. Pullman, Ivan W. Ratcliff Jr., Thomas G. Reinsch, Ernest D. Rivers, Sam J. Ross, Philip J. Schoeneberger, Leo G. Shields, Christopher W. Smith, Terrence M. Sobecki, John A. Thompson, George W. Threlkeld, Larry T. West, Candiss Williams, Michael A. Wilson, Douglas A. Wysocki, Ronald D. Yeck, and Keith K. Young.

Physical Science Analysts

Michelle A. Etmund, Diane G. Hooper, Jennifer Ingham, Patricia E. Jones, Christopher W. Lee, Kevin Loeffelmann, Scarlett Murphy, David Parks, Amber M. Shinn-Kenjar, Adrien Spidell-Metcalf, Kathyrn L. Newman, Michael J. Pearson, Susan J. Reidel, Crystal A. Schaecher, Aaron Shropshire, and Pamela A. Van Neste.

NONDISCRIMINATION STATEMENT

In accordance with Federal civil rights law and U.S. Department of Agriculture (USDA) civil rights regulations and policies, the USDA, its Agencies, offices, and employees, and institutions participating in or administering USDA programs are prohibited from discriminating based on race, color, national origin, religion, sex, gender identity (including gender expression), sexual orientation, disability, age, marital status, family/parental status, income derived from a public assistance program, political beliefs, or reprisal or retaliation for prior civil rights activity, in any program or activity conducted or funded by USDA (not all bases apply to all programs). Remedies and complaint filing deadlines vary by program or incident.

Persons with disabilities who require alternative means of communication for program information (e.g., Braille, large print, audiotape, American Sign Language, etc.) should contact the responsible Agency or USDA's TARGET Center at (202) 720-2600 (voice and TTY) or contact USDA through the Federal Relay Service at (800) 877-8339. Additionally, program information may be made available in languages other than English.

To file a program discrimination complaint, complete the USDA Program Discrimination Complaint Form, AD-3027, found online at How to File a Program Discrimination Complaint and at any USDA office or write a letter addressed to USDA and provide in the letter all of the information requested in the form. To request a copy of the complaint form, call (866) 632-9992. Submit your completed form or letter to USDA by:

(1) mail: U.S. Department of Agriculture
Office of the Assistant Secretary for Civil Rights
1400 Independence Avenue, SW
Washington, D.C. 20250-9410;

(2) fax: (202) 690-7442; or

(3) email: program.intake@usda.gov.

USDA is an equal opportunity provider, employer, and lender.

OBSOLETE METHODS OF ANALYSIS

SSIR 42, Part 2, describes the methods that are no longer used at the Kellogg Soil Survey Laboratory (KSSL). These methods were described in earlier versions of Soil Survey Investigations Report (SSIR) No. 42 (1989, 1992, 1996, 2004, and 2014) and in SSIR No. 1, "Procedures for Collecting Soil Samples and Methods of Analysis for Soil Survey" (1972, 1982, and 1984). Some of these procedures are in the old format. Information is not available to describe some of these obsolete procedures in the same detail as used to describe the current methods in the laboratory. Also included in the appendix of this manual are examples of earlier versions of the KSSL data sheet (appendix fig. 1) and pedon description (appendix fig. 2).

Since the publication of SSIR No. 42 (1996), the number and kinds of methods performed at the KSSL have increased significantly, resulting in a re-structuring of the laboratory method codes. This re-structuring is observed beginning in the 2004 version of SSIR No. 42 to present. Some of the methods described in SSIR No. 1, 1972, 1982, and 1984, as well as in SSIR No. 42, 1989, 1992, and 1996, carry the old method codes, which may not necessarily be the same as current method codes. These older method codes have a maximum of four characters, e.g., 6A2b.

Documentation and archiving of these obsolete methods creates an important reference since many older SSIRs and scientific publications report these methods. The intent of this documentation is to provide a historical linkage for the KSSL core methods. The following sections of this manual document the obsolete methods based on the last version in which the methods were current.

Section I: SSIR No. 42, Soil Survey Laboratory Methods Manual, Version 5.0 (2014)

Section II: SSIR No. 42, Soil Survey Laboratory Methods Manual, Version 4.0 (2004)

Section III: SSIR No. 42, Soil Survey Laboratory Methods Manual, Version 3.0 (1996)

Section IV: SSIR No. 42, Soil Survey Laboratory Methods Manual, Versions 1.0 and 2.0 (1989, 1992, respectively)

Section V: SSIR No. 1, Procedures for Collecting Soil Samples and Methods of Analysis for Soil Survey (1972, 1982, 1984)

INDEX TO OBSOLETE METHODS

Obsolete Methods That Have the New Method Code Structure

Index to Obsolete Methods, New Code Structure—continued

Index to Obsolete Methods, New Code Structure—continued

Index to Obsolete Methods, New Code Structure—continued

Obsolete Methods That Have the Old Method Code Structure

Index to Obsolete Methods, Old Code Structure—continued

Index to Obsolete Methods, Old Code Structure—continued

Index to Obsolete Methods, Old Code Structure—continued

Index to Obsolete Methods, Old Code Structure—continued

Index to Obsolete Methods, Old Code Structure—continued

Index to Obsolete Methods, Old Code Structure—continued

Index to Obsolete Methods, Old Code Structure—continued

Index to Obsolete Methods, Old Code Structure—continued

Index to Obsolete Methods, Old Code Structure—continued

Index to Obsolete Methods, Old Code Structure—continued

Index to Obsolete Methods, Old Code Structure—continued

OBSOLETE METHODS SECTION I: SSIR NO. 42, SOIL SURVEY LABORATORY METHODS MANUAL, VERSION 5.0 (2014)

SOIL AND WATER CHEMICAL EXTRACTIONS AND ANALYSES (4)

Ion Exchange and Extractable Cations (4B)

Displacement after Washing, NH_4OAc, pH 7 (4B1a)

Automatic Extractor (4B1a1)

Atomic Absorption Spectrophotometer (4B1a1b)

Calcium, Magnesium, Potassium, and Sodium (4B1a1b1-4)

Air-Dry or Field-Moist, <2-mm (4B1a1b1-4a-b1)

1. Application

The extractable bases (Ca^{2+}, Mg^{2+}, K^+, and Na^+) from the NH_4OAc extraction (method 4B1a1) are generally assumed to be those exchangeable bases on the cation exchange sites of the soil. The term “extractable” rather than “exchangeable” bases is used because any additional source of soluble bases influences the results. The abundance of these cations usually occurs in the sequence of $Ca^{2+} > Mg^{2+} > K^+ > Na^+$. Deviation from this usual order signals that some factor or factors, e.g., free $CaCO_3$ or gypsum, serpentine (high Mg^{2+}), or natric material (high Na^+), have altered the soil chemistry. The most doubtful cation extractions with this method are Ca^{2+} in the presence of free $CaCO_3$ and gypsum and K^+ in soils that are dominated by mica or vermiculite (Thomas, 1982).

2. Summary of Method

The NH_4OAc extract from method 4B1a1 is diluted with an ionization suppressant (La_2O_3). The analytes are measured by an atomic absorption spectrophotometer (AAS). The analyte is measured by absorption of the light from a hollow cathode lamp. An automatic sample changer is used to aspirate a series of samples. The AAS converts absorption to analyte concentration. Data are automatically recorded by a microcomputer and printer. The NH_4OAc extracted cations, Ca^{2+}, Mg^{2+}, K^+, and Na^+, are reported in meq 100 g^{-1} soil or (cmol (+) kg^{-1}) in methods 4B1a1b1-4, respectively.

3. Interferences

Four types of interferences (matrix, spectral, chemical, and ionization) affect the analyses of these cations. These interferences vary in importance, depending upon the particular analyte selected. Do not use borosilicate tubes because of potential leaching of analytes.

4. Safety

Wear protective clothing and safety glasses. Exercise special care when preparing reagents. Restrict the use of concentrated HCl to a fume hood. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts.

Follow standard laboratory procedures when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene gas is highly 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 AAS.

5. Equipment

5.1 Electronic balance, ±1.0-mg sensitivity

5.2 Atomic absorption spectrophotometer (AAS), double-beam optical system, AAnalyst, 400, Perkin-Elmer Corp., Norwalk, CT

5.3 Autosampler, S-10, Perkin-Elmer Corp., Norwalk, CT

5.4 Computer, with AA WinLab software, Perkin-Elmer Corp., Norwalk, CT, and printer

5.5 Single-stage regulator, acetylene

5.6 Digital diluter/dispenser, with syringes 10,000-µL and 1000-µL, gas tight, Microlab 500, Hamilton Co., Reno, NV

5.7 Plastic test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer

5.8 Containers, polyethylene

5.9 Peristaltic pump

6. Reagents

6.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

6.2 Hydrochloric acid (HCl), concentrated 12 *N*

6.3 HCl, 1:1 HCl:RODI, 6 *N*. Carefully mix 1 part of concentrated HCl to 1 part RODI water.

6.4 NH_4OH, reagent-grade, specific gravity 0.90

6.5 Glacial acetic acid, 99.5%

6.6 Ammonium acetate solution (NH_4OAc), 1 *N*, pH 7.0. Add 1026 mL of glacial acetic acid (CH_3COOH) to 15 L RODI water. Add 1224 mL of concentrated ammonium hydroxide (NH_4OH). Cool. Allow to stand one day to equilibrate to room temperature. Mix and adjust to pH 7.0 with CH_3COOH (typically,

≈40 mL) or NH_4OH and dilute with RODI water to 18 L. The NH_4OAc solution is used for extraction of cations (method 4B1a1).

6.7 NH_4OAc solution, 2.0 *N*, pH 7.0. Mix 228 mL of glacial acetic acid in 1200 mL of RODI water. While stirring, carefully add 272 mL of concentrated NH_4OH. Cool. Allow to stand 1 day to equilibrate to room temperature. Mix and adjust pH 7.0 using CH_3COOH or NH_4OH. Dilute to 2 L with RODI water.

6.8 Stock lanthanum ionization suppressant solution (SLISS), 65,000 mg L^{-1}. Wet 152.4 g lanthanum oxide (La_2O_3) with 100 mL RODI water. Slowly and cautiously add 500 mL of 6 *N* HCl to dissolve the La_2O_3. Cooling the solution is necessary. Dilute to 2 L with RODI water. Filter solution. Store in polyethylene container.

6.9 Working lanthanum ionization suppressant solution (WLISS), 2000 mg L^{-1}. Dilute 61.5 mL of SLISS with 1800 mL of RODI water (1:10). Dilute to 2 L with RODI water. Store in polyethylene container.

6.10 Primary stock standards solutions (PSSS), high purity, 1000 mg L^{-1}: Ca, Mg, K, and Na

6.11 Working stock mixed standards solution (WSMSS), High, Medium, Low, Low/Low, and Blank. In five 500-mL volumetric flasks, add 250 mL of 2 *N* NH_4OAc and the following designated amounts of Ca PSSS, Mg PSSS, K PSSS, and Na PSSS. Dilute to volume with RODI. Invert to thoroughly mix. Store in polyethylene containers. Prepare fresh weekly. Store in the refrigerator. Allow to equilibrate to room temperature before use. Prepare WSMSS as follows:

6.11.1 High Standard WSMSS: 90 mL Ca PSSS, 7.5 mL Mg PSSS, 20.0 mL K PSSS, and 100.0 mL Na PSSS = 180 mg L^{-1} Ca, 15 mg L^{-1} Mg, 40 mg L^{-1} K, and 200 mg L^{-1} Na

6.11.2 Medium Standard WSMSS: 60 mL Ca PSSS, 5.0 mL Mg PSSS, 10.0 mL K PSSS, and 50.0 mL Na PSSS = 120 mg L^{-1} Ca, 10 mg L^{-1} Mg, 20 mg L^{-1} K, and 100 mg L^{-1} Na

6.11.3 Low Standard WSMSS: 30 mL Ca PSSS, 2.5 mL Mg PSSS, 5.0 mL K PSSS, and 10.0 mL Na PSSS = 60 mg L^{-1} Ca, 5 mg L^{-1} Mg, 10 mg L^{-1} K, and 20 mg L^{-1} Na

6.11.4 Low/Low Standard WSMSS: 12.5 mL Ca PSSS, 0.25 mL Mg PSSS, 0.30 mL K PSSS, and 5.0 mL Na PSSS = 25 mg L^{-1} Ca, 0.5 mg L^{-1} Mg, 0.60 mg L^{-1} K, and 10 mg L^{-1} Na

6.11.5 Blank WSMSS: 0 mL of Ca, Mg, K, and Na PSSS

6.12 Mixed calibration standard solutions (MCSS), High, Medium, Low, Very Low, and Blank. Dilute 1 part WSMSS with 19 parts of WLISS (1:20) dilution with resulting concentrations for MCSS as follows:

6.12.1 MCSS High Standard: 9.0 mg L^{-1} Ca, 0.75 mg L^{-1} Mg, 2.0 mg L^{-1} K, and 10.0 mg L^{-1} Na

6.12.2 MCSS Medium Standard: 6.0 mg L^{-1} Ca, 0.5 mg L^{-1} Mg, 1.0 mg L^{-1} K, and 5.0 mg L^{-1} Na

6.12.3 MCSS Low Standard: 3.0 mg L^{-1} Ca, 0.25 mg L^{-1} Mg, 0.5 mg L^{-1} K, and 1.0 mg L^{-1} Na

6.12.4 MCSS Very Low Standard: 1.25 mg L^{-1} Ca, 0.025 mg L^{-1} Mg, 0.030 K, and 0.5 mg L^{-1} Na

6.12.5 Blank MCSS: 0 mg L^{-1} Ca, Mg, K, and Na

6.13 Compressed air with water and oil traps

6.14 Acetylene gas, purity 99.6%

7. Procedure

Dilution of Calibration Standards and Sample Extracts

7.1 The 10-mL syringe is for diluent (WLISS). The 1-mL syringe is for the MCSS and NH_4OAc extracts (method 4B1a1). Set the digital diluter at a 1:20 dilution. See reagents for preparation of the MCSS (High, Medium, Low, Very Low, and Blank). Dilute 1 part NH_4OAc sample extract with 19 parts of WLISS (1:20 dilution).

7.2 Dispense the diluted sample solutions into test tubes which have been placed in the sample holders of the sample changer.

AAS Set-up and Operation

7.3 Refer to the manufacturer's manual for operation of the AAS. The following are only very general guidelines for instrument conditions for the various analytes.

Analyte	Conc.	Burner & angle	Wavelength	Slit	Fuel/Oxidant (C_2H_2/Air)
	(mg L^{-1})		*(nm)*	*(mm)*	
Ca	9.0	10 cm @ 0°	422.7	0.7	1.5/10.0
Mg	0.75	10 cm @ 0°	285.2	0.7	1.5/10.0
K	2.0	10 cm @ 0°	766.5	0.7	1.5/10.0
Na	10.0	10 cm @ 30°	589.0	0.2	1.5/10.0

7.4 Use the computer and printer to set instrument parameters and to collect and record instrument readings.

AAS Calibration and Analysis

7.5 Calibrate the instrument by using the MCSS (High, Medium, Low, Very Low, and Blank). The data system then associates the concentrations with the instrument responses for each MCSS. Rejection criterion for MCSS is R^2 <0.99.

7.6 If sample exceeds calibration standard, the sample is diluted 1:5, 1:20, 1:100, etc., with 1 *N* NH_4OAc followed by 1:20 dilution with WLISS.

7.7 Perform one quality control (QC) (Low Standard MCSS) every 12 samples. If reading is not within 10%, the instrument is re-calibrated and QC re-analyzed.

7.8 Record analyte readings to 0.01 unit.

8. Calculations

The instrument readings for analyte concentration are in mg L^{-1}. These analyte concentrations are converted to meq 100 g^{-1} as follows:

Soil Analyte Concentration (meq 100 g^{-1}) =

$$\{A \times [(B1 - B2) / B3] \times C \times R \times 100\} / (1000 \times E \times F)$$

where:

A = Analyte (Ca, Mg, 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 cm^{-3})

C = Dilution, if performed

100 = Conversion factor (100-g basis)

R = Air-dry/oven-dry ratio (method 3D1) or field-moist/oven-dry ratio (method 3D2)

1000 = mL L^{-1}

E = Soil sample weight (g)

F = Equivalent weight (mg meq^{-1})

where:

Ca^{+2} = 20.04 mg meq^{-1}

Mg^{+2} = 12.15 mg meq^{-1}

Na^{+1} = 22.99 mg meq^{-1}

K^{+1} = 39.10 mg meq^{-1}

9. Report

Report the extractable Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} to the nearest 0.1 meq 100 g^{-1} (cmol (+) kg^{-1}).

10. Precision and Accuracy

Precision and accuracy data are available from the KSSL upon request.

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)

Displacement after Washing, NH4Cl (4B1b)

Automatic Extractor (4B1b1)

Atomic Absorption Spectrophotometer (4B1b1b)

Calcium, Magnesium, Potassium, and Sodium (4B1b1b1-4)

Air-dry or Field-Moist, <2-mm (4B1b1b1-4a-b1)

1. Application

The extractable bases (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) from the NH_4Cl extraction (method 4B1b1) are generally assumed to be those exchangeable bases on the cation exchange sites of the soil. The abundance of these cations usually occurs in the sequence of $Ca^{2+} > Mg^{2+} > K^{+} > Na^{+}$. Deviation from this usual order signals that some factor or factors, e.g., free $CaCO_3$ or gypsum, serpentine (high Mg^{2+}), or natric material (high Na^{+}), have altered the soil chemistry. The most doubtful cation extractions with this method are Ca^{2+} in the presence of free $CaCO_3$ or gypsum and K^{+} in soils that are dominated by mica or vermiculite (Thomas, 1982).

2. Summary of Method

The NH_4Cl extract from method 4B1b1 is diluted with an ionization suppressant (La_2O_3). The analytes are measured by an atomic absorption spectrophotometer (AAS). The analyte is measured by absorption of the light from a hollow cathode lamp. An automatic sample changer is used to aspirate a series of samples. The AAS converts absorption to analyte concentration. Data are automatically recorded by a microcomputer and printer. The NH_4Cl extracted cations, Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}, are reported in meq 100 g^{-1} soil or (cmol (+) kg^{-1}) in methods 4B1b1b1-4, respectively.

3. Interferences

Four types of interferences (matrix, spectral, chemical, and ionization) affect the analyses of these cations. These interferences vary in importance, depending upon the particular analyte selected. Do not use borosilicate tubes because of potential leaching of analytes.

4. Safety

Wear protective clothing and safety glasses. Exercise special care when preparing reagents. Restrict the use of concentrated HCl to a fume hood. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts.

Follow standard laboratory methods when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene gas is highly 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 AAS.

5. Equipment

5.1 Electronic balance, ±1.0-mg sensitivity

5.2 Atomic absorption spectrophotometer (AAS), double-beam optical system, AAnalyst, 400, Perkin-Elmer Corp., Norwalk, CT

5.3 Autosampler, S-10, Perkin-Elmer Corp., Norwalk, CT

5.4 Computer, with AA WinLab software, Perkin-Elmer Corp., Norwalk, CT, and printer

5.5 Single-stage regulator, acetylene

5.6 Digital diluter/dispenser, with syringes 10,000-µL and 1000-µL, gas tight, Microlab 500, Hamilton Co., Reno, NV

5.7 Plastic test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer

5.8 Containers, polyethylene

5.9 Peristaltic pump

6. Reagents

6.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

6.2 Hydrochloric acid (HCl), concentrated 12 *N*

6.3 HCl, 1:1 HCl:RODI, 6 *N*. Carefully mix 1 part of concentrated HCl to 1 part RODI water.

6.4 Ammonium chloride solution (NH_4Cl), 1 *N*. Dissolve 535 g of NH_4Cl reagent in RODI water and dilute to 10 L.

6.5 Stock lanthanum ionization suppressant solution (SLISS), 65,000 mg L^{-1}. Wet 152.4 g lanthanum oxide (La_2O_3) with 100 mL RODI water. Slowly and cautiously add 500 mL of 6 *N* HCl to dissolve the La_2O_3. Cooling the solution is necessary. Dilute to 2 L with RODI water. Filter solution. Store in polyethylene container.

6.6 Working lanthanum ionization suppressant solution (WLISS), 2000 mg L^{-1}. Dilute 61.5 mL of SLISS with 1800 mL of RODI water (1:10). Dilute to 2 L with RODI water. Store in polyethylene container.

6.7 Primary stock standards solutions (PSSS), high purity, 1000 mg L^{-1}: Ca, Mg, K, and Na.

6.8 Working stock mixed standards solution (WSMSS), High, Medium, Low, Very Low, and Blank. In five 500-mL volumetric flasks, add 250 mL of 2 *N* NH_4Cl and the following designated amounts of Ca PSSS, Mg PSSS, K PSSS, and Na PSSS. Dilute to volume with RODI. Invert to thoroughly mix. Store in polyethylene containers. Prepare fresh weekly. Store in the refrigerator. Allow to equilibrate to room temperature before use. Prepare WSMSS as follows:

6.8.1 High Standard WSMSS: 90 mL Ca PSSS, 7.5 mL Mg PSSS, 20.0 mL K PSSS, and 100.0 mL Na PSSS = 180 mg L^{-1} Ca, 15 mg L^{-1} Mg, 40 mg L^{-1} K, and 200 mg L^{-1} Na

6.8.2 Medium Standard WSMSS: 60 mL Ca PSSS, 5.0 mL Mg PSSS, 10.0 mL K PSSS, and 50.0 mL Na PSSS = 120 mg L^{-1} Ca, 10 mg L^{-1} Mg, 20 mg L^{-1} K, and 100 mg L^{-1} Na

6.8.3 Low Standard WSMSS: 30 mL Ca PSSS, 2.5 mL Mg PSSS, 5.0 mL K PSSS, and 10.0 mL Na PSSS = 60 mg L^{-1} Ca, 5 mg L^{-1} Mg, 10 mg L^{-1} K, and 20 mg L^{-1} Na

6.8.4 Very Low Standard WSMSS: 12.5 mL Ca PSSS, 0.25 mL Mg PSSS, 0.30 mL K PSSS, and 5.0 mL Na PSSS = 25 mg L^{-1} Ca, 0.5 mg L^{-1} Mg, 0.60 mg L^{-1} K, and 10 mg L^{-1} Na

6.8.5 Blank WSMSS: 0 mL of Ca, Mg, K, and Na PSSS

6.9 Mixed calibration standard solutions (MCSS), High, Medium, Low, Very Low, and Blank. Dilute 1 part WSMSS with 19 parts of WLISS (1:20) dilution with resulting concentrations for MCSS as follows:

6.9.1 MCSS High Standard: 9.0 mg L^{-1} Ca, 0.75 mg L^{-1} Mg, 2.0 mg L^{-1} K, and 10.0 mg L^{-1} Na

6.9.2 MCSS Medium Standard: 6.0 mg L^{-1} Ca, 0.5 mg L^{-1} Mg, 1.0 mg L^{-1} K, and 5.0 mg L^{-1} Na

6.9.3 MCSS Low Standard: 3.0 mg L^{-1} Ca, 0.25 mg L^{-1} Mg, 0.5 mg L^{-1} K, and 1.0 mg L^{-1} Na

6.9.4 MCSS Very Low Standard: 1.25 mg L^{-1} Ca, 0.025 mg L^{-1} Mg, 0.030 K, and 0.5 mg L^{-1} Na

6.9.5 Blank MCSS: 0 mg L^{-1} Ca, Mg, K, and Na

6.10 Compressed air with water and oil traps

6.11 Acetylene gas, purity 99.6%

7. Procedure

Dilution of Calibration Standards and Sample Extracts

7.1 The 10-mL syringe is for diluent (WLISS). The 1-mL syringe is for the MCSS and NH_4Cl extracts (method 4B1b). Set the digital diluter at a 1:20 dilution. See reagents for preparation of the MCSS (High, Medium, Low, Very Low, and Blank). Dilute 1 part NH_4Cl sample extract with 19 parts of WLISS (1:20 dilution).

7.2 Dispense the diluted sample solutions into test tubes that have been placed in the sample holders of the sample changer.

AAS Set-up and Operation

7.3 Refer to the manufacturer's manual for operation of the AAS. The following are only very general guidelines for instrument conditions for the various analytes.

Analyte	Conc.	Burner & angle	Wavelength	Slit	Fuel/Oxidant (C_2H_2/Air)
	(mg L^{-1})		*(nm)*	*(mm)*	
Ca	9.0	10 cm @ 0°	422.7	0.7	1.5/10.0
Mg	0.75	10 cm @ 0°	285.2	0.7	1.5/10.0
K	2.0	10 cm @ 0°	766.5	0.7	1.5/10.0
Na	10.0	10 cm @ 30°	589.0	0.2	1.5/10.0

7.4 Use the computer and printer to set instrument parameters and to collect and record instrument readings.

AAS Calibration and Analysis

7.5 Calibrate the instrument by using the MCSS (High, Medium, Low, Very Low, and Blank). The data system then associates the concentrations with the instrument responses for each MCSS. Rejection criterion for MCSS is R^2 <0.99.

7.6 If sample exceeds calibration standard, the sample is diluted 1:5, 1:20, 1:100, etc., with 1 *N* NH_4Cl followed by 1:20 dilution with WLISS.

7.7 Perform one quality control (QC) (Low Standard MCSS) every 12 samples. If reading is not within 10%, the instrument is re-calibrated and QC re-analyzed.

7.8 Record analyte readings to 0.01 unit.

8. Calculations

The instrument readings for analyte concentration are in mg L^{-1}. These analyte concentrations are converted to meq 100 g^{-1} as follows:

Soil Analyte Concentration (meq 100 g^{-1})=

$$\{A \times [(B_1 - B_2)/B_3] \times C \times R \times 100\}/(1000 \times E \times F)$$

where:

A = Analyte (Ca, Mg, K, Na) concentration in extract (mg L^{-1})

B_1 = Weight of extraction syringe and extract (g)

B_2 = Weight of tared extraction syringe (g)

B_3 = Density of 1 *N* NH_4Cl at 20 °C (1.0166 g cm^{-3})

C = Dilution, if performed

100 = Conversion factor (100-g basis)

R = Air-dry/oven-dry ratio (method 3D1) or field-moist/oven-dry ratio (method 3D2)

1000 = mL L^{-1}

E = Soil sample weight (g)

F = Equivalent weight (mg meq^{-1})

where:

Ca^{+2} = 20.04 mg meq^{-1}

Mg^{+2} = 12.15 mg meq^{-1}

Na^{+1} = 22.99 mg meq^{-1}

K^{+1} = 39.10 mg meq^{-1}

9. Report

Report the extractable Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+} to the nearest 0.1 meq 100 g^{-1} (cmol (+) kg^{-1}).

10. Precision and Accuracy

Precision and accuracy data are available from the KSSL upon request.

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.

Soil Test Analyses (4D)

Aqueous Extraction (4D2)

Single-Point Extraction (4D2a)

1:5, 23-h, 1-h (4D2a2)

Cadmium-Copper Reduction (4D2a2c)

Sulfanilamide N-1-Naphthylethylenediamine Dihydrochloride (4D2a1c1)

Flow-Injection, Automated Ion Analyzer (4D2a2c1a)

Nitrate (4D2a2c1a1)

Air-Dry or Field-Moist, <2 mm (4D2a2c1a1a-b1)

1. Application

The 1:5 aqueous extraction of nitrate is used in soil taxonomy as criterion for two taxa of the Gelisols order. The subgroups of Nitric Anhyorthels and Nitric Anhyturbels are defined by a minimum nitrate concentration of 118 mmol (−)/L in a horizon at least 15 cm thick. A additional part of the criterion uses a simple calculation of the nitrate content times the horizon thickness to connote a significant amount of nitrate accumulation. The product of nitrate concentration times thickness (cm) must be ≥3500. Based on this calculation, a horizon that is only 15 cm thick must have a nitrate concentration of 233 mmol (−)/L to qualify, whereas a horizon with a nitrate concentration of only 118 mmol (−)/L must be twice as thick (i.e., 30 cm) to meet the criterion (Soil Survey Staff, 2014).

2. Summary of Method

A 2.5-g soil sample is mechanically shaken for 30 min in 25 mL of reverse osmosis deionized water (RODI). The sample is then filtered through Whatman No. 42 filter paper. A flow injection automated ion analyzer is used to measure the soluble inorganic nitrate (NO_3^-). The nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide followed by coupling with N-1-naphthylethylenediamine dihydrochloride. The resulting water soluble dye has a magenta color, which is read at 520 nm. Absorbance is proportional to the concentration of NO_3^- in the sample. Data are reported as mmol (−) L^{-1} as NO_3^- (4D2a2c1a1).

3. Interferences

Nitrite is oxidized by air to nitrate in a few days. If analysis can be made within 24 h, the sample should be preserved by refrigeration at 4 ºC. When samples must be stored for more than 24 h, they should be preserved with sulfuric acid (2 mL concentrated H_2SO_4 per liter) and refrigerated (LACHAT, 2003). Low results can be obtained for samples that contain high concentration of Fe, Cu, or other metals. In this method, EDTA is added to the buffer to reduce this interference (LACHAT, 2003).

4. Safety

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses). Exercise special care when preparing reagents. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts. Restrict the use of NH_4OH and concentrated HCl to a fume hood. Use safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids. Cadmium is toxic and carcinogenic. Wear gloves and follow the precautions described on the Material Safety Data Sheet. If the cadmium-copper reduction column is repacked, all transfers should be done over a special tray or beaker dedicated to this purpose. Preferably, send the cadmium-copper column to LACHAT for repacking.

5. Equipment

5.1 Electronic balance, ±1.0-mg sensitivity

5.2 Centrifuge tubes, 25-mL, polyethylene, Oak Ridge

5.3 Mechanical reciprocating shaker, 200 oscillations min^{-1}, 1½ in strokes, Eberbach 6000, Eberbach Corp., Ann Arbor, MI

5.4 Centrifuge, 50-mL, polyethylene

5.5 Pipettes, electronic digital, 2500-µL and 10-mL, with tips, 2500-µL and 10-mL

5.6 Filter paper, Whatman 42, 150-mm

5.7 Funnel, 60° angle, long stem, 50-mm diameter

5.8 Volumetric flasks, 1-L and 250-mL

5.9 Bottles, plastic, dark, 1-L

5.10 Cups, plastic

5.11 Dispenser, 30-mL or 10-mL

5.12 Flow Injection Automated Ion Analyzer, QuikChem 8500, LACHAT Instruments, Loveland, CO, with computer and printer

5.13 Sampler, LACHAT Instruments, Loveland, CO

5.14 Reagent Pump, LACHAT Instruments, Loveland, CO

5.15 Automated Dilution Station, LACHAT Instruments, Loveland, CO

5.16 Sample Processing Module (SPM) or channel, QuikChem Method (12-107-04-1-B, nitrate in 1 *M* KCl 0.025 to 20.0 mg N L^{-1}), LACHAT Instruments, Loveland, CO

5.17 Computer, with QuikChem software, LACHAT Instruments, Loveland, CO, and printer

5.18 Vials, plastic, 25-mL (standards)

5.19 Culture tubes, glass, 10-mL (samples)

6. Reagents

6.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

6.2 Helium, compressed gas

6.3 15 *M* NaOH. In a 500-mL container, add 250 mL RODI water. Slowly add 300 g NaOH. (CAUTION: The solution will get very hot!) Swirl until dissolved. Cool and store in a plastic bottle. Use to adjust ammonium chloride buffer to pH 8.5 (Reagent 6.4).

6.4 Ammonium chloride buffer, pH 8.5. In a hood, add 500 mL RODI to a 1-L volumetric flask. Add 105 mL concentrated HCl, 90 mL ammonium hydroxide (NH_4OH), and 1.0 g disodium EDTA. Dissolve and dilute to mark. Invert to mix. Degas with helium ≈5 min.

6.5 Sulfanilamide color reagent. To a 1-L volumetric flask, add 600 mL RODI H_2O followed by 100 mL 85 percent phosphoric acid (H_3PO_4), 40.0 g sulfanilamide, and 1.0 g N-1-naphthylethylenediamine dihydrochloride (NED). Shake to wet and stir to dissolve 20 min. Dilute to mark, invert to thoroughly mix. Degas with helium ≈5 min. Store in dark bottle and discard when pink.

6.6 1 *M* KCl extracting solution, carrier, and standards diluent. Dissolve 74.5 g potassium chloride (KCl) in 800 mL RODI water. Dilute to mark and invert to thoroughly mix. The extracting solution is used also as the carrier and a component of the N standards. Degas with helium ≈5 min.

6.7 The following are standards for a 1-channel system determining $NO_2^- + NO_3^-$ or NO_2^- and a 2-channel system where one channel is used for determining $NO_2^- + NO_3^-$ and the other channel is used for determining NO_2^-. For the 1-channel system, either NO_2^- or NO_3^- standards may be used. It is recommended that when running a 1 channel method for $NO_2^- + NO_3^-$ that NO_3^- standards are used. For the 2-channel system, the use of both $NO_2^- + NO_3^-$ standard sets is recommended.

6.7.1 Stock standard nitrate solution ($SSNO_3S$), 200.0 mg N L^{-1} as NO_3^- in 1 *M* KCl. In a 1-L volumetric flask, dissolve 1.444 g potassium nitrate (KNO_3) (dried in an oven for 2 h at 110 °C) and 74.5 g KCl in 600 mL RODI water. Dilute to mark with RODI water and invert to thoroughly mix. Store in polyethylene containers in a refrigerator. Make fresh weekly.

6.7.2 Working stock standard nitrate solution ($WSSNO_3S$), 20.0 mg N L^{-1} as NO_3^- in 1 *M* KCl. To a 1-L volumetric flask, add 100 mL $SSNO_3S$. Dilute to mark with 1 *M* KCl and invert to thoroughly mix. Make fresh daily.

6.7.3 Standard nitrate calibration standards (SNO_3CS), or working standards, 10.00, 1.00, 0.80, 0.08, and 0.00 mg N L^{-1} as NO_3^- in 1 *M* KCl. Make fresh daily. To five 250-mL volumetric flasks, add as follows:

6.7.3.1 10.00 mg N L^{-1} = 125.0 mL $WSSNO_3S$

6.7.3.2 1.00 mg N L^{-1} = 12.5 mL $WSSNO_3S$

6.7.3.3 0.80 mg N L^{-1} = 10.0 mL $WSSNO_3S$

6.7.3.4 0.08 mg N L^{-1} = 1.00 mL $WSSNO_3S$

6.7.3.5 0.00 mg N L^{-1} = 0.0 mL $WSSNO_3S$ (blank)

Dilute each SNO_3CS to the mark with 1 *M* KCl and invert to thoroughly mix. Do not degas.

6.7.4 Stock standard nitrite solution ($SSNO_2S$), 200.0 mg N L^{-1} as NO_2^- in 1 *M* KCl. In a 1-L volumetric flask, dissolve 74.5 g KCl and either 0.986 g sodium nitrite ($NaNO_2$) or 1.214 g potassium nitrite (KNO_2) in 800 mL RODI water. Dilute to mark with RODI water and invert to thoroughly mix. Store in polyethylene containers in a refrigerator. Make fresh weekly.

6.7.5 Working stock standard nitrite solution ($WSSNO_2S$), 20.0 mg N L^{-1} as NO_2^- in 1 *M* KCl. To a 1-L volumetric flask, add 100 mL $SSNO_2S$. Dilute to mark with 1 *M* KCl and invert to thoroughly mix. Make fresh daily.

6.7.6 Standard nitrite calibration standards (SNO_2CS), or working standards, 10.00, 1.00, 0.80, 0.08, and 0.00 mg N L^{-1} as NO_3^- in 1 *M* KCl. Make fresh daily. To five 250-mL volumetric flasks, add as follows:

6.7.6.1 10.00 mg N L^{-1} = 125.0 mL $WSSNO_2S$

6.7.6.2 1.00 mg N L^{-1} = 12.5 mL $WSSNO_2S$

6.7.6.3 0.80 mg N L^{-1} = 10.0 mL $WSSNO_2S$

6.7.6.4 0.08 mg N L^{-1} = 1.00 mL $WSSNO_2S$

6.7.6.5 0.00 mg N L^{-1} = 0.0 mL $WSSNO_2S$ (blank)

Dilute each SNO_2CS to the mark with 1 *M* KCl and invert to thoroughly mix. Do not degas.

7. Procedure

Extraction

7.1 Weigh 2.5 g of <2-mm or fine-grind, air-dry soil to the nearest mg and place into a 50-mL centrifuge tube. If sample is moist, weigh enough soil to achieve ≈2.5 g of air-dry soil.

7.2 Add ≈25 mL of RODI water to sample. Transfer the sample to a shaker. Shake for 30 min at 200 oscillations min^{-1} at room temperature (20 ±2 °C).

7.3 Remove the sample from the shaker. Decant, filter, and collect extract in receiving cups. If extracts are not to be determined immediately after collection, then store samples at 4 °C. Analyze samples within 24 h.

Flow Injection Set-up and Operation

7.4 Transfer sample extracts into culture tubes and place in sample trays marked “Samples.”

7.5 Transfer working calibration standards into plastic vials and place in descending order in sample trays marked “Standards.”

7.6 Refer to the operating and software reference manuals for LACHAT for set-up and operation. Refer to LACHAT Method QuikChem Method 12-107-04-1-B for data system parameters, such as analyte and calibration data and sampler and valve timing.

7.7 Run samples using calibration curve. Sample concentration is calculated from the regression equations. Report results to the nearest 0.01 unit for the sample extract and each standard nitrogen calibration standard.

7.8 If samples are outside calibration range, dilute samples with extracting solution and re-analyze.

7.9 Upon completion of run, place the transmission lines into RODI water and pump for approximately 20 min before proceeding with the normal shut-down procedure.

7.10 KCl may accumulate and cause clogs in the manifold tubing and the fittings over time. The valves and fittings therefore need to be washed with RODI water upon completion of analysis. Some fittings may need to be soaked overnight or placed in a sonic bath for 10 to 15 min to remove KCl accumulations.

8. Calculations

Convert extract N (mg L^{-1}) to mmol (+) L^{-1} as follows:

Soil N = (A x B) / C

where:

A = Sample extract reading (mg N L^{-1})

B = Dilution, if performed

C = Molecular weight (NO_3^-) = 62.0 mg $mmol^{-1}$

9. Report

Report data to the nearest 0.1 mmol (−) L^{-1} as NO_3^-.

10. Precision and Accuracy

Precision and accuracy data are available from the KSSL upon request.

11. References

LACHAT Instruments. 2003. QuikChem method 12-107-04-1-B, nitrate in 2 M KCl soil extracts by flow injection analysis, 0.025 to 20.0 mg N L^{-1}. LACHAT Instruments, Loveland, CO.

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

Soil Test Analyses (4D)

1 *M* KCl Extraction (4D9)

Cadmium-Copper Reduction (4D9a)

Sulfanilamide N-1-Naphthylethylenediamine Dihydrochloride (4D9a1)

Flow-Injection, Automated Ion Analyzer (4D9a1a)

Nitrate (4D9a1a1)

Air-Dry or Field-Moist, <2 mm (4D9a1a1a-b1)

1. Application

The inorganic combined N in soils is predominantly NH_4^+ and NO_3^- (Keeney and Nelson, 1982). Nitrogen in the form of ammonium ions and nitrate are of particular concern because they are very mobile forms of nitrogen and are most likely to be lost to the environment (National Research Council, 1993). All forms of nitrogen, however, are subject to transformation to ammonium ions and nitrate as part of the nitrogen cycle in agro-ecosystems, and all can contribute to residual nitrogen and nitrogen losses to the environment (National Research Council, 1993).

2. Summary of Method

A 2.5-g soil sample is mechanically shaken for 30 min in 25 mL of 1 *M* KCl solution. The sample is then filtered through Whatman No. 42 filter paper. A flow injection automated ion analyzer is used to measure the soluble inorganic nitrate (NO_3^-). The nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide followed by coupling with N-1-naphthylethylenediamine dihydrochloride. The resulting water soluble dye has a magenta color which is read at 520 nm. Absorbance is proportional to the concentration of NO_3^- in the sample. Data are reported as mg N kg^{-1} soil as NO_3^- (4D9a1a1).

3. Interferences

Nitrite is oxidized by air to nitrate in a few days. If analysis can be made within 24 h, the sample should be preserved by refrigeration at 4 ºC. When samples must be stored for more than 24 h, they should be preserved with sulfuric acid (2 mL concentrated H_2SO_4 per liter) and refrigerated (LACHAT, 2003). Low results can be obtained for samples that contain high concentration of Fe, Cu, or other metals. In this method, EDTA is added to the buffer to reduce this interference (LACHAT, 2003).

4. Safety

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses). Exercise special care when preparing reagents. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts. Restrict the use of NH_4OH and concentrated HCl to a fume hood. Use safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids. Cadmium is toxic and carcinogenic. Wear gloves and follow the precautions described on the Material Safety Data Sheet. If the cadmium-copper reduction column is repacked, all transfers should be done over a special tray or beaker dedicated to this purpose. Preferably, send the cadmium-copper column to LACHAT for repacking.

5. Equipment

5.1 Electronic balance, ±1.0-mg sensitivity

5.2 Centrifuge tubes, 25-mL, polyethylene, Oak Ridge

5.3 Mechanical reciprocating shaker, 200 oscillations min^{-1}, 1½ in strokes, Eberbach 6000, Eberbach Corp., Ann Arbor, MI

5.4 Centrifuge, 50-mL, polyethylene

5.5 Pipettes, electronic digital, 2500-µL and 10-mL, with tips, 2500-µL and 10-mL

5.6 Filter paper, Whatman 42, 150-mm

5.7 Funnel, 60° angle, long stem, 50-mm diameter

5.8 Volumetric flasks, 1-L and 250-mL

5.9 Bottles, plastic, dark, 1-L

5.10 Cups, plastic

5.11 Dispenser, 30-mL or 10-mL

5.12 Flow Injection Automated Ion Analyzer, QuikChem 8500, LACHAT Instruments, Loveland, CO, with computer and printer

5.13 Sampler, LACHAT Instruments, Loveland, CO

5.14 Reagent Pump, LACHAT Instruments, Loveland, CO

5.15 Automated Dilution Station, LACHAT Instruments, Loveland, CO

5.16 Sample Processing Module (SPM) or channel, QuikChem Method (12-107-04-1-B, nitrate in 2 *M* KCl soil extracts by flow injection analysis, 0.025 to 20.0 mg N L^{-1}), LACHAT Instruments, Loveland, CO

5.17 Computer, with QuikChem software, LACHAT Instruments, Loveland, CO, and printer

5.18 Vials, plastic, 25-mL (standards)

5.19 Culture tubes, glass, 10-mL (samples)

6. Reagents

6.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

6.2 Helium, compressed gas

6.3 15 *M* NaOH. In a 500-mL container, add 250 mL RODI water. Slowly add 300 g NaOH. (CAUTION: The solution will get very hot!) Swirl until dissolved. Cool and store in a plastic bottle. Use to adjust ammonium chloride buffer to pH 8.5 (Reagent 6.4).

6.4 Ammonium chloride buffer, pH 8.5. In a hood, add 500 mL RODI to a 1-L volumetric flask. Add 105 mL concentrated HCl, 90 mL ammonium hydroxide (NH_4OH), and 1.0 g disodium EDTA. Dissolve and dilute to mark. Invert to mix. Degas with helium ≈5 min.

6.5 Sulfanilamide color reagent. To a 1-L volumetric flask, add 600 mL RODI H_2O followed by 100 mL 85 percent phosphoric acid (H_3PO_4), 40.0 g sulfanilamide, and 1.0 g N-1-naphthylethylenediamine dihydrochloride (NED). Shake to wet and stir to dissolve 20 min. Dilute to mark and invert to thoroughly mix. Degas with helium ≈5 min. Store in dark bottle and discard when pink.

6.6 1 *M* KCl extracting solution, carrier and standards diluent. Dissolve 74.5 g potassium chloride (KCl) in 800 mL RODI water. Dilute to mark and invert to thoroughly mix. The extracting solution is used also as the carrier and a component of the N standards. Degas with helium ≈5 min.

6.7 The following are standards for a 1-channel system determining $NO_2^- + NO_3^-$ or NO_2^- and a 2-channel system where one channel is used for $NO_2^- + NO_3^-$ and the other channel is used for determining NO_2^-. For the 1-channel system, either NO_2^- or NO_3^- standards may be used. It is recommended that when running a 1 channel method for $NO_2^- + NO_3^-$ that NO_3^- standards are used. For the 2-channel system, the use of both $NO_2^- + NO_3^-$ standard sets are recommended.

6.7.1 Stock Standard Nitrate Solution ($SSNO_3S$), 200.0 mg N L^{-1} as NO_3^- in 1 *M* KCl. In a 1-L volumetric flask, dissolve 1.444 g potassium nitrate (KNO_3) (dried in an oven for 2 h at 110 °C) and 74.5 g KCl in 600 mL RODI water. Dilute to mark with RODI water and invert to thoroughly mix. Store in polyethylene containers. Make fresh weekly. Store in a refrigerator.

6.7.2 Working Stock Standard Nitrate Solution ($WSSNO_3S$), 20.0 mg N L^{-1} as NO_3^- in 1 *M* KCl. To a 1-L volumetric flask, add 100 mL $SSNO_3S$. Dilute to mark with 1 *M* KCl and invert to thoroughly mix. Make fresh daily.

6.7.3 Standard Nitrate Calibration Standards (SNO_3CS), or working standards, 10.00, 1.00, 0.80, 0.08, and 0.00 mg N L^{-1} as NO_3^- in 1 *M* KCl. Make fresh daily. To five 250-mL volumetric flasks, add as follows:

6.7.3.1 10.00 mg N L^{-1} = 125.0 mL $WSSNO_3S$

6.7.3.2 1.00 mg N L^{-1} = 12.5 mL $WSSNO_3S$

6.7.3.3 0.80 mg N L^{-1} = 10.0 mL $WSSNO_3S$

6.7.3.4 0.08 mg N L^{-1} = 1.00 mL $WSSNO_3S$

6.7.3.5 0.00 mg N L^{-1} = 0.0 mL $WSSNO_3S$ (blank)

Dilute each SNO_3CS to the mark with 1 *M* KCl and invert to thoroughly mix. Do not degas.

6.7.4 Stock Standard Nitrite Solution ($SSNO_2S$), 200.0 mg N L^{-1} as NO_2^- in 1 *M* KCl. In a 1-L volumetric flask, dissolve 74.5 g KCl and either 0.986 g sodium nitrite ($NaNO_2$) or 1.214 g potassium nitrite (KNO_2) in 800 mL RODI water. Dilute to mark with RODI water and invert to thoroughly mix. Store in polyethylene containers in a refrigerator. Make fresh weekly.

6.7.5 Working Stock Standard Nitrite Solution ($WSSNO_2S$), 20.0 mg N L^{-1} as NO_2^- in 1 *M* KCl. To a 1-L volumetric flask, add 100 mL

$SSNO_2S$. Dilute to mark with 1 *M* KCl and invert to thoroughly mix. Make fresh daily.

6.7.6 Standard Nitrite Calibration Standards (SNO_2CS), or working standards, 10.00, 1.00, 0.80, 0.08, and 0.00 mg N L^{-1} as NO_3^- in 1 *M* KCl. Make fresh daily. To five 250-mL volumetric flasks, add as follows:

6.7.6.1 10.00 mg N L^{-1} = 125.0 mL $WSSNO_2S$

6.7.6.2 1.00 mg N L^{-1} = 12.5 mL $WSSNO_2S$

6.7.6.3 0.80 mg N L^{-1} = 10.0 mL $WSSNO_2S$

6.7.6.4 0.08 mg N L^{-1} = 1.00 mL $WSSNO_2S$

6.7.6.5 0.00 mg N L^{-1} = 0.0 mL $WSSNO_2S$ (blank)

Dilute each SNO_2CS to the mark with 1 *M* KCl and invert to thoroughly mix. Do not degas.

7. Procedure

Extraction

7.1 Weigh 2.5 g of <2-mm or fine-grind, air-dry soil to the nearest mg and place into a 50-mL centrifuge tube. If sample is moist, weigh enough soil to achieve ≈2.5 g of air-dry soil.

7.2 Add ≈25 mL of 1 *M* KCl to sample. Transfer the sample to a shaker. Shake for 30 min at 200 oscillations min^{-1} at room temperature (20 ±2 °C).

7.3 Remove the sample from the shaker. Decant, filter, and collect extract in receiving cups. If extracts are not to be determined immediately after collection, then store samples at 4 °C. Analyze samples within 24 h.

Flow Injection Set-up and Operation

7.4 Transfer sample extracts into culture tubes and place in sample trays marked “Samples.”

7.5 Transfer WNCS standards into plastic vials and place in descending order in sample trays marked “Standards.”

7.6 Refer to the operating and software reference manuals for LACHAT for set-up and operation. Refer to LACHAT Method QuikChem Method 12-107-04-1-B for data system parameters, such as analyte and calibration data and sampler and valve timing.

7.7 Run samples using calibration curve. Sample concentration is calculated from the regression equations. Report results to the nearest 0.01 unit for the sample extract and each SPCS.

7.8 If samples are outside calibration range, dilute samples with extracting solution and re-analyze.

7.9 Upon completion of run, place the transmission lines into RODI water and pump for approximately 20 min before proceeding with the normal "Shut-down" procedure.

7.10 KCl may accumulate and cause clogs in the manifold tubing and the fittings over time. The valves and fittings therefore need to be washed with RODI water upon completion of analysis. Some fittings may need to be soaked overnight or placed in a sonic bath for 10 to 15 min to remove any KCl accumulations.

8. Calculations

Convert extract N (mg L^{-1}) to soil N (mg kg^{-1}) as follows:

Soil N = (A x B x C x R x 1000) / E

where:

A = Sample extract reading (mg N 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)

1000 = Conversion factor to kg-basis

E = Sample weight (g)

9. Report

Report data to the nearest 0.1 mg N kg^{-1} soil as NO_3^-.

10. Precision and Accuracy

Precision and accuracy data are available from the KSSL upon request.

11. References

Keeney, D.R., and D.W. Nelson. 1982. p. 643–698. Nitrogen–inorganic forms. *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.

LACHAT Instruments. 2003. QuikChem method 12-107-04-1-B, nitrate in 2 *M* KCl soil extracts by flow injection analysis, 0.025 to 20.0 mg N L^{-1}. LACHAT Instruments, Loveland, CO.

National Research Council. 1993. Soil and water quality. An agenda for agriculture. Committee on Long-Range Soil and Water Conservation. Natl. Acad. Press, Washington, DC.

Soil Test Analyses (4D)

Anaerobic Incubation (4D10)

2 *M* KCl Extraction (4D10a)

Ammonia–Salicylate (4D10a1)

Flow Injection, Automated Ion Analyzer (4D10a1a)

N as NH_3 (Mineralizable N) (4D10a1a1)

Air-Dry or Field-Moist, <2 mm (4D10a1a1a-b1)

1. Application

The most satisfactory methods currently available for obtaining an index for the availability of soil N are those involving the estimation of the N formed when soil is incubated under conditions that promote mineralization of organic N by soil microorganisms (USEPA, 1992). The method described herein for estimating mineralizable N is an anaerobic incubation and is suitable for routine analysis of soils. This method involves estimation of the ammonium produced by a 1-week period of incubation of soil at 40 °C (Keeney and Bremner, 1966) under anaerobic conditions to provide an index of N availability.

2. Method Summary

An aliquot of air-dry, homogenized soil is placed in a test tube with water, stoppered, and incubated at 40 °C for 1 week. The contents are rinsed with 2 *M* KCl. A flow injection automated ion analyzer is used to measure the ammonium produced in the soil after incubation. Absorbance of the solution is read at 660 nm. Data are reported as mg N kg^{-1} soil as NH_3 by method 4D10a1a1.

3. Interferences

The temperature and incubation period must remain constant for all samples. The test can be performed on field-moist or air-dry soil samples. Ammonia is volatile and slowly leaves the sample even through polyethylene bottles. Samples should be run within 24 h of extraction. If this cannot be done, the samples should be adjusted to pH 3–5 with dilute sulfuric acid (LACHAT, 2003). The pH of the standards solutions should approximate that of the samples, i.e., if samples have been preserved with sulfuric acid, then the preservation acid should be added in standards preparation (LACHAT, 2003). Remove interfering turbidity by filtration. Soil extracts can contain sufficient concentrations of calcium and magnesium to cause precipitation during analysis. EDTA is added to eliminate this problem (Keeney and Nelson, 1982).

4. Safety

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses) when preparing reagents, especially concentrated acids and bases. Dispense concentrated acids and bases in a fume hood. Thoroughly wash hands after handling reagents. Use safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids.

5. Equipment

5.1 Electronic balance, ±1.0-mg sensitivity

5.2 Test tubes, 16-mm x 150-mm

5.3 PVC stoppers

5.4 Incubator, Model 10-140, Quality Lab Inc., Chicago, IL

5.5 Centrifuge, 50-mL, polyethylene

5.6 Filter paper, Whatman 42, 150-mm

5.7 Funnel, 60° angle, long stem, 50-mm diameter

5.8 Flow Injection Automated Ion Analyzer, QuikChem 8500, LACHAT Instruments, Loveland, CO

5.9 Sampler, LACHAT Instruments, Loveland, CO

5.10 Reagent Pump, LACHAT Instruments, Loveland, CO

5.11 Automated Dilution Station, LACHAT Instruments, Loveland, CO

5.12 Sample Processing Module (SPM) or channel, QuikChem Method (12-107-06-2-A, ammonia (salicylate) in 2 *M* KCl soil extracts, 0.1 to 20.0 mg N L^{-1}), LACHAT Instruments, Loveland, CO

5.13 Computer, with QuikChem software, LACHAT Instruments, Loveland, CO, and printer

5.14 Vials, plastic, 25-mL (standards)

5.15 Culture tubes, glass, 10-mL (samples)

6. Reagents

6.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

6.2 Helium, compressed gas

6.3 Potassium chloride (KCl), 2 *M,* carrier and standards diluent. Dissolve 150 g KCl in RODI water and dilute to 1-L volume. Mix thoroughly. Degas with helium.

6.4 EDTA (ethylene tetraacetic acid disodium salt dihydrate), 6% solution. Dissolve 66 g EDTA in 900 mL RODI water. Dilute to 1 L and invert to mix thoroughly. Degas with helium.

6.5 NaOH, buffer. Dissolve 28.0 g NaOH and 50.0 g sodium phosphate dibasic heptahydrate ($Na_2HPO_4 \cdot 7H_2O$) in 900 mL RODI water. Dilute to 1 L and invert to mix thoroughly. Degas with helium.

6.6 Salicylate-Nitroprusside Color Reagent. Dissolve 150 g sodium salicylate [salicylic acid sodium salt ($C_6H_4(OH)(COO)Na$)] and 1.0 g sodium nitroprusside [sodium nitroferricyanide dihydrate ($Na_2Fe(CN)_5NO \cdot 2H_2O$)] in 800 mL RODI water. Dilute to 1 L and invert to mix thoroughly. Degas with helium. Store in dark bottle in a refrigerator.

6.7 Hypochlorite Reagent. In a 500-mL volumetric, dilute 250 mL of 5.25% sodium hypochlorite (NaOCl) to mark with RODI water. Invert to mix thoroughly. Degas with helium.

6.8 Stock Standard N Solution (SSNS), 100.0 mg N L^{-1}. In a 1-L volumetric flask, dissolve 150 g potassium chloride (KCl) and 0.3819 g of ammonium chloride (NH_4Cl) (dried for 2 h at 110 °C) in about 800 mL RODI water. Dilute to volume with RODI water and invert to thoroughly mix. Do not degas with helium. Store in polyethylene containers. Make fresh weekly. Store in a refrigerator.

6.9 Standard N Calibration Solutions (SNCS), or working standards, 20.0, 8.00, 2.00, 0.50, 0.10, 0.00 mg N L^{-1}. Make fresh daily. To six 250-mL volumetric flasks, add as follows:

6.9.1 20.00 mg P L^{-1} = 50.0 mL SSNS

6.9.2 8.00 mg P L^{-1} = 20.0 mL SSNS

6.9.3 2.00 mg P L^{-1} = 5.0 mL SSNS

6.9.4 0.50 mg P L^{-1} = 1.25 mL SSNS

6.9.5 0.10 mg P L^{-1} = 0.25 mL SSNS

6.9.6 0.00 mg P L^{-1} = 0.0 mL SSNS (blank)

Dilute to mark with 2 M KCl. Invert to mix thoroughly.

7. Procedure

Anaerobic Incubation of Soil Sample

7.1 Weigh 5 g of <2 mm, air-dry soil to the nearest mg into a 16 mm x 150 mm test tube. If soil is fine-grind, weigh 1.25 g. If sample is moist, weigh enough soil to achieve ≈5 or 1.25 g, respectively, of air-dry soil.

7.2 Add 12.5 ±1 mL of RODI water. Do not add ethanol to overcome any wetting difficulties because ethanol interfere with microbial activity. Stopper

the tube, shake, and place in a 40 °C constant-temperature incubator for 7 days. Refer to the manufacturer's instructions for set-up and operation of the incubator.

7.3 At the end of 7 days, remove the tube and shake for 15 s.

7.4 Transfer the contents of the test tube to another test tube. Complete the transfer by rinsing the tube 3 times with 4 mL of 2 *M* KCl, using a total of 12.5 ±1 mL of the KCl. Filter contents into a centrifuge tube. If extracts are not to be determined immediately after collection, then store samples at 4 °C. Analyze samples within 24 h. Ammonia is volatile and slowly leaves the sample, even through the polyethylene bottles.

Flow Injection Set-up and Operation

7.5 Transfer sample extracts into culture tubes and place in XYZ sample trays marked "Samples."

7.6 Transfer WNCS standards into plastic vials and place in descending order in XYZ sample trays marked "Standards."

7.7 Refer to the operating and software reference manuals for LACHAT for set-up and operation. Refer to LACHAT Method QuikChem Method 12-107-06-2-A for data system parameters, such as analyte and calibration data and sampler and valve timing.

7.8 Run samples using calibration curve. Sample concentration is calculated from the regression equations. Report results to the nearest 0.01 unit for the sample extract and each SNCS.

7.9 If samples are outside calibration range, dilute samples with extracting solution and re-analyze.

7.10 Upon completion of run, place the transmission lines into the 1 *M* HCl. Pump the solution for approximately 5 min to remove any precipitated reaction products, and then place the lines in RODI water and pump for an additional 5 min before proceeding with the normal "Shut-down" procedure.

8. Calculations

Convert extract N (mg L^{-1}) to soil N (mg kg^{-1}) as follows:

$$\text{Soil N} = (A \times B \times C \times R \times 1000)/E$$

where:

A = Analyte 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)

1000 = Conversion factor to kg-basis

E = Sample weight (g)

9. Report

Report data to the nearest mg N kg^{-1} soil as NH_3.

10. Precision and Accuracy

Precision and accuracy data are available from the KSSL upon request.

11. References

Keeney, D.R., and J.M. Bremner. 1966. Comparison and evaluation of laboratory methods of obtaining an index of soil nitrogen availability. Agron. J. 58:498–503.

Keeney, D.R., and D.W. Nelson. 1982. p. 643–698. Nitrogen–inorganic forms. *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.

LACHAT Instruments. 2003. QuikChem method (12-107-06-2-A, ammonia (salicylate) in 2 *M* KCl soil extracts by flow injection analysis, 0.1 to 20.0 mg N L^{-1}), LACHAT Instruments, Loveland, CO.

U.S. Environmental Protection Agency (USEPA). 1992. Handbook of laboratory methods for forest health monitoring. G.E. Byers, R.D. Van Remortel, T.E. Lewis, and M. Baldwin (eds.) Part III. Soil analytical laboratory. Section 10. Mineralizable N. U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Las Vegas, NV.

Electrical Conductivity and Soluble Salts (4F)

Saturated Paste (4F2)

Saturated Paste Extraction (4F2c)

Automatic Extractor (4F2c1)

Atomic Absorption Spectrophotometry (4F2c1a)

Calcium, Magnesium, Potassium, and Sodium (4F2c1a1-4)

Air-Dry, <2 mm (4F2c1a1-4a1)

1. Application

The commonly determined soluble cations are Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}. In soils with a low saturation pH, measurable amounts of Fe and Al may be present. Determination of soluble cations is used to obtain the relations between total cation concentration and other properties of saline solutions, such as electrical

conductivity and osmotic pressure (U.S. Salinity Laboratory Staff, 1954). The relative concentrations of the various cations in the soil-water extracts also provide information on the composition of the exchangeable cations in the soil. Complete analyses of the soluble ions provide a means to determine total salt content of the soils and salt content at field moisture conditions.

2. Summary of Method

The saturation extract from method 4F2c1 is diluted with an ionization suppressant (La_2O_3). The analytes are measured by an atomic absorption spectrophotometer (AAS). The data are automatically recorded by a computer and printer. The saturation extracted cations, Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}, are reported in meq L^{-1} (mmol (+) L^{-1}) in methods 4F2c1a1-4, respectively.

3. Interferences

There are four types of interferences (matrix, spectral, chemical, and ionization) in the analysis of these cations. These interferences vary in importance, depending upon the particular analyte selected. Do not use borosilicate tubes because of potential leaching of analytes.

4. Safety

Wear protective clothing and eye protection. Exercise special care when preparing reagents. Restrict the use of concentrated HCl to a fume hood. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts.

Follow standard laboratory procedures when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene is highly 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 AAS.

5. Equipment

5.1 Electronic balance, ±1.0-mg sensitivity

5.2 Atomic absorption spectrophotometer (AAS), double-beam, AAnalyst 400, Perkin-Elmer Corp., Norwalk, CT

5.3 Autosampler, S-10, Perkin-Elmer Corp., Norwalk, CT

5.4 Computer, with AA WinLab software, Perkin-Elmer Corp., Norwalk, CT, and printer

5.5 Single-stage regulator, acetylene

5.6 Digital diluter/dispenser, with syringes 10,000-µL and 1000-µL, gas tight, Microlab 500, Hamilton Co., Reno, NV

5.7 Plastic test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer

5.8 Containers, polyethylene

5.9 Peristaltic pump

6. Reagents

6.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

6.2 Hydrochloric acid (HCl), concentrated 12 *N*

6.3 HCl, 1:1 HCl:RODI, 6 *N*. Carefully mix 1 part of concentrated HCl to 1 part RODI water.

6.4 Stock lanthanum ionization suppressant solution (SLISS), 65,000 mg L^{-1}. Wet 152.4 g of lanthanum oxide (La_2O_3) with 100 mL RODI water. Slowly and cautiously add 500 mL of 6 *N* HCl to dissolve the La_2O_3. Cooling the solution is necessary. Dilute to 2 L with RODI water. Filter solution. Store in polyethylene container.

6.5 Working lanthanum ionization suppressant solution (WLISS), 2000 mg L^{-1}. Dilute 61.5 mL of SLISS with 1800 mL of RODI water (1:10). Make up to volume with RODI water. Invert to mix thoroughly. Store in polyethylene container.

6.6 Primary Stock Standards Solution (PSSS), high purity, 1000 mg L^{-1}: Ca, Mg, K, and Na.

6.7 Working Stock Mixed Standards Solution (WSMSS) for Ca, Mg, and K. In a 500-mL volumetric flask, add 250 mL Ca PSSS, 25 mL Mg PSSS, and 100 mL K PSSS = 500 mg L^{-1} Ca, 50 mg L^{-1} Mg, and 200 mg L^{-1} K. Dilute to volume with RODI water. Invert to thoroughly mix. Store in polyethylene containers. Prepare fresh weekly. Store in the refrigerator.

6.8 Mixed Calibration Standards Solution (MCSS), High, Medium, Low, Very Low, and Blank as follows:

6.8.1 MCSS High Standard (1:100): Dilute WSMSS 1:100 with WLISS. Invert to mix thoroughly mix. Store in polyethylene containers. Prepare fresh weekly. Store in a refrigerator. Allow to equilibrate to room temperature before use. Final concentrations are 5 mg L^{-1} Ca, 0.5 mg L^{-1} Mg, and 2 mg L^{-1} K.

6.8.2 MCSS Medium Standard (1:200): To a 100-mL volumetric flask, add 50 mL of WSMSS and bring to volume with RODI water. Dilute 1:100 with WLISS. Invert to thoroughly mix. Store in polyethylene containers. Prepare fresh weekly. Store in a refrigerator. Allow to equilibrate to room temperature before use. Final concentrations are 2.5 mg L^{-1} Ca, 0.25 mg L^{-1} Mg, and 1 mg L^{-1} K.

6.8.3 MCSS Low Standard (1:400): To a 100-mL volumetric flask, add 25 mL of WSMSS and bring to volume with RODI water. Dilute 1:100 with WLISS. Invert to mix thoroughly. Store in polyethylene containers. Prepare fresh weekly. Store in a refrigerator. Allow to equilibrate to room temperature before use. Final concentrations are 1.25 mg L^{-1} Ca, 0.125 mg L^{-1} Mg, and 0.5 mg L^{-1} K.

6.8.4 MCSS Very Low Standard (1:600): To a 100-mL volumetric flask, add 16.65 mL of WSMSS and bring to volume with RODI water. Dilute 1:100 with WLISS. Invert to mix thoroughly. Store in polyethylene containers. Prepare fresh weekly. Store in a refrigerator. Allow to equilibrate to room temperature before use. Final concentrations are 0.83 mg L^{-1} Ca, 0.08 mg L^{-1} Mg, and 0.33 mg L^{-1} K.

6.8.5 MCSS Blank: 0 mL of Ca, Mg, and K. Dilute RODI water 1:100 with WLISS.

6.9 Na Calibration Standards Solution (NaCSS), High, Medium, Low, and Very Low as follows:

6.9.1 NaCSS High Standard (1:100): Dilute Na PSMSS (1000 mg L^{-1}) 1:100 with WLISS. Invert to thoroughly mix. Store in polyethylene containers. Prepare fresh weekly. Store in a refrigerator. Allow to equilibrate to room temperature before use. Final concentration is 10 mg L^{-1} Na.

6.9.2 NaCSS Medium Standard (1:200): In a 50-mL volumetric, add 25 mL of Na PSMSS and bring to volume with RODI water. Dilute 1:100 with WLISS. Invert to mix thoroughly. Store in polyethylene containers. Prepare fresh weekly. Store in a refrigerator. Allow to equilibrate to room temperature before use. Final concentration is 5 mg L^{-1} Na.

6.9.3 NaCSS Low Standard (1:400): In a 50-mL volumetric flask, add 12.5 mL of PSMSS and bring to volume with RODI water. Dilute 1:100 with WLISS. Invert to thoroughly mix. Store in polyethylene containers. Prepare fresh weekly. Store in a refrigerator. Allow to equilibrate to room temperature before use. Final concentration is 2.5 mg L^{-1} Na.

6.9.4 NaCSS Very Low Standard (1:600): In a 50-mL volumetric flask, add 8.35 mL of PSMSS and bring to volume with RODI water. Dilute 1:100 with WLISS. Invert to thoroughly mix. Store in polyethylene containers. Prepare fresh weekly. Store in a refrigerator. Allow to equilibrate before use. Final concentration is 1.67 mg L^{-1} Na.

6.9.5 NaCSS Blank: 0 mL Na PSMSS. Dilute RODI water 1:100 with WLISS.

6.10 Compressed air with water and oil traps

6.11 Acetylene gas, purity 99.6%

7. Procedure

Dilution of Calibration Standards and Sample Extracts

7.1 The 10-mL syringe is for diluent (WLISS). The 1-mL syringe is for the MCSS and saturation sample extracts (method 4F2c1). Set the digital diluter at a 1:100 dilution. See reagents for the preparation of the MCSS and the NaCSS. Dilute the saturation extract sample with 100 parts of WLISS (1:100).

7.2 Dispense the diluted sample solutions into test tubes that have been placed in the sample holders of the sample changer.

AAS Set-up and Operation

7.3 Refer to the manufacturer's manual for operation of the AAS. The following are only very general guidelines for instrument conditions for the various analytes.

Analyte	Conc.	Burner & angle	Wavelength	Slit	Fuel/Oxidant (C_2H_2/Air)
	(mg L^{-1})		*(nm)*	*(mm)*	
Ca	5.0	10 cm @ 0°	422.7	0.7	1.5/10.0
Mg	0.5	10 cm @ 0°	285.2	0.7	1.5/10.0
K	2.0	10 cm @ 0°	766.5	0.7	1.5/10.0
Na	10.0	10 cm @ 30°	589.0	0.2	1.5/10.0

7.4 Use the computer and printer to set instrument parameters and to collect and record instrument readings.

AAS Calibration and Analysis

7.5 Calibrate the instrument by using the MCSS and NaCSS. The data system then associates the concentrations with the instrument responses for each MCSS. Rejection criterion for MCSS is R^2 <0.99.

7.6 If sample exceeds calibration standard, the sample is diluted 1:5, 1:20, 1:100, etc., with RODI water followed by 1:100 dilution with WLISS.

7.7 Perform one quality control (QC) (Low Standard) for every 12 samples. If reading is not within 10%, the instrument is re-calibrated and QC re-analyzed.

7.8 Record analyte readings to 0.01 mg L^{-1}.

8. Calculations

The instrument readings for analyte concentration are in mg L^{-1}. These analyte concentrations are converted to meq L^{-1} as follows:

Analyte Concentration in Soil (meq L^{-1}) = (A x B) / C

where:

A = Analyte (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}) concentration in extract (mg L^{-1})

B = Dilution ratio, if needed

C = Equivalent weight

where:

Ca^{+2} = 20.04 mg meq^{-1}

Mg^{+2} = 12.15 mg meq^{-1}

Na^{+1} = 22.99 mg meq^{-1}

K^{+1} = 39.10 mg meq^{-1}

9. Report

Report the saturation extraction cations of Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} to the nearest 0.1 meq L^{-1} (mmol (+) L^{-1}).

10. Precision and Accuracy

Precision and accuracy data are available from the KSSL upon request.

11. References

U.S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. L.A. Richards (ed.) U.S. Dept. of Agric. Handb. 60. U.S. Govt. Print. Office, Washington, DC.

Selective Dissolutions (4G)

Dithionite-Citrate Extraction (4G1)

Atomic Absorption Spectrophotometer (4G1a)

Aluminum, Iron, and Manganese (4G1a1-3)

Air-Dry or Field-Moist, <2 mm (4G1a1-3a-b1)

1. Application

Dithionite-citrate (CD) is used as a selective dissolution extractant for organically complexed Fe and Al, noncrystalline hydrous oxides of Fe and Al, and amorphous aluminosilicates (Wada, 1989). The CD solution is a poor extractant of crystalline hydrous oxides of Al, allophane, and imogolite. The CD solution does

not extract opal, Si, or other constituents of crystalline silicate minerals (Wada, 1989).

This extraction is also sometimes referred to as citrate-dithionite or sodium citrate-dithionite. The method (4G1a1-3) described herein is not the same extraction as described in the Soil Survey Investigations Report (SSIR) No. 1 (1972), method 6C3. This obsolete SSL method (6C3) incorporated sodium bicarbonate as a buffer (pH 7.3) in the dithionite-citrate method, resulting in a buffered neutral citrate-bicarbonate-dithionite (Aguilera and Jackson, 1953; Mehra and Jackson, 1960; Jackson, 1969), commonly referred to as the CBD method.

2. Summary of Method

A soil sample is mixed with sodium dithionite, sodium citrate, and reverse osmosis deionized (RODI) water and shaken overnight. Solution is centrifuged, and a clear extract obtained. The CD extract is diluted with RODI water. The analytes are measured by an atomic absorption spectrophotometer (AAS). The data are automatically recorded by a computer and printer. The AAS converts absorption to analyte concentration. The percent CD extractable Al, Fe, and Mn are reported in methods 4G1a1-3, respectively.

3. Interferences

There are four types of interferences (matrix, spectral, chemical, and ionization) in the AAS analyses of these elements. These interferences vary in importance, depending upon the particular analyte selected.

The redox potential of the extractant is dependent upon the pH of the extracting solution and the soil system. Sodium citrate complexes the reduced Fe and usually buffers the system to a pH of 6.5 to 7.3. Some soils may lower the pH, resulting in the precipitation of Fe sulfides.

Filtered extracts can yield different recoveries of Fe, Mn, and Al, relative to unfiltered extracts.

4. Safety

Wear protective clothing (coats, aprons, sleeve guards, and gloves); eye protection (face shields, goggles, or safety glasses); and a breathing filter when handling dry sodium dithionite. Sodium dithionite may spontaneously ignite if allowed to become moist, even by atmospheric moisture. Keep dithionite in a fume hood.

Follow standard laboratory practices when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene gas is highly 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 AAS.

5. Equipment

5.1 Electronic balance, ±1.0-mg sensitivity

5.2 Mechanical reciprocating shaker, 200 oscillations min^{-1}, 1½ in strokes, Eberbach 6000, Eberbach Corp., Ann Arbor, MI

5.3 Atomic absorption spectrophotometer (AAS), double-beam optical system, AAnalyst, 400, Perkin-Elmer Corp., Norwalk, CT, with computer and printer

5.4 Autosampler, AS-93 Plus, Perkin-Elmer Corp., Norwalk, CT

5.5 Peristaltic pump

5.6 Single-stage regulators, acetylene and nitrous oxide

5.7 Centrifuge, Centra, GP-8, Thermo IEC, Needham Heights, MA

5.8 Digital diluter/dispenser, with syringes 10,000-µL and 1000-µL, gas tight, Microlab 500, Hamilton Co., Reno, NV

5.9 Dispenser, 30-mL

5.10 Test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer

5.11 Containers, polypropylene

5.12 Volumetrics, Class A, 100-mL, 250-mL, and 1000-mL

5.13 Measuring scoop, handmade, 0.4 g calibrated

5.14 Centrifuge tubes, 50-mL

6. Reagents

6.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

6.2 Sodium dithionite ($Na_2S_2O_4$), purified powder

6.3 Sodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), crystal, reagent. Dissolve 336 g sodium citrate in approximately 1 L RODI water, followed by diluting to 2 L with RODI water. Final concentration is 0.57 *M* sodium citrate.

6.4 Sulfuric acid (H_2SO_4), concentrated

6.5 Phosphoric acid (H_3PO_4), concentrated (85%). For Fe analysis, samples are diluted 1:50 prior to analysis. A diluting solution for Fe analysis (for a final concentration of 0.5% H_3PO_4 in samples) may be made by adding 6.12 mL of concentrated H_3PO_4 to 500 mL volume of RODI water, diluting to 1000 mL, and mixing thoroughly. (Note: 1:5 sample dilutions for Al and Mn are in RODI water.)

6.6 Primary Stock Standard Solution (PSSS), high purity, 1000 mg L^{-1}: Fe, Mn, and Al.

6.7 Calibration standards for Fe (Section 6.8): To each 100 mL volume of blank, calibration, and quality control (QC) standards, add 25 mL of the following matrix matching mixture. This mixture is made by combining 20 mL Na citrate extracting solution, 0.21 mL H_2SO_4, and 6 mL H_3PO_4 and diluting to 250 mL volume with RODI water. Invert to mix thoroughly. (Note: Matrix of standards is prepared to match a 1:50 dilution of samples. Also, H_2SO_4 substitutes for dithionite.)

6.8 Standard Fe Calibration Solutions (SFeCS), or working standards, (25.0, 20.0, 15.0, 10.0, 5.0, 1.0, and 0.0 mg Fe L^{-1}) and QC (12.5 mg L^{-1}). Prepare fresh weekly. In seven 100-mL volumetric flasks, add as follows:

6.8.1 25.0 mg Fe L^{-1}=2.5 mL $PSSS_{Fe}$

6.8.2 20.0 mg Fe L^{-1}=2.0 mL $PSSS_{Fe}$

6.8.3 15.0 mg Fe L^{-1}=1.5 mL $PSSS_{Fe}$

6.8.4 10.0 mg Fe L^{-1}=1.0 mL $PSSS_{Fe}$

6.8.5 5.0 mg Fe L^{-1}=0.5 mL $PSSS_{Fe}$

6.8.6 1.0 mg Fe L^{-1}=0.1 mL $PSSS_{Fe}$

6.8.7 0.0 mg Fe L^{-1}=0.0 mL $PSSS_{Fe}$ (blank)

6.8.8 12.5 m Fe L^{-1}=1.25 mL $PSSS_{Fe}$ (QC)

Fill to volume with RODI water and invert to mix thoroughly. After dissolution, transfer solution to a plastic bottle.

6.9 Calibration standards for Mn (Section 6.10): To each 100 mL volume of blank, calibration, and quality control (QC) standards, add 25 mL of the following matrix matching mixture. This mixture is made by combining 200 mL Na citrate extracting solution, 2.1 mL H_2SO_4, and diluting to 250-mL volume with RODI water. Invert to mix thoroughly. (Note: Matrix of standards is prepared to match a 1:5 dilution of samples. Also, H_2SO_4 substitutes for dithionite.)

6.10 Standard Mn Calibration Solutions (SMnCS), or working standards, (15.0, 10.0, 5.0, 2.5, 1.5, and 0.0 mg Mn L^{-1}) and QC (6.5 mg L^{-1}). Prepare fresh weekly. In six 100-mL volumetric flasks, add as follows:

6.10.1 15.0 mg Mn L^{-1}=1.5 mL $PSSS_{Mn}$

6.10.2 10.0 mg Mn L^{-1}=1.0 mL $PSSS_{Mn}$

6.10.3 5.0 mg Mn L^{-1}=0.5 mL $PSSS_{Mn}$

6.10.4 2.5 mg Mn L^{-1}=0.25 mL $PSSS_{Mn}$

6.10.5 1.5 mg Mn L^{-1}=0.15 mL $PSSS_{Mn}$

6.10.6 0.0 mg Mn L^{-1}=0.0 mL $PSSS_{Mn}$ (blank)

6.10.7 6.5 mg Mn L^{-1}=0.65 mL $PSSS_{Mn}$ (QC)

Fill to volume with RODI water and invert to mix thoroughly. After dissolution, transfer solution to a plastic bottle.

6.11 Calibration standards for Al (Section 6.12): To each 100 mL volume of blank, calibration, and quality control (QC) standards, add 25 mL of the following matrix matching mixture. This mixture is made by combining 200 mL Na citrate extracting solution, 2.1 mL H_2SO_4, and then diluting to 250-mL volume with RODI water. Invert to mix thoroughly. (Note: Matrix of standards is prepared to match a 1:5 dilution of samples—same as with Mn. Also, H_2SO_4 substitutes for dithionite.)

6.12 Standard Al Calibration Solutions (SAlCS), or working standards, (100.0, 80.0, 60.0, 40.0, 20.0, 10.0, and 0.0 mg Al L^{-1}) and QC (50.0 mg L^{-1}). Prepare fresh weekly. In seven 100-mL volumetric flasks, add as follows:

6.12.1 100.0 mg Al L^{-1} = 10.0 mL $PSSS_{Al}$

6.12.2 80.0 mg Al L^{-1} = 8.0 mL $PSSS_{Al}$

6.12.3 60.0 mg Al L^{-1} = 6.0 mL $PSSS_{Al}$

6.12.4 40.0 mg Al L^{-1} = 4.0 mL $PSSS_{Al}$

6.12.5 20.0 mg Al L^{-1} = 2.0 mL $PSSS_{Al}$

6.12.6 10.0 mg Al L^{-1} = 1.0 mL $PSSS_{Al}$

6.12.7 0.0 mg Al L^{-1} = 0.0 mL $PSSS_{Al}$ (blank)

6.12.8 50.0 mg Al L^{-1} = 5.0 mL $PSSS_{Al}$ (QC)

Fill to volume with RODI water and invert to mix thoroughly. After dissolution, transfer solution to a plastic bottle.

6.13 Acetylene gas, purity 99.6%

6.14 Nitrous oxide, USP

6.15 Compressed air with water and oil traps

7. Procedure

Extraction of Al, Fe, and Mn

7.1 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.

7.2 Add 0.4 g of sodium dithionite (use one calibrated scoop) and 25 mL of sodium citrate solution.

7.3 Cap tubes and shake briefly by hand to dislodge soil from tube bottom. Place tubes in rack.

7.4 Place rack in shaker and shake overnight (12 to 16 h) at 200 oscillations min^{-1} at room temperature (20 ±2 °C).

7.5 Remove tubes from shaker and manually shake tubes to dislodge any soil from cap. Allow samples to sit overnight.

7.6 The following day, centrifuge at 4000 rpm for 15 min. The Fe, Mn, and Al are determined on the AAS from a clear aliquot of solution.

Dilution of Sample Extracts

7.7 No ionization suppressant is required because the Na in the extractant is sufficient in quantity. For a 1:50 dilution of samples for Fe analysis, use the H_3PO_4 diluting solution (see Section 6.5). The dilution of Fe results in a final solution concentration of 0.5% H_3PO_4. Dilute 1 part CD sample extract with 49 parts of H_3PO_4 diluting solution (1:50 dilution).

7.8 A 1:5 dilution in RODI water is used for Al and Mn. Dilute 1 part CD sample extract with 4 parts RODI water.

7.9 Dispense the diluted sample solutions into test tubes that have been placed in the holders of the sample changer.

AAS Set-up and Operation

7.10 Refer to the manufacturer's manual for operation of the AAS. The following are only very general guidelines for instrument conditions for the various analytes.

Analyte	Concen-tration	Wave-length	Burner head	Slit	Fuel/Oxidant
	(mg L^{-1})	*(nm)*		*(mm)*	
Fe	25.0	248.8	10-cm parallel	0.2	3.0 C_2H_2/15.7 Air
Mn	15.0	279.8	10-cm parallel	0.2	3.0 C_2H_2/15.7 Air
Al	100.0	309.3	5-cm parallel	0.7	8.5 C_2H_2/15.7 N_2O

Typical read delay is 3 s, and integration time is 3 s but can vary depending on soil type. Three replicates are average for each sample.

7.11 Use the computer and printer to set instrument parameters and to collect and record instrument readings.

7.12 The instrument readings are programmed to display analyte concentration in mg L^{-1} (ppm).

AAS Calibration and Analysis

7.13 Each element is analyzed during separate runs on the AAS. Use the calibration reagent blank and calibration standards to calibrate the AAS. Calibrations are linear with calculated intercept.

7.14 Use the QC after every 12th sample. It must pass within 15% to continue. If it fails, recalibrate and reread the QC. The QC is also read at the end of each run.

7.15 If samples are outside the calibration range, a serial dilution is performed. A 1:5 dilution of the sample using the calibration blank, followed by the typical dilution (1:5 dilution with RODI water for Al and Mn, and 1:50 dilution with the H_3PO_4 diluting solution for Fe). Maintain matrix match between standards and diluted samples by performing this extra dilution with calibration blank.

7.16 Record analyte readings to 0.01 unit.

8. Calculations

Convert analyte concentrations (mg L^{-1}) to percent in soil as follows:

Soil Fe, Al, Mn (%) = (A x B x C x R x 100) / (E x 1000)

where:

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

1000 = mg g^{-1}

9. Report

Report percent CD extractable Al, Fe, and Mn to the nearest 0.1 of a percent.

10. Precision and Accuracy

Precision and accuracy data are available from the KSSL upon request.

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.

Mehra, O.P., and M.L. Jackson. 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. Clays Clay Miner. 7:317–327.

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

Wada, K. 1989. Allophane and imogolite. p. 1051–1087. In J.B. Dixon and S.B. Weed (eds.) Minerals in soil environments. 2nd ed. Soil Sci. Am. Book Series No. 1. ASA and SSSA, Madison, WI.

Ground and Surface Water Analyses (4l)

Electrical Conductivity and Salts (4l2)

Atomic Absorption Spectrophotometer (4l2b)

Calcium, Magnesium, Potassium, and Sodium (4l2b1-4)

1. Application

Nutrients (nitrogen and phosphorus), sediments, pesticides, salts, or trace elements in ground 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. Summary of Method

The water sample is filtered and diluted with an ionization suppressant (La_2O_3). The analytes are measured by an atomic absorption spectrophotometer (AAS). The data are automatically recorded by a computer and printer. The saturation extracted cations Ca^{2+}, Mg^{2+}, K^+, and Na^+ are reported in meq L^{-1} (mmol (+) L^{-1}) in methods 4l2b1-4, respectively.

3. Interferences

There are four types of interferences (matrix, spectral, chemical, and ionization) in the analysis of these cations. These interferences vary in importance, depending upon the particular analyte selected. Do not use borosilicate tubes because of potential leaching of analytes.

4. Safety

Wear protective clothing and eye protection. Exercise special care when preparing reagents. Restrict the use of concentrated HCl to a fume hood. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts.

Follow standard laboratory procedures when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene is highly 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 AAS.

5. Equipment

5.1 Electronic balance, ±1.0-mg sensitivity

5.2 Syringe filters, 0.45-µm diameter, Whatman, Clifton, NJ

5.3 Tubes, 50-mL, with caps

5.4 Atomic absorption spectrophotometer (AAS), double-beam, AAnalyst 400, Perkin-Elmer Corp., Norwalk, CT

5.5 Autosampler, S-10, Perkin-Elmer Corp., Norwalk, CT

5.6 Computer, with AA WinLab software, Perkin-Elmer Corp., Norwalk, CT, and printer

5.7 Single-stage regulator, acetylene

5.8 Digital diluter/dispenser, with syringes 10,000-µL and 1000-µL, gas tight, Microlab 500, Hamilton Co., Reno, NV

5.9 Plastic test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer

5.10 Containers, polyethylene

5.11 Peristaltic pump

6. Reagents

6.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

6.2 Hydrochloric acid (HCl), concentrated 12 *N*

6.3 HCl, 1:1 HCl:RODI, 6 *N*. Carefully mix 1 part of concentrated HCl to 1 part RODI water.

6.4 Stock Lanthanum Ionization Suppressant Solution (SLISS), 65,000 mg L^{-1}. Wet 152.4 g of lanthanum oxide (La_2O_3) with 100 mL RODI water. Slowly and cautiously add 500 mL of 6 *N* HCl to dissolve the La_2O_3. Cooling the solution is necessary. Dilute to 2 L with RODI water. Filter solution. Store in polyethylene container.

6.5 Working Lanthanum Ionization Suppressant Solution (WLISS), 2000 mg L^{-1}. Dilute 61.5 mL of SLISS with 1800 mL of RODI water (1:10). Make to 2-L volume with RODI water. Invert to mix thoroughly. Store in polyethylene container.

6.6 Primary Stock Standards Solution (PSSS), high purity, 1000 mg L^{-1}: Ca, Mg, K, and Na.

6.7 Working Stock Mixed Standards Solution (WSMSS) for Ca, Mg, and K. In a 500-mL volumetric flask, add 250 mL Ca PSSS, 25 mL Mg PSSS, and 100 mL K PSSS = 500 mg L^{-1} Ca, 50 mg L^{-1} Mg, and 200 mg L^{-1} K. Dilute

to volume with RODI water. Invert to thoroughly mix. Store in polyethylene containers. Prepare fresh weekly. Store in the refrigerator.

6.8 Mixed Calibration Standards Solution (MCSS), High, Medium, Low, Very Low, and Blank as follows:

6.8.1 MCSS High Standard (1:100): Dilute WSMSS 1:100 with WLISS. Invert to mix thoroughly mix. Store in polyethylene containers. Prepare fresh weekly. Store in a refrigerator. Allow to equilibrate to room temperature before use. Final concentrations are 5 mg L^{-1} Ca, 0.5 mg L^{-1} Mg, and 2 mg L^{-1} K.

6.8.2 MCSS Medium Standard (1:200): To a 100-mL volumetric flask, add 50 mL of WSMSS and bring to volume with RODI water. Dilute 1:100 with WLISS. Invert to thoroughly mix. Store in polyethylene containers. Prepare fresh weekly. Store in a refrigerator. Allow to equilibrate to room temperature before use. Final concentrations are 2.5 mg L^{-1} Ca, 0.25 mg L^{-1} Mg, and 1 mg L^{-1} K.

6.8.3 MCSS Low Standard (1:400): To a 100-mL volumetric flask, add 25 mL of WSMSS and bring to volume with RODI water. Dilute 1:100 with WLISS. Invert to mix thoroughly. Store in polyethylene containers. Prepare fresh weekly. Store in a refrigerator. Allow to equilibrate to room temperature before use. Final concentrations are 1.25 mg L^{-1} Ca, 0.125 mg L^{-1} Mg, and 0.5 mg L^{-1} K.

6.8.4 MCSS Very Low Standard (1:600): To a 100-mL volumetric flask, add 16.65 mL of WSMSS and bring to volume with RODI water. Dilute 1:100 with WLISS. Invert to mix thoroughly. Store in polyethylene containers. Prepare fresh weekly. Store in a refrigerator. Allow to equilibrate to room temperature before use. Final concentrations are 0.83 mg L^{-1} Ca, 0.08 mg L^{-1} Mg, and 0.33 mg L^{-1} K.

6.8.5 MCSS Blank: 0 mL of Ca, Mg, and K. Dilute RODI water 1:100 with WLISS.

6.9 Na Calibration Standards Solution (NaCSS), High, Medium, Low, and Very Low as follows:

6.9.1 NaCSS High Standard (1:100): Dilute Na PSMSS (1000 mg L^{-1}) 1:100 with WLISS. Invert to thoroughly mix. Store in polyethylene containers. Prepare fresh weekly. Store in a refrigerator. Allow to equilibrate to room temperature before use. Final concentration is 10 mg L^{-1} Na.

6.9.2 NaCSS Medium Standard (1:200): In a 50-mL volumetric, add 25 mL of Na PSMSS and bring to volume with RODI water.

Dilute 1:100 with WLISS. Invert to mix thoroughly. Store in polyethylene containers. Prepare fresh weekly. Store in a refrigerator. Allow to equilibrate to room temperature before use. Final concentration is 5 mg L^{-1} Na.

6.9.3 NaCSS Low Standard (1:400): In a 50-mL volumetric flask, add 12.5 mL of PSMSS and bring to volume with RODI water. Dilute 1:100 with WLISS. Invert to thoroughly mix. Store in polyethylene containers. Prepare fresh weekly. Store in a refrigerator. Allow to equilibrate to room temperature before use. Final concentration is 2.5 mg L^{-1} Na.

6.9.4 NaCSS Very Low Standard (1:600): In a 50-mL volumetric flask, add 8.35 mL of PSMSS Na (1000 ppm) and bring to volume with RODI water. Dilute 1:100 with WLISS. Invert to thoroughly mix. Store in polyethylene containers. Prepare fresh weekly. Store in a refrigerator. Allow to equilibrate before use. Final concentration is 1.67 mg L^{-1} Na.

6.9.5 NaCSS Blank: 0 mL Na PSMSS. Dilute RODI water 1:100 with WLISS.

6.10 Compressed air with water and oil traps

6.11 Acetylene gas, purity 99.6%

7. Procedure

7.1 Water sample is filtered into a 50-mL tube and capped. If extracts are not to be determined immediately after collection, then store samples at 4 °C. Analyze samples within 72 h.

Dilution of Calibration Standards and Sample Extracts

7.2 The 10-mL syringe is for diluent (WLISS). The 1-mL syringe is for the MCSS and water sample. Set the digital diluter at a 1:100 dilution. See Sections 6.8 and 6.9 for preparation of the MCSS and NaCSS. Dilute the saturation extract sample with 100 parts of WLISS (1:100).

7.3 Dispense the diluted sample solutions into test tubes that have been placed in the sample holders of the sample changer.

AAS Set-up and Operation

7.4 Refer to the manufacturer's manual for operation of the AAS. The following are only very general guidelines for instrument conditions for the various analytes.

Analyte	Conc.	Burner & angle	Wavelength	Slit	Fuel/Oxidant (C_2H_2/Air)
	(mg L^{-1})		*(nm)*	*(mm)*	
Ca	5.0	10 cm @ 0 °	422.7	0.7	1.5/0.0
Mg	0.5	10 cm @ 0 °	285.2	0.7	1.5/10.0
K	2.0	10 cm @ 0 °	766.5	0.7	1.5/10.0
Na	10.0	10 cm @ 30 °	589.0	0.2	1.5/10.0

7.5 Use the computer and printer to set instrument parameters and to collect and record instrument readings.

AAS Calibration and Analysis

7.6 Calibrate the instrument by using the MCSS and NaCSS. The data system then associates the concentrations with the instrument responses for each MCSS and NaCSS. Rejection criterion for MCSS and NaCSS is R^2 <0.99.

7.7 If sample exceeds calibration standard, the sample is diluted 1:5, 1:20, 1:100, etc., with RODI water followed by 1:100 dilution with WLISS.

7.8 Perform one quality control (QC) (Low Standard) for every 12 samples. If reading is not within 10%, the instrument is re-calibrated and QC re-analyzed.

7.9 Record analyte readings to 0.01 mg L^{-1}.

8. Calculations

The instrument readings for analyte concentration are in mg L^{-1}. These analyte concentrations are converted to meq L^{-1} as follows:

Analyte Concentration in Soil (meq L^{-1}) = (A x B) / C

where:

A = Analyte (Ca, Mg, K, Na) concentration in extract (mg L^{-1})

B = Dilution ratio, if needed

C = Equivalent weight

where:

Ca^{+2} = 20.04 mg meq^{-1}

Mg^{+2} = 12.15 mg meq^{-1}

K^{+1} = 39.10 mg meq^{-1}

Na^{+1} = 22.99 mg meq^{-1}

9. Report

Report the saturation extraction cations Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+} to the nearest 0.1 meq L^{-1} (mmol (+) L^{-1}).

10. Precision and Accuracy

Precision and accuracy data are available from the KSSL upon request.

11. References

National Research Council. 1993. Soil and water quality. An agenda for agriculture. Natl. Acad. Press, Washington, DC.

OBSOLETE METHODS SECTION II: SSIR NO. 42, SOIL SURVEY LABORATORY METHODS MANUAL, VERSION 4.0 (2004)

SAMPLE COLLECTION AND PREPARATION (1)

Laboratory Sample Collection and Preparation (1B)
Soils (1B1)
Soil Bulk Sample Preparation (1B1b)
Air-Dry Preparation (1B1b2)
<2-mm Fraction (1B1b2b)
Presence of Carbonates (1B1b2b5)

7.32 Use a sub-sample of the ADOD sample (method 1B1b2b4) and check for the presence of carbonates. Reference samples (knowns) are available for comparisons. Place 1 g of the air-dry fine-earth fraction in porcelain spot plate, add reverse osmosis water, and stir to remove entrapped air. Add 1 *N* HCl to soil, observe amount of effervescence, and record as follows:

None.—No visual effervescence.

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. Do not mistake trapped air bubbles for a positive test. Generally, these air bubbles appear immediately after the addition of 1 *N* HCl.

Slight.—More small bubbles, and possibly a few larger bubbles, appear throughout the sample than with a *very slight* reaction.

Strong.—More large bubbles are evident than with a *slight* reaction. Often the reaction is violent at first and then quickly decreases to a reaction that produces many small bubbles.

Violent.—The sample effervesces violently. Many large bubbles appear to burst from the spot plate.

SOIL AND WATER CHEMICAL EXTRACTIONS AND ANALYSES (4)

Ion Exchange and Extractable Cations (4B)

$BaCl_2$-Triethanolamine, pH 8.2 Extraction (4B2)

Automatic Extractor (4B2a)

Automatic Titrator (4B2a1)

Back Titration with HCl (4B2a1a)

Extractable Acidity (4B2a1a1)

Air-Dry or Field-Moist, <2 mm (4B2a1a1a-b1)

1. Application

The extractable acidity is the acidity released from the soil by a barium chloride-triethanolamine ($BaCl_2$-TEA) solution buffered at pH 8.2 and includes all the acidity generated by replacement of the H and Al from permanent and pH dependent exchange sites. Extractable acidity may be measured at any pH, and a variety of methods have been used to measure it. The Soil Conservation Service adopted a pH of 8.2 because it 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. Although other pH values are valid for some types of soils, and the $BaCl_2$-TEA, pH 8.2 method (4B2a1a1) may not always accurately reflect the nature of soils as they occur in the environment, this method has become a standard reference to which other methods are compared.

2. Summary of Method

A soil sample is leached with a $BaCl_2$-TEA solution buffered at pH 8.2. Sample is allowed to stand overnight and extracted using a mechanical vacuum extractor (Holmgren et al., 1977). The extract is back-titrated with HCl. The difference between a blank and the extract is the extractable acidity. Extractable acidity is reported in meq 100 g^{-1} soil or (cmol (+) kg^{-1}).

3. Interferences

No significant interferences are known to exist with this method. However, for some very acid soils, the buffer capacity of the $BaCl_2$-TEA solution may be exceeded.

4. Safety

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses) when preparing reagents, especially concentrated acids and bases. Dispense concentrated acids in a fume hood. Thoroughly wash hands after handling reagents. Use the safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids.

5. Equipment

5.1 Electronic balance, ±1.0-mg sensitivity

5.2 Mechanical vacuum extractor, 24 place, Sampletek, Mavco Industries, Lincoln, NE

5.3 Pipettes or dispenser, adjustable volume to 20 mL

5.4 Titration beakers, 250-mL, plastic, Metrohm Ltd., Brinkmann Instruments Inc.

5.5 Automatic titrator, with control unit, sample changer, and dispenser, Metrohm Ltd., Brinkmann Instruments, Inc.

5.6 Combination pH-reference electrode, Metrohm Ltd., Brinkmann Instruments, Inc.

5.7 Computer, with Titrino Workcell software, Metrohm Ltd., Brinkmann Instruments, Inc., and printer

5.8 Titration beakers, 250-mL, plastic, Metrohm Ltd., Brinkmann Instruments Inc.

5.9 Tubes, 60-mL, polypropylene, for extraction, with 0.45-µm filter

5.10 Rubber tubing, 3.2 ID x 6.4 OD x 25.4 mm, (⅛ ID x $^1/_{16}$ OD x 1 in) for connecting syringe barrels

6. Reagents

6.1 Reverse osmosis deionized (RODI) water

6.2 Reverse osmosis (RO) water

6.3 Hydrochloric acid (HCl), concentrated, 12 *N*

6.4 HCl, 0.13 *N*, standardized. Dilute 193 mL of concentrated HCl to 16-L volume with RODI water.

6.5 Buffer solution [0.5 *N* $BaCl_2$, 0.2 *N* Triethanolamine (TEA), pH 8.2]. Dissolve 977 g of $BaCl_2 \cdot 2H_2O$ in 8 L of RODI water. Dissolve 477 g of TEA in 4 L of RODI water. Mix two solutions and bring to nearly 16-L volume with RODI water. Adjust to pH 8.2 with ≈33 mL of concentrated HCl or barium hydroxide. Bring to 16-L volume with RODI water.

6.6 Replacement solution. Dissolve 977 g of $BaCl_2 \cdot 2H_2O$ in 8 L of RODI water. Add 80 mL of buffer solution and dilute 16-L volume with RODI water.

7. Procedure

Extraction of Acidity

7.1 Weigh 2.5 g of <2-mm or fine-grind, air-dry soil to the nearest mg and place in a labeled extraction (ET_1). If sample is moist, weigh enough soil

to achieve ≈2.5 g of air-dry soil. Prepare at least one reagent blank (no sample in syringe) and one quality control check sample per 24 samples.

7.2 Place labeled ET on extractor and connect to corresponding extraction tube ($ET_{Acidity}$) with rubber tubing.

7.3 Use a dispenser to add 20.00 mL of $BaCl_2$-TEA solution to the ET_1. During the addition, wash the sides of the tube and wet the sample. For organic soils, shaking, swirling, or stirring may be required to wet the sample.

7.4 Let ET_1 tube stand overnight.

7.5 Set the extractor for a 30-min extraction rate. Extract solution to a 0.5- to 1.0-cm height above the sample. Turn off the extractor. Do not allow the sample to become dry.

7.6 Use a dispenser to add 20.00 mL of replacement solution to ET_1. Extract the sample at 30-min rate, pulling the solution almost completely through the sample.

7.7 Add a second 20.00-mL aliquot of replacement solution to ET_1. Extract at 30-min rate until all the solution has been drawn through the sample.

7.8 Carefully remove $ET_{Acidity}$. Leave rubber tubing on the ET_1.

Titration of $BaCl_2$-TEA Extract

7.9 Transfer the $BaCl_2$-TEA extract from the $ET_{Acidity}$ to a 250-mL polyethylene titration beaker.

7.10 Add 100 mL of RO water to the beaker. The solution is ready to be titrated.

7.11 Refer to manufacturer's manual for operation of the automatic titrator.

7.12 Calibrate automatic titrator with 9.18, 7.00, and 4.00 pH 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 4.60
Dyn change pH	1.5 units
Drift	0.4 mV s^{-1}
Time delay	10 s
Drift	0.4 mV s^{-1}
Temp	25 °C
Stop volume	75 mL

7.13 If pre-titration pH is 0.3 units lower than the average pH of the blanks, re-run using a 0.25 g sample.

7.14 Record the titer to the nearest 0.01 mL. Record the normality of the HCl solution. Average the titer of the reagent blanks and record.

8. Calculations

Extractable acidity (meq 100 g^{-1}) = {[(B − T) x *N* x R] / C} x 100

where:

B = Average reagent blank titer (mL)

T = Sample titer (mL)

N = Normality of HCl

C = Sample weight (g)

100 = Conversion factor (100-g basis)

R = Air-dry/oven-dry ratio (method 3D1) or field-moist/oven-dry ratio (method 3D2)

9. Report

Report extractable acidity to the nearest 0.1 meq 100 g^{-1} (cmol (+) kg^{-1}).

10. Precision and Accuracy

Precision and accuracy data are available from the KSSL upon request.

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.

Soil Test Analyses (4D)

Aqueous Extraction (4D2)

Single-Point Extraction (4D2a)

1:10, 30 min (4D2a1)

Flow Injection, Automated Ion Analyzer (4D2a1b)

Phosphorus (4D2a1b1)

Air-Dry or Field-Moist, <2 mm (4D2a1b1a-b1)

1. Application

Phosphorus occurs in soil in both the solution and solid phase. These forms are well documented, but questions still remain concerning the exact nature of the constituents and ionic forms found in water, soils, and sediments (National Research Council, 1993). These forms influence P availability in relation to root absorption and plant growth; runoff and water quality problems; and P loadings.

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, there is evidence that some organic P is also included (Rigler, 1968).

The water or dilute salt extracts represent an attempt to approximate the soil solution P concentration. As an index of P availability, the objectives of this method are (1) to determine the P concentration level in the soil extract that limits plant growth (Olsen and Sommers, 1982) and (2) to determine the composition of the soil solution so that the chemical environment of the plant roots may be defined in quantitative terms (Adams, 1974). The sum of water soluble P and pH 3 extractable P has also been defined as the available P in runoff (Jackson, 1958).

2. Summary of Method

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 (RODI). The sample is then centrifuged until solution is free of soil mineral particles and then filtered until clear extracts are obtained.

A flow injection automated ion analyzer is used to measure the orthophosphate ion (PO_4^{3-}). This ion reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex. This complex is reduced with ascorbic acid to form a blue complex which absorbs light at 880 nm. Absorbance is proportional to the concentration of PO_4^{3-} in the sample. Data are reported as mg P kg^{-1} soil (4D2a1b1).

3. Interferences

Silica forms a pale blue complex which also absorbs at 880 nm. This interference is generally insignificant as a Si concentration of approximately 30 mg SiO_2 L^{-1} would be required to produce a 0.005 mg P L^{-1} positive error in orthophosphate (LACHAT, 1993).

Glassware contamination is a problem in low-level P determinations. Glassware should be washed with 1:1 HCl and rinsed with deionized water. Commercial detergents should rarely be needed but, if they are used, use P-free preparation for lab glassware (LACHAT, 1993).

Concentrations of ferric ion >50 mg L^{-1} will cause a negative error due to competition with the complex for the reducing agent ascorbic acid. Samples high in Fe can be pretreated with sodium bisulfite to eliminate this interference. Treatment with bisulfite will also remove the interference due to arsenates (LACHAT, 1993).

4. Safety

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses). When preparing reagents, exercise special care. Many metal salts are extremely toxic and may be fatal if

ingested. Thoroughly wash hands after handling these metal salts. Restrict the use of concentrated H_2SO_4 and HCl to a fume hood. Use safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids.

5. Equipment

5.1 Electronic balance, ±1.0-mg sensitivity

5.2 Centrifuge tubes, 50-mL, polyethylene

5.3 Mechanical reciprocating shaker, 200 oscillations min^{-1}, 1½ in strokes, Eberbach 6000, Eberbach Corp., Ann Arbor, MI

5.4 Centrifuge, Centra GP-8, Thermo IEC, Needham Heights, MA

5.5 Filter paper, Whatman No. 42, 150 mm

5.6 Funnel, 60° angle, long stem, 50-mm diameter

5.7 Volumetric flasks, 1-L and 250-mL

5.8 Bottles, plastic, dark, 1-L

5.9 Cups, plastic

5.10 Flow Injection Automated Ion Analyzer, QuikChem AE, LACHAT Instruments, Milwaukee, WI, with computer and printer

5.11 XYZ Sampler, LACHAT Instruments, Milwaukee, WI

5.12 Reagent Pump, LACHAT Instruments, Milwaukee, WI

5.13 Automated Dilution Station, LACHAT Instruments, Milwaukee, WI

5.14 Sample Processing Module (SPM) or channel, QuikChem Method (10-115-01-1-A, orthophosphate in waters, 0.01 to 2.0 mg P L^{-1}), LACHAT Instruments, Milwaukee, WI

5.15 Computer, with QuikChem software, LACHAT Instruments, Milwaukee, WI, and printer

5.16 Pipettes, electronic digital, 2500 µL and 10 mL, with tips, 2500 µL and 10 mL

5.17 Vials, plastic, 25-mL (standards)

5.18 Culture tubes, glass, 10-mL (samples)

5.19 Dispenser, 30 mL or 10 mL

6. Reagents

6.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

6.2 Helium, compressed gas

6.3 Sulfuric acid (H_2SO_4), concentrated, 36 *N*, trace pure grade

6.4 Stock ammonium molybdate solution. In 1-L volumetric flask dissolve 40.0 g ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$] in approximately 800 mL RODI water. Dilute to the mark with RODI water and invert to thoroughly mix. Stir for 4 h. Store in plastic and refrigerate.

6.5 Stock antimony potassium tartrate solution. In 1-L flask, dissolve 3.0 g antimony potassium tartrate (potassium antimony tartrate hemihydrate [$K(SbO)C_4H_4O_6\bullet ½H_2O$] in approximately 800 mL RODI water. Dilute to the mark and invert to thoroughly mix. Store in dark bottle and refrigerate.

6.6 Molybdate color reagent. In 1-L volumetric flask, add about 500 mL RODI water, then add 35.0 mL concentrated sulfuric acid (CAUTION: The solution will get very hot!) Swirl to mix. When it can be comfortably handled, add 72 mL stock antimony potassium tartrate solution and 213 mL stock ammonium molybdate solution. Dilute to volume with RODI water and invert three times. Degas with helium ≈5 min.

6.7 Ascorbic acid reducing solution. In 1-L volumetric flask, dissolve 60.0 g ascorbic acid in about 700 mL RODI water. Dilute to volume with RODI water and invert three times. Degas with helium ≈5 min. Optional: After dilution to volume and degassing, dissolve 1.0 g dodecyl sulfate ($CH_3(CH_2)_{11}OSO_3Na$). Prepare fresh weekly.

6.8 Sodium hydroxide-EDTA rinse. Dissolve 65 g sodium hydroxide (NaOH) and 6 g tetrasodium ethylenediamine tetraacetic acid (Na_4EDTA) in 1.0 L RODI water.

6.9 Stock standard P solution (SSPS), 100.0 mg P L^{-1} (ppm). In a 1-L volumetric flask, dissolve 0.4394 g primary standard grade anhydrous potassium dihydrogen phosphate (KH_2PO_4) that has been dried for 2 h at 110 °C in about 800 mL RODI water. Dilute to volume and invert to thoroughly mix. Do not degas. Store in polyethylene containers. Make fresh weekly. Store in a refrigerator.

6.10 Working stock standard P solution (WSSPS), 10.0 mg P L^{-1}. In a 1-L volumetric flask, dilute 100.0 mL SSPS to mark with RODI water. Invert to thoroughly mix. Make fresh daily.

6.11 Standard P calibration solutions (SPCS) or working standards, 2.0, 1.0, 0.5, 0.20, 0.05, 0.01, and 0.00 mg P L^{-1}. Make fresh daily. To seven 250-mL volumetric flasks add as follows:

6.11.1 2.0 mg P L^{-1} = 50.0 mL WSSPS

6.11.2 1.0 mg P L^{-1} = 25.0 mL WSSPS

6.11.3 0.5 mg P L^{-1} = 12.5 ml WSSPS

6.11.4 0.20 mg P L^{-1} = 5.0 mL WSSPS

6.11.5 0.05 mg P L^{-1} = 1.25 mL WSSPS

6.11.6 0.01 mg P L^{-1} = 0.25 mL WSSPS

6.11.7 0.00 mg P L^{-1} = 0 mL WSSPS (blank)

Dilute each SPCS to the mark with RODI water and invert to thoroughly mix. Do not degas.

7. Procedure

7.1 Weigh 2.5 g of <2-mm or fine-grind, air-dry soil to nearest mg on an electronic balance and place into a 50-mL centrifuge tube. If sample is moist, weigh enough soil to achieve ≈2.5 g of air-dry soil.

7.2 Add 25.0 mL of RODI water to sample. Transfer the sample to the shaker. Shake for 30 min at 200 oscillations min^{-1} at room temperature (20 °C ±2 °C).

7.3 Remove the sample from the shaker. Centrifuge at 2000 rpm for 10 min. Decant, filter, and collect extract in receiving cup.

7.4 Transfer sample extracts into culture tubes and place in XYZ sample trays marked “Samples”. If extracts are not to be determined immediately after collection, then store samples at 4 °C. Analyze samples within 24 h.

7.5 Transfer SPCS standards into plastic vials and place in descending order in XYZ sample trays marked “Standards”.

7.6 Refer to the operating and software reference manuals for LACHAT set-up and operation.

7.7 Turn main power switch “ON” and allow 15 min for heater module to warm up to 37 °C.

7.8 On reagent pump, set speed to 35. Pump RODI water through system for 20 min.

7.9 On computer main menu, select “Methods” and then “Analysis Select and Download.” On method list, select water soluble P method. System unit receives the downloaded method and initializes it.

7.10 Pump reagents into manifold. Continue this step and observe baseline. A good baseline needs to be smooth and at zero absorbance. Scatter is indicative of air bubbles and irregular reagent flow. Also observe for any back-pressure in manifold tubing.

7.11 On computer main menu, select “Samples,” “Tray Definition and Submit,” and then “Edit” to create new sample tray followed by “Submit” to run new sample tray.

7.12 Method parameters specific to water soluble P are defined within the “Method Definition” menu. Some of these parameters have been modified from the QuikChem Method 10-115-01-1-A, orthophosphate in waters

(U.S. Environmental Protection Agency, 1983; LACHAT Instruments, 1993; U.S. Department of Interior, Geological Survey 1993). Modifications are primarily related to the criteria and strategies for calibration standards and to injection timing.

7.13 Some of the method parameters as they relate to calibration standards are as follows:

7.13.1 There are 7 calibration standards (2.00, 1.00, 0.50, 0.20, 0.05, 0.01, and 0.00 mg P L^{-1}) with a data format of ####.###, i.e., data rounded to 3 places.

7.13.2 The segments/boundaries for the calibration standards are A–D (2.0 to 0.20 mg P L^{-1}) and D–G (0.20 to 0.00 mg P L^{-1}).

7.13.3 The protocol (replications) for the calibration standards is as follows: AA BB CCC DDDD EEEE FFFF GG

7.13.4 The check standard is 2.0 mg P L^{-1}. Maximum number of consecutive trays between check standard is one; maximum number of consecutive samples between check standard is 60; and maximum elapse time between check standards is 2 h.

7.13.5 Calibration strategy for segments A–D and D–G are normal. The normal strategy requires a minimum correlation coefficient of 0.99. Both segments require a maximum standard deviation in slope of 50%. A calibration passes only when both criteria are met. Strategies are user designated. In addition, calibration strategies are based on the full chord. Chord 0 is full chord, and chords 1–5 are sections of peak from start of peak to end of peak.

7.13.6 The instrument is calibrated with the injection of SPCS. The data system then associates the concentrations with the instrument response for each SPCS.

7.14 Method parameters in relation to timing are as follows:

7.14.1 Cycle period: 40 s

7.14.2 Inject to start of peak period: 18 s. To see if peaks are being timed correctly, scan across correlation coefficients for all chords 1–5. The most peak area should be between chords 2–4 with the most signal-to-noise ratio in chords 1 and 5.

7.14.3 Inject to end of peak period: 52 s

7.14.4 Automatic timing, where standard assumptions are in effect; no manual timing

7.15 Method parameters in relation to data presentation are as follows:

7.15.1 Top Scale Response: 0.50 abs

7.15.2 Bottom Scale Response: 0.00 abs

7.16 Method parameters in relation to data results are as follows:

7.16.1 Set Default Chord to 3. This change must be made to both the sample and the calibration RDF's.

7.17 Refer to the "Method Definition" for water soluble P for other method parameters not discussed here.

7.18 Run samples using calibration curve. Sample concentration is calculated from the regression equations. Report results to the nearest 0.01 unit for the sample extract and each SPCS.

7.19 If samples are outside calibration range, dilute samples with extracting solution and re-analyze.

7.20 Upon completion of run, place the transmission lines into the NaOH-EDTA solution. Pump the solution for approximately 5 min to remove any precipitated reaction products. Then place these lines in RODI water and pump for an additional 5 min and proceed with the normal "Shut-down" procedure.

8. Calculations

Convert extract P (mg L^{-1}) to soil P (mg kg^{-1}) as follows:

Soil P (mg kg^{-1}) = [(A x B x C x R x 1000 / E]

where:

A = Sample extract reading (mg L^{-1})

B = Extract volume (L)

D = Dilution, if performed

R = Air-dry/oven-dry ratio (method 3D1) or field-moist/oven-dry ratio (procedure 3D2)

1000 = Conversion factor to kg-basis

E = Sample weight (g)

9. Report

Report data to the nearest 0.1 mg P kg^{-1} soil.

10. Precision and Accuracy

Precision and accuracy data are available from the KSSL upon request.

11. References

Adams, F. 1974. Soil solution. p. 441–481. *In* E.W. Carson (ed.) The plant root and its environment. Univ. Press of Virginia, Charlottesville.

Jackson, M.L. 1958. Soil chemical analysis. Prentice-Hall, Inc., Englewood Cliffs, NJ.

LACHAT Instruments. 1993. QuikChem method 10-115-01-1-A, orthophosphate in waters, 0.02 to 2.0 mg P L^{-1}. LACHAT Instruments, 6645 West Mill Rd., Milwaukee, WI.

National Research Council. 1993. Soil and water quality. An agenda for agriculture. Committee on long-range soil and water conservation. Natl. Acad. Press, Washington, DC.

Olsen, S.R., and L.E. Sommers. 1982. Phosphorus. p. 403–430. *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.

Rigler, F.W. 1968. Further observations inconsistent with the hypothesis that the molybdenum blue method measures orthophosphate in lake water. Limnology and Oceanography 13:7–13.

Sharpley, A.N., and R.G. Menzel. 1987. The impact of soil and fertilizer phosphorus on the environment. Adv. Agron. 41:297–324.

U.S. Department of the Interior, U.S. Geological Survey. 1993. Methods for determination of inorganic substances in water and fluvial sediments. Book 5. Chapter Al. Method I-2601-78.

U.S. Environmental Protection Agency. 1983. Methods for chemical analysis of water and wastes. EPA-600/4-79-020. Revised March, 1983, Method 353.2.

Soil Test Analyses (4D)

Bray P-1 Extraction (4D3)

Flow-Injection, Automated Ion-Analyzer (4D3b)

Phosphorus (4D3b1)

Air-Dry or Field-Moist, <2 mm (4D3b1a-b1)

1. Application

The Bray P-1 procedure is widely used as an index of available P in the soil. Bray and Krutz (1945) originally designed the Bray P-1 extractant to selectively remove a portion of the adsorbed form of P with the weak, acidified ammonium fluoride solution. Adsorbed phosphorus is in the anion form adsorbed by different charged surface functional groups that have varying degrees of adsorption affinity. In general, this method has been most successful on acid soils (Olsen and Sommers, 1982). The acid solubilizes calcium and aluminum phosphates and partially extracts iron phosphates compounds. The NH_4F complexes the aluminum in solution and limits re-adsorption of P on iron oxides (Kuo, 1996). The Bray P-1 has limited ability to extract P in calcareous soils due to the neutralization of the dilute acid by carbonates. For most soils, Bray P-1 and Mehlich No. 3 are nearly comparable in their abilities to extract native P but exceed Olsen sodium-bicarbonate method by two- to three-fold, indicating that predictive models for Bray

P-1, Mehlich No. 3, and Olsen sodium-bicarbonate are closely associated with pH buffering of extractant (acid versus alkaline) (Burt et al., 2002).

2. Summary of Method

A 2.5-g soil sample is mechanically shaken for 15 min in 25-mL of Bray P-1 extracting solution. The sample is then centrifuged until solution is free of soil mineral particles and then filtered until clear extracts are obtained.

A flow injection automated ion analyzer is used to measure the orthophosphate ion (PO_4^{3-}). This ion reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex. This complex is reduced with ascorbic acid to form a blue complex which absorbs light at 660 nm. Absorbance is proportional to the concentration of PO_4^{3-} in the sample. Data are reported as mg P kg^{-1} soil (4D3b1).

3. Interferences

Silica forms a pale blue complex which also absorbs at 660 nm. This interference is generally insignificant as a silica concentration of approximately 4000 mg L^{-1} would be required to produce a 1 mg L^{-1} positive error in orthophosphate (LACHAT Instruments, 1989).

Concentrations of ferric iron greater than 50 mg L^{-1} will cause a negative error due to competition with the complex for the reducing agent ascorbic acid. Samples high in iron can be pretreated with sodium bisulfite to eliminate this interference. Treatment with bisulfite will also remove the interference due to arsenates (LACHAT Instruments, 1989).

The determination of phosphorus is sensitive to variations in acid concentrations in the sample since there is no buffer. With increasing acidity, the sensitivity of the method is reduced. Samples, standards, and blanks should be prepared in a similar matrix.

4. Safety

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses). When preparing reagents, exercise special care. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts. Restrict the use of concentrated HCl, NH_4F, and H_2SO_4 to a fume hood. Use safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids.

5. Equipment

5.1 Electronic balance, ±1.0-mg sensitivity

5.2 Centrifuge tubes, 50-mL, polyethylene

5.3 Mechanical reciprocating shaker, 200 oscillations min^{-1}, 1½ in strokes, Eberbach 6000, Eberbach Corp., Ann Arbor, MI

5.4 Centrifuge, Centra GP-8, Thermo IEC, Needham Heights, MA

5.5 Filter paper, Whatman No. 42, 150 mm

5.6 Funnel, 60° angle, long stem, 50-mm diameter

5.7 Volumetric flasks, 1-L and 250-mL

5.8 Bottles, plastic, dark, 1-L

5.9 Cups, plastic

5.10 Dispenser, 30 mL or 10 mL

5.11 Flow Injection Automated Ion Analyzer, QuikChem AE, LACHAT Instruments, Milwaukee, WI, with computer and printer

5.12 XYZ Sampler, LACHAT Instruments, Milwaukee, WI

5.13 Reagent Pump, LACHAT Instruments, Milwaukee, WI

5.14 Automated Dilution Station, LACHAT Instruments, Milwaukee, WI

5.15 Sample Processing Module (SPM) or channel, QuikChem Method (12-115-01-1-A, orthophosphate in waters, 0.4 to 20 mg P L^{-1}), LACHAT Instruments, Milwaukee, WI

5.16 Computer, with QuikChem software, LACHAT Instruments, Milwaukee, WI, and printer

5.17 Pipettes, electronic digital, 2500 µL and 10 mL, with tips 2500 µL and 10 mL

5.18 Vials, plastic, 25-mL (standards)

5.19 Culture tubes, glass, 10-mL (samples)

6. Reagents

6.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

6.2 Helium, compressed gas

6.3 Hydrochloric acid (HCl), concentrated, 12 *N,* trace pure grade

6.4 Sulfuric acid (H_2SO_4), concentrated, 36 *N*, trace pure grade

6.5 HCl, 1 *N*. Carefully add 83.33 mL of concentrated HCl to RODI water and dilute to 1-L volume.

6.6 Bray No. 1 Extracting Solution. 0.025 *M* HCl, and 0.03 *M* NH_4F. Dissolve 8.88 g of NH_4F in 4 L RODI water. Add 200 mL of 1.0 *N* HCl and dilute to 8 L with RODI water. The solution pH should be 2.6 ±0.05. Store in a polyethylene bottle.

6.7 Stock ammonium molybdate solution. In 1-L volumetric flask dissolve 40.0 g ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}•4H_2O$] in approximately 800 mL RODI water. Dilute to the mark with RODI water and invert to thoroughly mix. Stir for 4 h. Store in plastic and refrigerate.

6.8 Stock antimony potassium tartrate solution. In 1-L flask, dissolve 3.0 g antimony potassium tartrate (potassium antimony tartrate hemihydrate [$K(SbO)C_4H_4O_6•½H_2O$] in approximately 800 mL RODI water. Dilute to the mark and invert to thoroughly mix. Store in dark bottle and refrigerate.

6.9 Molybdate color reagent. In 1-L volumetric flask, add 72 mL stock antimony potassium tartrate solution and 213 mL stock ammonium molybdate solution. Dilute to volume with RODI water and invert to thoroughly mix. Degas with helium ≈15 min.

6.10 Ascorbic acid reducing solution. In 1-L volumetric flask, dissolve 60.0 g ascorbic acid in about 700 mL RODI. Dilute to volume with RODI water and invert to thoroughly mix. Degas with helium ≈5 min. After dilution to volume and degassing, dissolve 1.0 g dodecyl sulfate ($CH_3(CH_2)_{11}OSO_3Na$). Prepare fresh daily.

6.11 0.8 *M* H_2SO_4 Carrier. To 1-L container, add 44.4 mL concentrated H_2SO_4 and bring to volume with RODI water. (CAUTION: The solution will get very hot!) Invert to thoroughly mix. Degas with helium ≈5 min.

6.12 Sodium hydroxide-EDTA rinse. Dissolve 65 g sodium hydroxide (NaOH) and 6 g tetrasodium ethylenediamine tetraacetic acid (Na_4EDTA) in 1.0 L RODI water.

6.13 Working stock standard P solution (WSSPS), 100.0 mg P L^{-1}. In a 1-L volumetric flask, dissolve 0.4394 g primary standard grade anhydrous potassium dihydrogen phosphate (KH_2PO_4) that has been dried for 2 h at 110 °C in about 800 mL extracting solution. Dilute to 1-L volume with extracting solution and invert to thoroughly mix. Store in polyethylene containers. Make fresh weekly. Store in a refrigerator.

6.14 Standard P calibration solutions (SPCS) or working standards, 20.00, 12.00, 4.00, 0.800, and 0.000 mg P L^{-1} as PO_4^{3-}. Make fresh weekly. Store in refrigerator. Allow to equilibrate to room temperature before use. To five 250-mL volumetric flasks add as follows:

6.14.1 20.00 mg P L^{-1} = 50 mL WSSPS

6.14.2 12.00 mg P L^{-1} = 30 mL WSSPS

6.14.3 4.00 mg P L^{-1} = 10 ml WSSPS

6.14.4 0.80 mg P L^{-1} = 2 mL WSSPS

6.14.5 0.00 mg P L^{-1} = 0 mL WSSPS (blank)

Dilute each SPCS to the mark with extracting solution and invert to thoroughly mix. Do not degas.

7. Procedure

7.1 Weigh 2.5 g of <2-mm or fine-grind, air-dry soil to nearest mg on an electronic balance and place into a 50-mL centrifuge tube. If sample is moist, weigh enough soil to achieve ≈2.5 g of air-dry soil.

7.2 Dispense 25.0 mL of extracting solution to tube.

7.3 Transfer the sample to the shaker. Shake for 15 min at 200 oscillations min^{-1} at room temperature (20 °C ±2 °C).

7.4 Remove the sample from the shaker. Centrifuge at 2000 rpm for 10 min. Decant, filter, and collect extract in receiving cup. If extracts are not to be determined immediately after collection, then store samples at 4 °C. Analyze samples within 72 h.

7.5 Transfer sample extracts into culture tubes and place in XYZ sample trays marked “Samples”.

7.6 Transfer SPCS standards into plastic vials and place in descending order in XYZ sample trays marked “Standards”.

7.7 Refer to the operating and software reference manuals for LACHAT set-up and operation.

7.8 Turn main power switch “ON” and allow 15 min for heater module to warm up to 60 °C.

7.9 On reagent pump, set speed to 35.

7.10 On computer main menu, select “Methods” and then “Analysis Select and Download”. On method list, select Bray P-1 Method. System unit receives the downloaded method and initializes it.

7.11 Pump reagents into appropriate chambers of the manifold. Continue this step and observe baseline. A good baseline needs to be smooth and at zero absorbance. Scatter is indicative of air bubbles and irregular reagent flow. Also observe for any back-pressure in manifold tubing.

7.12 On computer main menu, select “Samples,” “Tray Definition and Submit,” and then “Edit” to create new sample tray followed by “Submit” to run new sample tray.

7.13 Method parameters specific to Bray P-1 are defined within the “Method Definition” menu. Some of these parameters have been modified from the QuikChem Method 12-115-01-1-A, orthophosphate in soils (U.S. Environmental Protection Agency, 1983; LACHAT Instruments, 1989; U.S. Department of the Interior, Geological Survey, 1993). Modifications are primarily related to the criteria and strategies for calibration standards and to injection timing.

7.14 Some of the method parameters as they relate to calibration standards are as follows:

7.14.1 There are 5 calibration standards (20.00, 12.00, 4.00, 0.80, and 0.00 mg P L^{-1}) with a data format of ####.###, i.e., data rounded to 3 places.

7.14.2 The segments/boundaries for the calibration standards are A–C (20.0 to 4.0 mg P L^{-1}); C–E (4.0 to 0.0 mg P L^{-1}).

7.14.3 The protocol (replications) for the calibration standards is as follows: AA BB CC DDD EEE.

7.14.4 The check standard is 20.0 mg P L^{-1}. Maximum number of consecutive trays between check standard is one; maximum number of consecutive samples between check standard is 60; and maximum elapse time between check standards is 2 h.

7.14.5 Calibration strategy for segments A–C and C–E are normal. The normal strategy requires a minimum correlation coefficient of 0.99. Both segments require a maximum standard deviation in slope of 50%. A calibration passes only when both criteria are met. Strategies are user designated. In addition, calibration strategies are based on the full chord. Chord 0 is full chord, and chords1–5 are sections of peak from start of peak to end of peak.

7.14.6 The instrument is calibrated with the injection of SPCS. The data system then associates the concentrations with the instrument response for each SPCS.

7.15 Method parameters in relation to timing are as follows:

7.15.1 Cycle period: 40 s

7.15.2 Inject to start of peak period: 18 s. To see if peaks are being timed correctly, scan across correlation coefficients for all chords 1–5. The most peak area should be between chords 2–4 with the most signal-to-noise ratio in chords 1 and 5.

7.15.3 Inject to end of peak period: 46 s

7.15.4 Automatic timing, where standard assumptions are in effect. Manual timing may be helpful in this method.

7.16 Method parameters in relation to data presentation are as follows:

7.16.1 Top Scale Response: 0.50 abs

7.16.2 Bottom Scale Response: 0.00 abs

7.17 Refer to the “Method Definition” for Bray P-1 for other method parameters not discussed here.

7.18 Run samples using calibration curve. Sample concentration is calculated

from the regression equations. Report results to the nearest 0.01 unit for the sample extract and each SPCS.

7.19 If samples are outside calibration range, dilute samples with extracting solution and re-analyze.

7.20 Upon completion of run, place the transmission lines into the NaOH-EDTA solution. Pump the solution for approximately 5 min to remove any precipitated reaction products. Then place these lines in RODI water and pump for an additional 5 min and proceed with the normal "Shut-down" procedure.

8. Calculations

Convert extract P (mg L^{-1}) to soil P (mg kg^{-1}) as follows:

$$\text{Soil P (mg kg}^{-1}\text{)} = [(A \times B \times C \times R \times 1000)/E]$$

where:

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)

1000 = Conversion factor to kg-basis

E = Sample weight (g)

9. Report

Report data to the nearest 0.1 mg P kg^{-1} soil.

10. Precision and Accuracy

Precision and accuracy data are available from the KSSL upon request.

11. References

Bray, R.H., and L.T. Kurtz. 1945. Determination of total, organic, and available forms of phosphorus in soils. Soil Sci. 59:39–45.

Burt, R., M.D. Mays, E.C. Benham, and M.A. Wilson. 2002. Phosphorus characterization and correlation with properties of selected benchmark soils of the United States. Commun. Soil Sci. Plant Anal. 33:117–141.

Kuo, S. 1996. Phosphorus. p. 869–919. *In* D.L. Sparks (ed.) Methods of soil analysis. Part 3. Chemical methods. No. 5. ASA and SSSA, Madison, WI.

LACHAT Instruments. 1989. QuikChem method 12-115-01-1-A, phosphorus as orthophosphate, 0.4 to 20 mg P L^{-1}. LACHAT Instruments, 6645 West Mill Rd., Milwaukee, WI.

Olsen, S.R., and L.E. Sommers. 1982. Phosphorus. p. 403–430. *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. Department of the Interior, U.S. Geological Survey. 1993. Methods for determination of inorganic substances in water and fluvial sediments. Book 5. Chapter Al. Method I-2601-78.

U.S. Environmental Protection Agency. 1983. Methods for chemical analysis of water and wastes. EPA-600/4-79-020. Revised March, 1983, Method 353.2.

Selective Dissolutions (4G)

Sodium Pyrophosphate Extraction (4G3)

Acid Digestion (4G3b)

$K_2Cr_2O_7$ + (H_2SO_4 + H_3PO_4 Digestion) (4G3b1)

CO_2 Evolution, Gravimetric (4G3b1a)

Organic Carbon (4G3b1a1)

Air-Dry or Field-Moist, <2 mm (4G3b1a1a-b1)

1. Application

Sodium pyrophosphate (0.1 *M* $Na_4P_2O_7$) is used as a selective dissolution extractant for organically complexed Fe and Al (Wada, 1989). The $Na_4P_2O_7$ solution is a poor extractant for allophane, imogolite, amorphous aluminosilicates, and noncrystalline hydrous oxides of Fe and Al. The $Na_4P_2O_7$ solution does not extract opal, crystalline silicates, layer silicates, and crystalline hydrous oxides of Fe and Al (Wada, 1989). Sodium pyrophosphate extractable organic C, Fe, and Al were former criteria for spodic placement in soil taxonomy (Soil Survey Staff, 1975). Sodium pyrophosphate extractable Al, Fe, and Mn are currently determined by method (4G3a1-3).

2. Summary of Method

The soil sample is mixed with 0.1 *M* $Na_4P_2O_7$ and shaken overnight. The solution is then allowed to settle overnight before centrifuging and filtering to obtain a clear extract. The organic C in the sodium pyrophosphate extract is wet oxidized in a fume hood and gravimetrically measured in method 4G3b1a1.

3. Interferences

There are several interferences with this procedure, especially the peptization and dispersion of microcrystalline iron oxide by pyrophosphate (Jeanroy and Guilet, 1981). The quantity of Fe extracted with pyrophosphate decreases with increasing centrifugation (McKeague and Schuppli, 1982); therefore uniform high-speed centrifugation or micropore filtration treatments are required (Schuppli et al., 1983; Loveland and Digby, 1984). Sodium pyrophosphate extraction works

best at pH 10 (Loeppert and Inskeep, 1996). The concentration of $Na_4P_2O_7$ solution must be close to 0.1 *M*. Variable amounts of organic C may be extracted by varying the pyrophosphate concentration.

4. Safety

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Restrict the use of concentrated HCl to a fume hood. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts.

5. Equipment

5.1 Electronic balance, ±0.1-mg sensitivity

5.2 Mechanical reciprocating shaker, 200 oscillations min^{-1}, 1½ in strokes, Eberbach 6000, Eberbach Corp., Ann Arbor, MI

5.3 Centrifuge, Centra, GP-8, Thermo IEC, Needham Heights, MA

5.4 Digital diluter/dispenser, with syringes 10,000 and 1000 µL, gas tight, Microlab 500, Hamilton Co., Reno, NV

5.5 Dispenser, 40 mL

5.6 Test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer

5.7 Containers, polypropylene

5.8 Volumetrics, Class A, 100, 250, and 1000-mL

5.9 Centrifuge tubes, 50-mL

5.10 Funnel, 60° angle, long stem, 50-mm diameter

5.11 Filter paper, Whatman 42, 150 mm

5.12 Absorption bulb, Nesbitt with stopper

5.13 Absorption bulb, Stetser-Norton

5.14 Flask, boiling, round bottom, short neck

5.15 Condenser, Allihn

5.16 Funnel, separatory, cylindrical, open top, with stopcock

5.17 Tube, drying, Schwartz

6. Reagents

6.1 Reverse osmosis deionized (RODI) water

6.2 Hydrochloric acid (HCl), concentrated, 12 *N*

6.3 Sodium pyrophosphate solution, 0.1 *M*. Dissolve 446.05 g of

$Na_4P_2O_7 \cdot 10H_2O$ in 10 L of RODI water. pH solution to 10.0 with either HCl or NaOH.

6.4 Potassium dichromate ($K_2Cr_2O_7$) reagent.

6.5 Potassium iodide solution. Dissolve 100 g of KI in 100 mL of RODI water.

6.6 Silver sulfate, saturate aqueous solution

6.7 Digestion acid mixture: Mix 600 mL of concentrated H_2SO_4 and 400 mL of 85% H_3PO_4.

6.8 Indicarb or Mikohibite

6.9 Soda lime

6.10 Zinc granules, 300 mesh

6.11 Anhydrone

6.12 Acetylene gas, purity 99.6%

6.13 Nitrous oxide gas, compressed

6.14 Compressed air with water and oil traps

7. Procedure

Extraction of Al, Fe, and Mn

7.1 Weigh 0.5 g <2-mm or fine-grind, air-dry soil to the nearest mg sample and place in a 50-mL centrifuge tube. If sample is moist, weigh enough soil to achieve ≈0.5 g of air-dry soil.

7.2 Add 30-mL of 0.1 *M* $Na_4P_2O_7$, pH 10.0 solution to centrifuge tube.

7.3 Cap tube and shake briefly by hand to dislodge soil from tube bottom. Place tube in rack.

7.4 Place rack in shaker and shake overnight (12 to 16 h) at 200 oscillations min^{-1} at room temperature (20 °C ±2°C).

7.5 Remove tubes from shaker and manually shake tubes to dislodge any soil from cap. Allow samples to sit overnight.

7.6 Next day centrifuge sample at 4000 rpm for 15 min. Filter if necessary.

Organic C Determination

7.7 Pipet 100 mL of the extract into a 100-ml flask.

7.8 Evaporate the extract to near dryness using a 50 °C water bath and a gentle stream of clean, filtered air.

7.9 Construct the wet combustion apparatus. Refer to figure 4G3-1 for the apparatus for gravimetric organic C determination.

7.10 Add 1 to 2 g of potassium dichromate.

7.11 Wash the neck of the flask with 3 mL of RODI H_2O and connect to condenser.

7.12 Attach a weighed Nesbitt bulb to the system and open the valve at the top.

7.13 Pour 25 mL of digestion-acid mixture into the funnel. Add the mixture to the flask and immediately close the stopcock. Use the digestion-acid mixture to lubricate the stopcock.

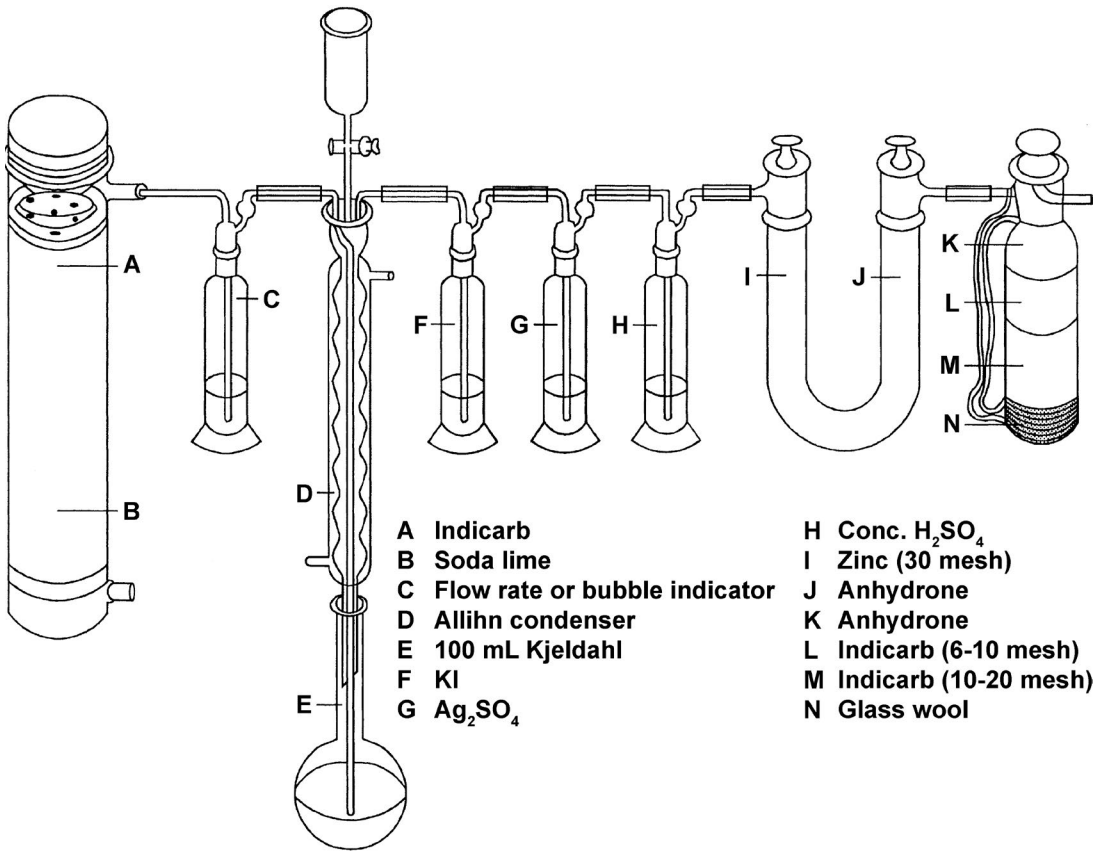


Figure 4G3-1.—Apparatus for gravimetric organic carbon determinations of 0.1 M sodium pyrophosphate extracts.

7.14 The tip of the air-delivery tube should be ≈0.5 cm below the digestion-acid mixture. Adjust the flow of the "carrier stream" to maintain 1 to 2 bubble s^{-1} rate throughout the digestion. Apply suction on the outlet side of the Nesbitt bulb. Gentle air pressure and needle valve on the air-pressure line aids flow-adjustment.

7.15 With a gas flame or a variable power-heating mantle, gently heat the flask until the mixture boils (≈3 to 4 min). Continue a gentle boiling for 10 min. Heating is too rapid if white fumes of SO_2 are visible above the second bulb of the reflux condenser.

7.16 Remove the heat and allow to aerate for 10 additional min at a rate of 6 to 8 bubbles s^{-1}.

7.17 Close the stopcock on the Nesbitt bulb, disconnect the bulb from the system, and weigh to the nearest 0.0001g.

8. Calculations

8.1 Organic C (%) = $[(Wt_F - Wt_I) \times 27.3 \times Volume \times R] / (Sample\ Weight\ (g) \times 236.6)$

where:

Wt_F = Nesbitt bulb weight after digestion (g)

Wt_I = Nesbitt bulb weight before digestion (g)

Volume = Extract volume digested (mL)

R = Air-dry/oven-dry ratio (method 3D1) or field-moist/oven-dry ratio (method 3D2)

27.3 = Conversion factor

236.6 = Total extract volume (mL)

9. Report

Report organic C the nearest 0.1 of a percent.

10. Precision and Accuracy

Precision and accuracy data are available from the SSL upon request.

11. References

Jeanroy, E., and B. Guillet. 1981. The occurrence of suspended ferruginous particles in pyrophosphate extracts of some soil horizons. Geoderma 26:95–105.

Loeppert, R.H., and W.P. Inskeep. 1996. Iron. p. 639–664. *In* D.L. Sparks (ed.) Methods of Soil Analysis. Part 3 – Chemical methods. Soil Sci. Am. Book Series No. 5. ASA and SSSA, Madison, WI.

Loveland, P.J., and P. Digby. 1984. The extraction of Fe and Al by 0.1*M* pyrophosphate solutions: A comparison of some techniques. J. Soil Sci. 35:243–250.

McKeague, J.A., and P.A. Schuppli. 1982. Changes in concentration of iron and aluminum in pyrophosphate extracts of soil and composition of sediment resulting from ultracentrifugation in relation to spodic horizon criteria. Soil Sci. 134:265–270.

Schuppli, P.A., G.J. Ross, and J.A. McKeague. 1983. The effective removal of suspended materials from pyrophosphate extracts of soils from tropical and temperate regions. Soil Sci. Soc. Am. J. 47:1026–1032.

Soil Survey Staff. 1975. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys. USDA–SCS Agric. Handb. 436. U.S. Govt. Print. Office, Washington, DC.

Wada, K. 1989. Allophane and imogolite. p. 1051–1087. *In* J.B. Dixon and S.B. Weed (ed.) Minerals in soil environments. 2nd ed. Soil Sci. Am. Book Series No. 1. ASA and SSSA, Madison, WI.

Total Analysis (4H)

Acid Digestion (4H1)

HNO_3 + HCl Digestion (4H1a)

Microwave (4H1a1)

Inductively Coupled Plasma Atomic Emission Spectrophotometer (4H1a1a)

Axial Mode (4H1a1a1)

####### Ultrasonic Nebulizer (4H1a1a1a)

######## Silver, Arsenic, Barium, Beryllium, Cadmium, Cobalt, Chromium, Copper, Manganese, Molybdenum, Nickel, Phosphorus, Lead, Antimony, Tin, Strontium, Thallium, Vanadium, Tungsten, and Zinc (4H1a1a1a1-20)

######### Air-Dry, <2 mm (4H1a1a1a1-20a1)

1. Application

The term of trace elements is widely applied to a variety of elements that are generally present in plants, soils, and water in low concentrations or what is termed background levels. Knowledge of these levels is important in understanding the consequences of increasing levels of trace elements in ecosystems (Tiller, 1989; Holmgren et al., 1993). These elements may become elevated in concentration due to natural (e.g., magmatic activity, mineral weathering, translocation through the soil or landscape) or through human-induced activities (e.g., pesticides, mining, smelting, manufacturing). The relative reactivity or bioavailability of these elements in soils is governed by a variety of chemical factors such as pH, redox potential, organic concentrations, and oxides (Pierzynski and Schwab, 1993; Gambrell, 1994; Keller and Vedy, 1994; Burt et al., 2002). Uses of elemental data in soil survey applications are broad and diverse, ranging from understanding natural (Wilcke and Amelung, 1996; Jersak et al., 1997) to human-induced distributions (Wilcke et al., 1998). Knowledge of the elemental amounts and distribution in soils and their relationships with other soil properties can enhance the understanding of the fate and transport of anthropogenic elements, thereby expanding the utility and application of soil survey knowledge in areas of environmental concern such as urban, mine spoil reclamation, smelter emissions, and agricultural waste applications (Burt et al., 2003).

2. Summary of Method

The approach of this digestion methodology is to maximize the extractable concentration of elements in digested soils while minimizing the matrix interferences such as found in digestion procedures that use HF acid. This method (4H1a1) follows EPA Method 3051A. A 500-mg <2-mm soil separate which has been air-dried and ground to <200 mesh (75 µm) is weighed into a 100-ml Teflon (PFA) sample digestion vessel. To the vessel, 9.0 mL HNO_3 and 3.0 mL HCl are added. The vessel is inserted into a protection shield and covered, and placed into a rotor with temperature control. Following microwave digestion, the rotor and samples are cooled, and digestate quantitatively transferred into a 50-ml glass volumetric high purity reverse osmosis deionized water. The volumetrics are allowed to stand overnight, filled to volume, and samples transferred into appropriate acid-washed polypropylene containers for analysis. The concentration of Ag, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, P, Pb, Sb, Sn, Sr, Tl, V, W, and Zn are determined using an inductively coupled plasma atomic emission spectrophotometer (ICP–AES) in axial mode by methods 4H1a1a1a1-20, respectively. Mercury is analyzed by a cold-vapor atomic absorption spectrophotometer (CVASS) (4H1a1c1), and As and Se are determined by flow through hydride-generation and atomic absorption spectrophotometer (HGAAS) (4H1a1b1a1-2), respectively.

3. Interferences

Organic constituents may contain metals and are difficult to digest if present in high concentrations. Certain elements are subject to volatile losses during digestion and transfer. Certain soil minerals (e.g., quartz, feldspars) are not soluble in HNO_3 + HCl.

Spectral and matrix interferences exist. Interferences are corrected or minimized by using both an internal standard and inter-elemental correction factors. Also, careful selection of specific wavelengths for data reporting is important. Background corrections are made by ICP software. Samples and standards are matrix-matched to help reduce interferences.

4. Safety

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Restrict the use of concentrated acids to the fume hood. Wash hands thoroughly after handling reagents. Filling the digestion vessel to greater than 25 percent of the free volume or adding organic reagents or oxidizing agents to the cup may result in explosion of the digestion microwave system.

5. Equipment

5.1 Electronic balance, ±1.0-mg sensitivity

5.2 Pipette(s) capable of delivering 3 and 9 mL, Omnifit Corp. manufacturers

variable volume, (10-ml maximum) pipettes suitable for HNO_3 and HCl delivery from 2.5 L bottles

5.3 Volumetric flasks, class A glass, 50 mL

5.4 Polypropylene bottles, 60 mL, with cap

5.5 Electronic balance (±0.1 mg sensitivity)

5.6 Microwave oven, CEM Mars 5, 14 position-HP500 Plus vessel and rotor (vessels composed of PFA, sleeves composed of advanced composite)

5.7 Volumetrics, 500, 250, and 50-mL class A glass

5.8 Containers, 500-mL, polypropylene, with screw caps

5.9 Pipettes, electronic digital, 250 µL and 10 mL, Rainin Instrument Co., Woburn, MA

5.10 Inductively coupled plasma atomic emission spectrophotometer (ICP–AES), Perkin-Elmer Optima 3300 Dual View (DV), Perkin-Elmer Corp., Norwalk, CT

5.11 RF generator, floor mounted power unit, 45 MHz free running, Perkin-Elmer Corp., Norwalk, CT

5.12 Computer, with WinLab software ver. 4.1, Perkin-Elmer Corp., Norwalk, CT, and printer

5.13 Recirculating chiller, Neslab, CFT Series

5.14 Compressed gasses, argon (minimum purity=99.996%) and nitrogen (minimum purity=99.999%)

5.15 Autosampler, AS-90, Perkin-Elmer Corp., Norwalk, CT

5.16 Quartz torch, Part No. N069-1662; alumina injector (2.0 mm id), Part No. N069-5362

5.17 Ultrasonic nebulizer, Model U-5000AT+ , CETAC Corp., Omaha, NE

5.18 Peristaltic pump (for automatic injection of internal standard)

6. Reagents

6.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

6.2 Concentrated hydrochloric acid (HCl), 12 N, trace pure grade

6.3 Concentrated nitric acid (HNO_3), 16 N, trace pure grade

6.4 Primary standards: 1000 mg L^{-1}, from High Purity Standards, Charleston, SC. Single elemental standards are manufactured in dilute HNO_3, HNO_3 + HF, or H_2O.

7. Procedure

Microwave Acid Digestion

7.1 About 500 mg of fine-earth (<2-mm) or a specific particle size separate ground to <200-mesh (75 µm) is weighed to the nearest 0.1 mg in a 100-mL digestion vessel.

7.2 Note: If sample is principally composed of organic materials (organic C > 15%), perform a preliminary digestion in the muffle furnace in an digestion crucible: 250°C for 15 min, 450 °C for 15 min, followed by 550 °C for 1 h.

7.3 Pipette 9.0 mL HNO_3 and 3.0 mL HCl into the sample and allow to completely wet. Add acids in the fume hood. Allow acids to react and vent in uncovered vessels for about 30 min.

7.4 Place covered vessels in protective sleeve, cover and place into rotor.

7.5 Place digestion rotor in the microwave oven and insert the temperature probe into the reference vessel. Attach the probe cable into the fitting in the top of the microwave. Connect the pressure monitor to the vessel.

7.6 Microwave settings are as follows:

1200 watts at 100% power for 5.5 min until 175 °C

Hold at 175 °C for 4.5 min

Cool for 5 min

7.7 After cooling, disconnect temperature probe and pressure sensor from microwave.

7.8 Remove rotor from oven, and place in fume hood.

7.9 Open each vessel carefully and then quantitatively transfer contents of vessel to a 50-mL volumetric flask with RODI water.

7.10 Cap flask and mix well by inverting. Allow to stand overnight. Finish filling to volume with RODI water.

7.11 Decant contents into a labeled 60-mL polypropylene container.

7.12 Prepare working standards of a blank, reference soil sample from the SSL repository, NIST or other standard reference material, and blank by the same digestion method. Run two of these standards or blank with each set of 14 samples.

ICP–AES Calibration Standards, Set-Up, and Operation

7.13 A primary mixed calibration standard (PMCS) is prepared from the respective primary elemental standards (1000 mg L^{-1}) to a 500-mL final volume. From this PMCS, three working calibration standards (WCS) are prepared. In addition, a single element standard for Tl (STl_1) is prepared

separately from a 1000 µg L^{-1} stock standard to a 50-mL final volume. Also, prior to diluting to volume, add 90 mL HNO_3 and 30 mL HCl to the PMCS and 9 mL HNO_3 and 3 mL HCl to the STI_1. Use RODI water to dilute to final volume for PMCS and STI_1. Invert to mix thoroughly. Store in polyethylene container in refrigerator. Make fresh on a routine basis. The amount of the primary standards (1000 mg L^{-1}) to make the PMCS, amount of the1000 µg L^{-1} TI stock standard to make the STI_1 and the final elemental concentrations of the PMCS and STI_1 are as follows:

Element	Concentration	Primary Standard Required
	(µg L^{-1})	*(mL)*
As	2,000	1
Ni	4,000	2
P	60,000	30
Cr	4,000	2
M	40,000	20
Cu	20,000	10
Zn	20,000	10
C	2,000	1
Pb	4,000	2
Co	4,000	2
A	400	0.2
Ba	120,000	60
Be	600	0.3
Sb	400	0.2
Sr	60,000	30
M	400	0.2
V	20,000	10
Sn	8,000	4
Tl	500	25
W	2,000	1

7.14 The WCS are made from dilution of the PMCS with the exception of single element Tl (STI_2), which is made up separately. The three WCS (Low, Medium, and High) require 0.625, 6.25, and 62.5 ml PMCS diluted to 250-mL final volume, respectively. Also, prior to diluting to volume, add 44.89, 43.88, and 33.75 mL HNO_3 and 14.96, 14.63, and 11.25 mL HCl to the WCS (Low, Medium, and High, respectively). The STI_2 requires 0.5, 5, and 50 mL of the STI_1 diluted to a 50-mL final volume. Also, prior to diluting to

volume, add 8.91 and 8.1 mL HNO_3 and 2.97 and 2.7 mL HCl for the Low and Medium $ST1_2$, respectively. Use RODI water to dilute to final volume for WCS and STI_2. Invert to mix thoroughly. Store in polyethylene container in a refrigerator. Make fresh on a routine basis. The elemental concentrations of the Low, Medium, and High WCS and the $ST1_2$ are as follows:

Element	Concentration		
	Low	Medium	High
	(µg L^{-1})		
Ni	10	100	1000
P	150	1500	15,000
Cr	10	100	1000
Mn	100	1000	10,000
Cu	50	500	5000
Zn	50	500	5000
Cd	5	50	500
Pb	10	100	1000
Co	10	100	1000
Ag	1	10	100
Ba	300	300	3000
Be	1.5	15	150
Sb	1.0	10	100
Sr	150	1500	15,000
Mo	1	10	100
V	50	500	5000
Sn	20	200	2000
Tl	5	50	500
W	5	50	500
As	5	50	500

7.15 Single element primary standards (1000 mg L^{-1}, Al, Fe, Mo, V, Mn) are required to create the inter-elemental correction (IEC) factors. These are prepared in the matrix of the digests and are combined into one solution for routine calibration. The single element IEC standards (SEIECS) are required to determine the IEC's. The mixed IEC standard (MIECS) is required for routine calibration. The SEIECS is based on a 50-mL final volume and the MIECS is based a 250-mL final volume. Use RODI water to dilute to final volume for SEIECS and MIECS. Invert to mix thoroughly. Store in polyethylene container in a refrigerator. Make fresh on routine basis. The amount of the primary standard (1000 mg L^{-1}) to make the

SEIECS and MIECS solutions and the final elemental concentration of these IEC solutions are as follows:

Element	IEC Solution Concentration	Primary Standard Required	
		MIECS	SEIECS
	mg L^{-1}	*mL*	
Al	100	25.00	5.0
Fe	100	25.00	5.0
Mo	5	1.25	0.25
V	10	2.50	0.50
Mn	10	2.50	0.50

7.16 To MIECS, add 45 and 15 mL HNO_3 and HCl, respectively. To SEIECS, add 9 and 3 mL HNO_3 and HCl, respectively. Use RODI water to dilute to final volume for MIECS and SEIECS.

7.17 The elements chosen for IEC factors are based on established spectral interferences with chosen analyte wavelengths. The SEIECS should initially be prepared in separate 50-mL volumetrics for establishment of IEC factors and then prepared (MIECS) in a single 250-mL volumetric for routine analysis. IEC factors are established via a procedure in the WinLab software in which the amount of interference on the analyte (in µg L^{-1}) is measured for each mg L^{-1} of interferent concentration in the digest.

7.18 A 10 mg L^{-1} Lu internal standard (read at 291.138 nm) is added to the blank, all calibration standards, and samples. It is prepared by adding 5.0 mL Lu primary standard (1000 mg L^{-1}) and 10 ml conc. HNO_3 to 500-mL volumetric flask, and diluting to volume with RODI water. Internal standard is automatically injected via the peristaltic pump and mixing block.

7.19 Use the ICP–AES in axial mode and ultrasonic nebulization to analyze sample. Internal standard is added via an external peristaltic pump at 15% pump speed using 0.44 mm id. pump tubing. Internal standard and samples or standards are mixed via a mixing block and coil prior to entering the ultrasonic nebulizer. 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.

7.20 Analyses are generally performed at two or more wavelengths for each element. The selected wavelengths are as follows (reported wavelength listed first and in boldface):

Element	Wavelength
	(nm)
Al	**237.312** 308.215
Fe	**302.107** 238.203
Mn	**260.570** 203.844
P	**178.221**, 213.620
Cr	**267.710**, 205.558
Cu	**324.753**, 327.396
Ni	**232.003**, 231.604
Zn	**213.857**, 206.197
Cd	**228.802**, 226.501
Pb	**220.353**, 216.998
Co	**228.614**
Sb	**217.582**, 206.833
Sr	**460.733,** 407.771
Ba	**233.525**, 455.507
Be	**313.104**, 313.046
As	**188.979**
Ag	**328.068**, 338.287
Mo	**202.031**, 203.845
V	**292.402**, 310.230
Sn	**189.927**, 235.485
W	**207.912**, 224.876
Tl	**190.801**, 276.787
Lu	**291.138** (Internal Standard)
Al (IEC)	**237.312**
Fe (IEC)	**302.107**
Mo (IEC)	**202.031**
V (IEC)	**292.402**
Mn (IEC)	**260.568**

7.21 Use the blank standard solution to dilute those samples with concentrations greater than the high standard. Rerun all elements and use only the data needed from the diluted analysis.

7.22 Establish detection limits using the blank standard solution. 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. Analyzed values lower than the detection limits are reported as “ND” or non-detected.

7.23 The extract obtained in this method (4H1a1) is used in method 4H1a1c1 for Hg analysis and in methods 4H1a1b1a1-2 for As and Se analysis, respectively.

8. Calculations

The calculation of mg kg^{-1} of an element in the soil from µg L^{-1} in solution is as follows:

Analyte concentration in soil (mg kg^{-1}) = [A x B x C x R x 1000] / E x 1000

A = Sample extract reading (µg L^{-1})

B = Extract volume (L)

C = Dilution, if performed

R = Air-dry/oven-dry ratio (method 3D1)

1000 = Conversion factor in numerator to kg-basis

E = Sample weight (g)

1000 = Factor in denominator (µg mg^{-1})

9. Report

Analyses are generally performed at two or more wavelengths for each element, with the one selected wavelength for reporting purposes. The particle-size fraction digested needs to be identified with each sample. Data are reported to the nearest 0.01 mg kg^{-1}.

10. Precision and Accuracy

Precision and accuracy data are available from the SSL upon request.

11. References

Burt, R., M.A. Wilson, T.J. Keck, B.D. Dougherty, D.E. Strom, and J.A. Lindhal. 2002. Trace element speciation in selected smelter-contaminated soils in Anaconda and Deer Lodge Valley, Montana, USA. Adv. Environ. Res. 8:51–67.

Burt, R., M.A. Wilson, M.D. Mays, and C.W. Lee. 2003. Major and trace elements of selected pedons in the USA. J. Environ. Qual. 32:2109–2121.

Gambrell, R.P. 1994. Trace and toxic metals in wetlands–A review. J. Environ. Qual. 23:883–891.

Holmgren, G.G.S., M.W. Meyer, R.L. Chaney, and R.B. Daniels. 1993. Cadmium, lead, zinc, copper, and nickel in agricultural soils of the United States of America. J. Environ. Qual. 22:335–348.

Jersak, J., R. Amundson, and G. Brimhall, Jr. 1997. Trace metal geochemistry in Spodosols of the Northeastern United States. J. Environ. Qual. 26:551–521.

Keller, C., and J.C. Vedy. 1994. Distribution of copper and cadmium fractions in two forest soils. J. Environ. Qual. 23:987–999.

Pierzynski, G.M., and A. P. Schwab. 1993. Bioavailability of zinc, cadmium, and lead in a metal-contaminated alluvial soil. J. Environ. Qual. 22:247–254.

Tiller, K.G. 1989. Heavy metals in soils and their environmental significance. *In* B.A. Stewart (ed.) Adv. Soil Sci. 9:113–142.

Wilcke, W., and W. Amelung. 1996. Small-scale heterogeneity of aluminum and heavy metals in aggregates along a climatic transect. Soil Sci. Soc. Am. Proc. 60:1490–1495.

Wilcke, W., S. Muller, N. Kanchanakool, and W. Zech. 1998. Urban soil contamination in Bangkok: Heavy metal and aluminum partitioning in topsoils. Geoderma 86:211–228.

Total Analysis (4H)

Acid Digestion (4H1)

HNO_3 + HCl Digestion (4H1a)

Microwave (4H1a1)

HCl Digestion (4H1a1b)

Water Bath (4H1a1b1)

Flow Through Hydride-Generation and Atomic Absorption Spectrophotometer (4H1a1b1)

Arsenic and Selenium (4H1a1b1a1-2)

Air-Dry, <2 mm (4H1a1b1a1-2a1)

1. Application

Arsenic is an extremely toxic element that is occurs in both organic and inorganic forms in soils. It is typically found in low concentrations, but has been widely applied to soils as a component in pesticides and herbicides and also via industrial pollution and smelting operations. The element is used in drugs, soaps, dyes, and metals, though 90% of industrial As in the U.S. is used in wood preservatives (Pinsker, 2001). Concerns exist for both short-term (acute) and long-term (chronic) soil exposure. Primary route for exposure is via soil ingestion or inhalation of air-borne particles. Data from As measurements in groundwater by U.S. Geological Survey and Environmental Protection Agency has suggested that most As in groundwater is related to natural sources (Ryker, 2001), i.e., from mineral dissolution from minerals in geologic formations and soils. For example, As released via pyrite oxidation is in part responsible for groundwater As levels in Bangladesh ranging between 50 and 2,500 µg/L in many wells. Soil applied As is

generally immobile, with soil chemistry similar to phosphorus. The element occurs as arsenate (As^{5+}) and arsenite (As^{3+}), and in soils, is in the form of the oxyanion, AsO_4^{3-}. The weathering of limestone and biological accumulation of the element by aquatic organisms is responsible for the high levels in wetland soils of Florida (Chen et. al., 2002).

Selenium is a naturally occurring element in rocks, but is especially concentrated in certain geologic formations, such as Mancos Shale in Colorado and Wyoming and in the shales of the Moreno and Kreyenhagen Formations of California (Martens and Suarez, 1997). Selenium occurs in four species (related to valance states): selenate (Se^{6+}), selenite (Se^{4+}), elemental Se (Se^0), and selenide (Se^{2-}). The bioavailability and toxicity is related to speciation. The oxidized species are more commonly found in soils and water. The element is important due to both deficiency (forages for animals) and toxicity (bioaccumulation) concerns (Huang and Fujii, 1996).

2. Summary of Method

A soil sample is digested with HNO_3 and HCl in a microwave oven (method 4H1a1). Following extraction, samples are diluted with water to a final 50-mL volume. A 6-mL aliquot of the digestate is combined with 6 mL concentrated H_2SO_4 and heated at 180 °C for 5 min in the microwave oven to eliminate the HNO_3. Then, the extract is combined with 14 mL of water and 20 mL of concentrated HCl and boiled for 30 min. Sample extracts are allowed to cool. Potassium iodide is added as a pre-reduction step for As analysis, with a final concentration of 1% in analysis solutions. Solutions are allowed to stand 1 h before analyzed for total As and/or Se, using flow through hydride-generation and atomic absorption spectrophotometer (HGAAS). Under acidic conditions, sodium borohydride ($NaBH_4$) reduces As and Se to form gaseous products that can be detected by atomic adsorption. For example:

$$3NaBH_4 + 4H_2SeO_3 \rightarrow 4H_2Se_{(g)} + 3H_3BO_4 + 3NaOH$$

The data are automatically recorded by a computer and printer. The As and Se concentrations are reported as mg kg^{-1} in the soil by methods 4H1a1b1a1-2, respectively.

3. Interferences

Oxidizing acids (e.g., nitric) can produce interferences, and inter-element interferences (e.g., Cu, Sn, Ni, Fe, Cr, Pb, Co) can affect determinations. Even small amounts of nitric acid produce suppressed, erratic absorbance signals and low recoveries, more so for As than Se. This interference can be effectively eliminated with either (1) addition of urea before the potassium iodide pre-reduction step, or (2) boiling the samples with H_2SO_4. Alternatively, if samples are boiled in HCl, the quantity of nitric acid can be sufficiently reduced to eliminate the need for urea. Hydride-forming elements may exist in more than one oxidation-state, affecting the signal. In general, As^{5+} methods produce a signal that may

be 20 to 50% of that produced by As^{3+}. There are typically more inter-element interferences for As^{5+} methods than for As^{3+}. Inter-element interferences can be reduced by using the lowest possible concentration of sodium borohydride. Best results can be obtained for difficult samples containing high concentrations of metals if the sodium borohydride concentration is reduced to 0.3% w/v.

4. Safety

Wear protective clothing (coats, aprons, sleeve guards, and gloves); eye protection (face shields, goggles, or safety glasses); and a breathing filter when handling As and Se solutions. These elements are extremely toxic.

Follow standard laboratory practices when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene gas is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the AA.

5. Equipment

5.1 Electronic balance, ±0.1-mg sensitivity

5.2 Atomic absorption spectrophotometer (AAS), PE Model Analyst 300, Perkin-Elmer Corp., Norwalk, CT

5.3 System 2 Electrodeless Discharge Lamp (EDL) Power Supply, with lamps for As and Se, Perkin-Elmer Corp., Norwalk, CT

5.4 Autosampler, Model 90A, Perkin-Elmer Corp., Norwalk, CT

5.5 WinLab Software, Ver. 4.1, Perkin-Elmer Corp., Norwalk, CT

5.6 Computer, Dell Optiplex GXM 333 MHz Pentium, Dell Computer Corp., 17 in color monitor

5.7 Printer, Hewlett-Packard LaserJet 880A

5.8 Single-stage regulator, acetylene service, part number E11-0-N511A, Air Products and Chemicals, Inc., Box 538, Allentown, PA

5.9 Double-stage regulator, argon service

5.10 Varian Vapor Generation Accessory, Model VGA-77

5.11 Tubes, 50-mL for calibration standards

5.12 Test tubes, 50-mL, Corning Pyrex, for sample digestion

5.13 Test tubes, 25-mL, 16 mm x 100, for sample dilution and autosampler

5.14 100, 250, and 1000-mL volumetrics, class A.

5.15 Containers, polypropylene and glass

5.16 Water bath, 95 °C-capability

6. Reagents

6.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

6.2 Sulfuric acid (H_2SO_4), 36 *M*, trace metal purity

6.3 Sodium hydroxide ($NaOH•3H_2O$)

6.4 Sodium borohydride ($NaBH_4$) pellets

6.5 Hydrochloric acid (HCl), 12 *M*, trace metal purity, assay 35–38%

6.6 Acetylene gas, purity 99.6%.

6.7 Compressed air with water and oil traps

6.8 Compressed argon

6.9 Primary standards, 1000 mg L^{-1} As and 1000 mg L^{-1} Se, High Purity Standards, Inc.

6.10 Primary mixed working standard (PMWS), 1000 µg L^{-1} As and Se: Add 500 mL RODI water to a 1-L volumetric. Add 1 mL of 1000 mg L^{-1} As, 1 mL of 1000 mg L^{-1} Se, and 10 mL concentrated HCl. Fill to volume with RODI water. Invert to mix thoroughly. Final concentration is ≈1% HCl. Store in polyethylene container in a refrigerator. Make fresh weekly.

6.11 Mixed Calibration Standards (MCS), 150, 100, 75, 50, 25, 12, and 0 µg L^{-1}: To seven 250-mL volumetrics, add PMWS and concentrated HCl as follows:

6.11.1 150 µg L^{-1} = 37.5 mL PMWS + 106 mL HCl

6.11.2 100 µg L^{-1} = 25.0 mL PMWS + 113 mL HCl

6.11.3 75 µg L^{-1} = 18.75 mL PMWS + 116 mL HCl

6.11.4 50 µg L^{-1} = 12.5 mL PMWS + 119 mL HCl

6.11.5 25 µg L^{-1} = 6.25 mL PMWS + 122 mL HCl

6.11.6 12 µg L^{-1} = 3.0 mL PMWS + 124 mL HCl

6.11.7 0 µg L^{-1} = 0 mL PMWS + 125 mL HCl

6.12 Bring to volume with RODI water and invert to mix thoroughly. Store in polyethylene container in a refrigerator. Standards will keep for 2 to 3 days with refrigeration. Quality Control (QC) check is MCS 100 µg L^{-1}. Final concentration of MCS and QC check is ≈6 *M* HCl.

6.13 Acid Carrier, 6 *M* HCl: Add 200 mL RODI water to a 500-mL volumetric. Carefully add 250 mL concentrated HCl and fill to volume with RODI water. Invert to mix thoroughly.

6.14 Reductant, 0.5% NaOH-0.3% $NaBH_4$: Add 200 mL RODI water to a 500-mL volumetric. Always stabilize the solution by first adding the NaOH. Add 2.5 g

NaOH and mix until dissolved. Add 1.5 g of $NaBH_4$, mix until dissolved, and fill to volume. Invert to mix thoroughly. Degas for 10 min. Make fresh daily.

6.15 Potassium iodide (KI) (10%) – ascorbic acid solution (10%): To a 500-mL volumetric, add 250 mL of RODI water. Dissolve 50 g of KI and 50 g of ascorbic acid and dilute to volume with RODI water. Invert to mix thoroughly. Make fresh daily. (Procedure requires 1-mL per sample.)

6.16 Diluent, 6 *M* HCl, for samples: Add 400 mL RODI water to a 1-L volumetric. Carefully add 500 mL concentrated HCl and fill to volume with RODI water. Invert to mix thoroughly.

6.17 QC Soil Standards: Loam C (certified reference material, purchased from High Purity Standards) and NIST SRM 2710 (National Institute of Standards and Technology, Standard Reference Material), all prepared to <200 mesh (75 µm).

7. Procedure

Digestion of Acid (HNO_3 + HCl) Extract

7.1 Prepare soil samples, soil standards, blanks, and spikes prepared in method 4H1a1 as follows: Pipette 6mL of acid (HNO_3 + HCl) extract and 6mL concentrated H_2SO_4 into a 50-mL Pyrex tube. Place in a glass beaker (4 tubes into each 250-mL beaker; maximum of 3 beakers, i.e., 12 samples, in microwave at one time). Heating program for microwave is as follows:

Parameter	Value
Stage	1
Max. Power (watts)	600
Heating Power (%)	100
Program Ramp (min)	5:00
Pressure (psi)	800
Temperature (°C)	180
Hold (min)	30:00

Place thermocouple (in thermowell) into one sample. Heat microwave until 180 °C is reached for 5 minutes. At that time, fuming (loss of HNO_3) should cease. Allow samples to cool and vent in the microwave for 5 minutes prior to removal.

7.2 To the microwave digested soil samples and MCS, pipette 15 mL of RODI water + 20 mL of concentrated HCl. Include one QC soil standard and blank in each sample rack. Soil samples and QC soil standards have a final concentration of ≈6 *M* HCl.

7.3 Digest the open tubes (do not cover) in a sample rack by submerging up to the neck of the tubes in a water bath (95 °C). Heat for 30 min and remove to cool.

7.4 Remove tubes, cool, fill to volume and cap. Mix well by inverting. (Note: digested soil samples and QC soil standards can be analyzed the same day, or placed into the refrigerator overnight for subsequent analysis the following day.) For As analysis, proceed to Section 7.5. For Se analysis, proceed to Section 7.7.

7.5 Arsenic (MCS): Pipette 36 mL of digested MCS + 4 mL of KI-ascorbic acid solution into test tubes that have been placed in the sample holder of the sample changer. Allow to stand 1 h before As analysis. Do not allow MCS to stand greater than 2 h before As analysis. For every sample extract rack, do a set of MCS.

7.6 Arsenic (sample extracts): Pipette 9 mL of sample extract + 1 mL of KI-ascorbic acid solution into test tubes that have been placed in the sample holder of the sample changer. Allow to stand 1 h before As analysis. Do not allow samples to stand longer than 2 h before As analysis.

7.7 Selenium (sample extracts and MCS): Pour sample extract and MCS (without KI-ascorbic acid solution) into test tubes that have been placed in the sample holder of the sample changer.

HGAAS Set-up and Operation

7.8 Each element is analyzed separately on the atomic absorption spectrometer. Refer to manufacturer's manual for operation of AAS. Connect EDL power supply to AAS. Allow EDL to warm up 20 to 30 minutes. Follow the manufacturer's operating procedures for AA EDL settings, warm-up, and adjustments to settings. Connect vapor generation accessory to AA. Follow the manufacturer's operating procedures for appropriate gas and liquid flow. Instrumental parameters for each element are as follows:

Element	Wavelength	Slit Width	EDL Current
	(nm)		*(mA)*
Arsenic	193.7	0.7	380
Selenium	196.0	2.0	250

The flame is required only for heating the gas flow tube and is maintained at as low a temperature as possible. Use an air/C_2H_2 mixture of 6.5 and 0.2 L min^{-1}.

7.9 For automated analysis (using the autosampler), the analysis is performed using atomic absorption with background correction, time average mode,

with a read delay of 48 s, BOC time of 5 s, and read time of 2 s. Rinse for 30 s between samples. Reported values are the average of five replications.

7.10 Use the computer and printer to set instrument parameters and to collect and record instrument readings.

7.11 The instrument readings are programmed to display analyte concentration in μg L^{-1} (ppb).

HGAAS Calibration

7.12 Each element is analyzed during separate runs on the AA. Use the calibration reagent blank and calibration standards to calibrate the AAS. Detection limits are 5 and 10 μg L^{-1} for As and Se, respectively.

7.13 Use the QC standards after every 12th sample. The QC is 100 μg L^{-1} for As and Se, respectively, with ±30% rejection criteria. If QC fails after three attempts, recalibrate and reread the QC. The QC is read at the end of each run.

7.14 If samples are outside the calibration range, a 1:5 serial dilution is performed using 6 *M* HCl. The QC soil standards (Loam C and SRM 2710) have As contents of 47±3 and 626±38, mg kg^{-1} soil, respectively, as consensus/certified values. These QC soil standards have automatic dilutions of 1:10 and 1:100, respectively.

Clean-up and Maintenance

7.15 Soak the absorption cell in dilute HNO_3 acid (0.1% w/v) for 30 min, rinse thoroughly with RODI water, and allow to dry.

7.16 If gas/liquid separator and tubing (including autosampler sipper) has been exposed to contamination with KI, pump a freshly prepared 1% sodium thiosulfate solution through the system for 10 min. The sodium thiosulfate solution must be removed by pumping RODI water through the system for 10 min.

7.17 If gas/liquid separator and tubing have not been exposed to contamination with KI, pump RODI water through the system for 10 min.

8. Calculations

Convert extract As and Se (μg L^{-1}) to soil As and Se (mg kg^{-1}) as follows:

$$\text{Soil As (mg kg}^{-1}\text{)} = [A \times B \times C \times R \times 1000] / E \times 1000$$

where:

A = Sample extract reading (μg L^{-1})

B = Extract volume (L) (0.05)

C = Dilution, if performed

1000 = Conversion factor in numerator to kg-basis

1000 = Factor in denominator (µg mg^{-1})

R = Air-dry/oven-dry ratio (method 3D1)

E = Sample weight (g) (0.5)

Soil Se (mg kg^{-1}) = [A x B x C x R x 1000]/E x 1000

where:

A = Sample extract reading (µg L^{-1})

B = Extract volume (L) (0.05)

C = Dilution, if performed

1000 = Conversion factor in numerator to kg-basis

1000 = Factor in denominator (µg mg^{-1})

R = Air-dry/oven-dry ratio (method 3D1)

E = Sample weight (g) (0.5)

9. Report

Report As and Se to the nearest 0.1 mg kg^{-1} soil.

10. Precision and Accuracy

Precision and accuracy data are available from the SSL upon request.

11. References

Anawar, H.M., J. Akai, K.M.G. Mostofa, S. Safiullah, and S.M. Tareq. 2002. Arsenic poisoning in groundwater: Health risk and geochemical sources in Bangladesh. Environ. Int. 27:597–604.

Chen, M., L.Q. Ma, and W.G. Harris. 2002. Arsenic concentrations in Florida surface soils: influence of soil type and properties. Soil Sci. Soc. Am. J. 66:632–640.

Huang, P.M., and R. Fujii. 1996. Selenium and arsenic. p. 793–831. *In* D.L. Sparks (ed.) Methods of soil analysis. Part 3 – Chemical Analysis. Soil Sci. Soc. Am. Book Series No. 5. ASA and SSSA, Madison, WI.

Martens, D.A., and D.L. Suarez. 1997. Selenium speciation of marine shales, alluvial soils, and evaporation basin soils of California. J. Environ. Qual. 26:424–432.

Office of Environmental Health Assessment Services. 1999. Hazards of short-term exposure to arsenic contaminated soil. State of Washington. Olympia, WA.

Pinsker, L.M. 2001. Health hazards: Arsenic. Geotimes. Nov. p. 32–33.

Ryker, S.J. 2001. Mapping arsenic in groundwater: a real need, but a hard problem. Geotimes. Nov. p. 34–36.

Total Analysis (4H)

Acid Digestion (4H1)

HNO_3 + HCl Digestion (4H1a)

Microwave (4H1a1)

Cold Vapor Atomic Absorption Spectrophotometer (4H1a1c)

Mercury (4H1a1c1)

Air-Dry, <2-mm (4H1a1c1a1)

1. Application

Mercury is highly toxic to both plants and animals, and enters the food chain primarily through atmospheric deposition (smelting, coal combustion, volcanic activity) and pesticide usage (Pais and Jones, 1997). Due to the absorption of Hg by both organic and inorganic soil components, many studies have been performed which have examined soil-Hg interactions (MacNaughton and James, 1974; Barrow and Cox, 1992; Yin et al., 1996) and ecosystem distributions (Hall et al., 1987; Inacio et al., 1998).

2. Summary of Method

Soil digests (HNO_3+HCl) from method 4H1a1 are analyzed for Hg using cold-vapor atomic absorption spectroscopy (CVAAS). This method is based on absorption of radiation at 253.7 nm wavelength by Hg vapor. The digest is mixed with stannous chloride to reduce Hg to the elemental state. Using argon as a carrier gas, the solution is passed over a gas-liquid separator in a closed system to separate the gaseous Hg from solution. The Hg vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration. Mercury data are reported as μg kg^{-1} soil by method 4H1a1c1.

3. Interferences

Copper, chlorides, and certain volatile organic materials may be interferences.

4. Safety

Soil digests contain acid and must be handled appropriately. Procedure uses a primary Hg standard that is diluted for working standards. Use gloves and avoid skin contact. Gasses exhausting from the Hg analyzer cabinet, prior to passing through the Hg vapor trap, may contain Hg vapor. Do not run the instrument unless the exhaust gas is properly scrubbed or removed.

5. Equipment

5.1 Cold-vapor atomic absorption spectrophotometer (CVAAS), CETAC M-6000A Mercury Analyzer, CETAC Corp., Omaha, NE

5.2 Autosampler, CETAC ASX-500 Model 510, CETAC Corp., Omaha, NE

5.3 Autodilutor Accessory, CETAC ADX-500, CETAC Corp., Omaha, NE

5.4 Nafion drying tube, CETAC Corp., Omaha, NE

5.5 Peristaltic Pump, CETAC Corp., Omaha, NE

5.6 Computer, Microsoft Windows 97, CETAC M-6000A Software, CETAC, Corp., Omaha, NE, and printer

5.7 Pipettors, electronic digital, Rainin Instrument Co., Woburn, MA, 2500 µL and 10 mL

5.8 Compressed argon gas

5.9 Calcium sulfate (anhydrous) or equivalent desiccant

6. Reagents

6.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

6.2 Concentrated hydrochloric acid (HCl), 12 *N*. Use trace pure HCl.

6.3 Concentrated nitric acid (HNO_3), 16 *N*. Use trace pure HNO_3.

6.4 Primary standard: 1000 mg L^{-1} Hg, High-Purity Standards, Charleston, SC

6.5 Stock standard, 500 µg L^{-1}: Add 0.25 mL primary standard to 500 mL volumetric and dilute to mark with RODI water and invert to mix thoroughly.

6.6 Standard Hg calibration solutions or working standards are 4.0, 3.0, 2.5, 1.0, 0.5, and 0.0 µg L^{-1}. To six 50-mL volumetric flasks add as follows:

6.6.1 0.0 µg L^{-1} = 9 mL HNO_3 + 3 mL HCl

6.6.2 0.5 µg L^{-1} = 0.05 mL stock standard + 9 mL HNO_3 + 3 mL HCl

6.6.3 1.0 µg L^{-1} = 0.1 mL stock standard + 9 mL HNO_3 + 3 mL HCl

6.6.4 2.5 µg L^{-1} = 0.25 mL stock standard + 9 mL HNO_3 + 3 mL HCl

6.6.5 3.0 µg L^{-1} = 0.3 mL stock standard + 9 mL HNO_3 + 3 mL HCl

6.6.6 4.0 µg L^{-1} = 0.4 mL stock standard + 9 mL HNO_3 + 3 mL HCl

Dilute each working standard to mark with RODI water and invert to mix thoroughly. These working standards are used for Normal and High Throughput Ranges.

6.7 Stannous chloride, reducing agent 10% stannous chloride solution ($SnCl_2$ in 7% HCl). Add 50 g of stannous chloride and 97.2 mL concentrated HCl

to 500 mL volumetric and dilute to mark with RODI water. Invert to mix thoroughly.

6.8 Diluent: Add 90 mL concentrated HNO_3 and 30 mL concentrated HCl to 500 mL volumetric and dilute to mark with RODI water. Invert to mix thoroughly.

6.9 Rinse (5% HNO_3): Add 71.4 mL HNO_3 to 1-L volumetric and dilute to mark with RODI water. Invert to mix thoroughly.

6.10 Potassium permanganate, solid, crystalline, fills safety trap for Hg vapor exhaust.

6.11 Glass wool. Fine glass wool only.

7. Procedure

7.1 Oven radiator temperature must be at 125 °C to maintain the actual gas temperature of 50 °C. Argon gas carrier must be supplied at 100 psig (6.9 bar). Liquid flow is always set at fixed flow of 4.0 mL min^{-1} (sample) and 0.8 mL min^{-1} (reagent).

7.2 Turn mercury analyzer and mercury lamp for warm-up (90 min) prior to analysis. Ensure integrity of lamp (there is some loss of performance at 13 mA but replace at 15 mA).

7.3 Turn on computer and choose Worksheet Template appropriate to range of analysis. Three ranges of analysis (Highest Sensitivity, Normal, and High Throughput) have been developed on the CETAC Mercury Analyzer. Method parameters for each of these ranges are saved on a different Worksheet Template. General parameters are as follows:

High Throughput Range	
Sampling Times	
Integration	1 s
Read Delay	35 s
Auto-Adjust Integration	
Replicates	4
Instrument Control	
Gas Flow	300 mL min^{-1}
Autosampler Setup	
Sip Duration	20 s
Rinse Time	20 s
Repeats	1

Sample Matrix	Liquid
Reslope Frequency	0
Reslope Standard	Standard No. 3 (check standard)
Detection Limit	0.050 µg L^{-1}
Baseline Correction	1 point

Normal Range	
Sampling Times	
Integration	1 s
Read Delay	50 s
Auto-Adjust Integration	
Replicates	4
Instrument Control	
Gas Flow	85 mL min^{-1}
Autosampler Setup	
Sip Duration	30 s
Rinse Time	45 s
Repeats	1
Sample Matrix	Liquid
Reslope Frequency	0
Reslope Standard	Standard No. 3 (check standard)
Detection Limit	0.015 µg L^{-1}
Baseline Correction	1 point

Highest Sensitivity Range	
Sampling Times	
Integration	1
Read Delay	50
Auto-Adjust Integration	
Replicates	4

Instrument Control	
Gas Flow	40 mL min^{-1}
Autosampler Setup	
Sip Duration	60 s
Rinse Time	140 s
Repeats	1
Sample Matrix	Liquid
Reslope Frequency	0
Reslope Standard	Standard No. 3 (check standard)
Detection Limit	0.001 µg L^{-1}
Baseline Correction	2 point

7.4 Prior to analysis ensure that the gas-liquid separator (GLS) post is fully wetted as follows:

7.4.1 Check the bottle supplying the ASX-500 rinse station is full of 5% HNO_3.

7.4.2 Use quick release mechanism and fully release clamp tension on lower two tube channels of peristaltic pump (drain channels).

7.4.3 Use sample and reagent tubes and pump 5% HNO_3 and stannous chloride reagent, respectively.

7.4.4 With drain pump tubes unclamped, GLS should begin to fill with 5% HNO_3.

7.4.5 Allow GLS to fill until liquid level reaches top of GLS center post or until gas bubble propels a meniscus upward to wet post all along its length, including apex.

7.4.6 Upon wetting, immediately reengage quick-release clamps on drain pump tubes.

7.4.7 Do not let liquid level overflow GLS into Nafion drying tube.

7.4.8 With drain tube clamps properly reengaged and pump running, liquid level normally stops rising and goes back down.

7.4.9 Once GLS has emptied, leave pump running (keep liquid flowing).

7.5 Zero analyzer to compensate for baseline offsets (due to microscopic dust buildup on the optics, dirty sample windows, and thermal drift).

7.6 Define Time Profile using Signal Profile Chart (sample time, and 1st and 2nd baseline correction points) as follows:

7.6.1 Current sample time on chart will start at dark green vertical line and stop at light red vertical line.

7.6.2 Using mouse, define sample time by clicking on chart and dragging to right.

7.6.3 Integration times will automatically be recalculated based on new total sample time.

7.6.4 Current 1st baseline correction point will start at light blue vertical line and stop at dark red line.

7.6.5 Use mouse and shift key and change point times by clicking on chart and dragging to right.

7.6.6 To do this, press and hold shift key.

7.6.7 Click with left mouse button on left limit of part of signal to be used on baseline correction point.

7.6.8 Light blue vertical cursor line will appear.

7.6.9 Without releasing shift key or left mouse button, drag mouse to right until portion of signal to be used as baseline correction point is between light blue and dark red cursor lines.

7.6.10 Release shift and mouse key and chart will update baseline times in worksheet.

7.6.11 Current 2nd baseline correction point on chart will start at light green vertical line and stop at purple line.

7.6.12 Use mouse and control key, change point times by clicking on chart and dragging to right.

7.7 Enter sample numbers, final volume, and weights in “Labels”.

7.8 Run calibration and analysis in “Analysis”.

7.9 After completion of analytical run, run RODI water through sample sipper tube and stannous chloride reagent lines. Pump all lines dry after rinsing.

7.10 Perform shutdown: turn off mercury lamp, argon gas, ASX-500, pump, M-6000 main power, close the M-6000A Software, and turn off the computer.

8. Calculations

Analytical data is reported by the instrument in μg mL^{-1} in solution. It is converted to μg kg^{-1} in soil as follows:

Hg in soil (μg kg^{-1}) = [A x B x C x R x 1000] / E

where:

A = Sample extract reading (μg L^{-1})

B = Extract volume (mL)

C = Dilution, if performed

1000 = Conversion factor in numerator to kg-basis

R = Air-dry/oven-dry ratio (method 3D1)

E = Sample weight (g)

9. Report

Hg data are reported to the nearest 0.1 µg kg^{-1}.

10. Precision and Accuracy

Precision and accuracy data are available from the SSL upon request.

11. References

Barrow, N.J., and V.C. Cox. 1992. The effects of pH and chloride concentration on mercury sorption: I. By goethite. J. Soil Sci. 43:295–304.

Hall, A., A.C. Duarte, M.T. Caldeeira, and M.F. Lucas. 1987. Sources and sinks of mercury in the coastal lagoon of Aveiro, Portugal. Sci. Total Environ. 64:75–87.

Inacio, M.M., V. Pereira, and M.S. Pinto. 1998. Mercury contamination in sandy soils surrounding an industrial emission source (Estarreja, Portugal). Geoderma 85:325–339.

MacNaughton, M.G., and R.O. James. 1974. Adsorption of aqueous mercury (II) complexes at the oxide/water interface. J. Colloid Interface Sci. 47:431–440.

Pais, Istvan, and J.B. Jones, Jr. 1997. The handbook of trace elements. St. Lucie Press. Boca Raton, FL. 223 pp.

Yin, Y., H.E. Allen, Y. Li, C.P. Huang, and P.F. Sanders. 1996. Adsorption of mercury(II) by soil: Effects of pH, chloride, and organic matter. J. Environ. Qual. 25(4):837–844

Ground and Surface Water Analyses (4I)

Total Analysis (4I3)

Inductively Coupled Plasma Atomic Emission Spectrophotometer (4I3a)

Axial Mode (4I3a1)

Ultrasonic Nebulizer (4I3a1a)

Aluminum, Iron, Manganese, Phosphorus, and Silicon (4I3d1a1-5)

1. Application

Nutrients (nitrogen and phosphorus), sediments, pesticides, salts, or trace elements in ground and surface water affect soil and water quality (National

Research Council, 1993). This procedure was developed for the analysis of the elemental content of ground or surface water.

2. Summary of Method

The water is filtered and acidified with HCl. Two calibration standards plus a blank are prepared for elemental analysis. An inductively coupled plasma atomic emission spectrophotometer (ICP–AES) in axial mode is used to determine the concentration of Al, Fe, Mn, P, and Si (mg L^{-1}) by methods 4I3d1a1-5, respectively.

3. Interferences

Spectral and matrix interferences exist. Interferences are corrected or minimized by using an internal standard. Also, careful selection of specific wavelengths for data reporting is important. Samples and standards are matrix matched to help reduce interferences.

4. Safety

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Restrict the use of concentrated acids to the fume hood. Wash hands thoroughly after handling reagents.

5. Equipment

5.1 Syringe filters, 0.45-µm diameter, Whatman, Clifton, NJ

5.2 Tubes, 50-mL, with caps

5.3 Volumetrics, 500-mL and 200 ml, class A glass

5.4 Containers, 500-mL, polypropylene, with screw caps

5.5 Pipettors, electronic digital, Rainin Instrument Co., Woburn, MA, 2500 µL and 10 mL

5.6 Inductively coupled plasma atomic emission spectrophotometer (ICP–AES), Perkin-Elmer Optima 3300 Dual View (DV), Perkin-Elmer Corp., Norwalk, CT.**5.7** Computer, with WinLab software, ver. 4.1, Perkin-Elmer Corp., Norwalk, CT, and printer

5.8 Compressed gasses, argon (minimum purity = 99.996%) and nitrogen (minimum purity = 99.999%)

5.9 Autosampler, AS-90, Perkin-Elmer Corp., Norwalk, CT

5.10 Quartz torch, alumina injector (2.0 mm id), Ultrasonic Nebulizer, Model U-5000AT+ , CETAC Corp., Omaha, NE

6. Reagents

6.1 Deionized, reverse osmosis (RODI) water, ASTM Type 1 grade of reagent water

6.2 Concentrated hydrochloric acid (HCl), 12 *N*. Use trace-pure grade that contains low levels of impurities.

6.3 Primary standards:1000 mg L^{-1}, High Purity Standards, Charleston, SC. Single elemental standards are manufactured in dilute HNO_3, HNO_3+HF, or H_2O.

6.4 Internal standard: HNO_3, trace pure

7. Procedure

7.1 Water sample is filtered into a 50-mL tube and capped. If extracts are not to be determined immediately after collection, then store samples at 4 °C. Analyze samples within 72 h.

7.2 The working calibration standards (WCS) are made from dilution of the primary standards. The low and high WCS for Al and Si are prepared as follows:

7.2.1 ALLO is 0.5, 2.5, and 2.5 mg L^{-1} of Al, Fe, and Mn, respectively. To a 500-mL volumetric flask, add 0.25, 1.25, and 1.25 mL of the Al, Fe, and Mn primary standard (1000 mg L^{-1}), respectively.

7.2.2 ALHI is 1.0, 5.0, and 5.0 mg L^{-1} of Al, Fe, and Mn, respectively. To a 500-mL volumetric flask, add 0.50, 2.50, and 2.50 mL of the Al, Fe, and Mn primary standard (1000 mg L^{-1}), respectively.

7.2.3 SILO is 0.5 and 0.5 mg L^{-1} of Si and P, respectively. To a 500-mL volumetric flask, add 0.25 and 0.25 mL of the Si and P primary standard (1000 mg L^{-1}), respectively.

7.2.4 SIHI is 1.0 and 1.0 mg L^{-1} of Si and P, respectively. To a 500-mL volumetric flask, add 0.50 and 0.50 mL of the Si and P primary standard (1000 mg L^{-1}), respectively.

7.3 Samples are treated with 0.5 mL HCl for each 10 mL water.

7.4 A 10 mg L^{-1} Lu internal standard (read at 291.138 nm) is added to the blank, all calibration standards, and samples. It is prepared by adding 5.0 mL Lu primary standard (1000 mg L^{-1}) and 10 mL conc. HNO_3 to a 500 ml volumetric flask, and diluting to volume with RODI water.

7.5 Use the ICP–AES spectrophotometer in axial mode to analyze elements. Use ultrasonic nebulization of sample. Internal standard is added via an external peristaltic pump at 15% pump speed using 0.44 mm id. pump tubing. Internal standard and samples or standards are mixed via a mixing block and coil prior to entering the ultrasonic nebulizer. Typically, no initial

dilutions of samples because of high concentrations 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.

7.6 Analyses are generally performed at two or more wavelengths for each element. The selected wavelengths are as follows (reported wavelength listed first and in boldface):

Element	Wavelength
	nm
Mn	**260.570**, 257.610, 403.075
P	**178.221**, 213.620, 214.910
Al	**308.215**, 167.022, 396.153
Fe	**238.203**, 239.562, 259.939
Si	**251.611**, 212.412, 288.158
Lu	**291.138** (Internal Standard)

7.7 Use the blank standard solution to dilute those samples with concentrations greater than the high standard. Rerun all elements and use only the data needed from the diluted analysis.

7.8 Establish detection limits using the blank standard solution. 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. Analyzed values lower than the detection limits are reported as “ND” or non-detected.

8. Calculations

With the HCl treatment (0.5 mL per 10 mL water) in the calculations, the concentrations are then reported directly, unless additional dilutions are performed because of high analyte concentrations.

9. Report

Data are reported to the nearest 0.01 mg L^{-1}.

10. Precision and Accuracy

Precision and accuracy data are available from the KSSL upon request.

11. References

National Research Council. 1993. Soil and Water Quality. An agenda for agriculture. Natl. Acad. Press, Washington, DC.

SOIL BIOLOGICAL AND PLANT ANALYSIS (6)

Soil Analyses (6A)

Sample Preparation (1B3b2b1)

0.5 M K_2SO_4 Extraction + Heating with Disodium Bicinchoninic Reagent (6A1)

UV-Visible Spectrophotometer, Dual Beam (6A1a)

Hot Water Extractable Organic Carbon (6A1a1)

Air-Dry, <2 mm (6A1a1a1)

1. Application

Hot water soluble soil carbohydrates are thought to be primarily extra-cellular polysaccharides of microbial origin. They help bind soil particles together into stable aggregates. Water stable aggregates reduce soil loss through erosion and increase organic matter and nutrient content. They also occur as part of the fast or labile organic carbon pool in soils. This labile pool contains the most available carbon for plant, animal and microbial use. The hot water soluble organic C makes up from 4 to 10% of the microbial biomass C determined by chloroform fumigation. It also makes up about 6 to 8% of the total carbohydrate content in the soil. This pool is the most easily depleted of the three organic C pools (Joergensen et al., 1996; Haynes and Francis, 1993).

2. Summary of Method

Water is added to a 10-g soil sample and autoclaved at 1 h at 121 °C. Extractable carbohydrates are measured by adding disodium bicinchoninic (BCA) reagent to a 0.5 M K_2SO_4 soil extract, heating to 60 °C for 2 h, cooling, and reading the absorbance at 562 nm using a spectrophotometer. Glucose is used as a standard and results expressed as glucose-C. Data are reported as mg glucose equivalent-carbon kg^{-1} soil by method 6A1a1.

3. Interferences

Carbohydrates from non-microbial sources can be avoided by using the BCA reagent that is selective for microbial carbohydrates. 0.5 *M* K_2SO_4 extracts of soil are usually supersaturated with $CaSO_4$, with the excess $CaSO_4$ precipitating during storage, especially if samples are frozen and during heating of the extract with BCA reagent (Joergensen et al., 1996). Sodium hexametaphosphate is added to buffer to prevent $CaSO_4$ precipitation (Joergensen et al., 1996). Aspartic acid is used to chelate Cu^{2+}, preventing undesirable oxidation and so improving precision (Sinner and Puls, 1978).

4. Safety

Wear safety glasses when preparing solutions and handling soil extracts. Use oven mitts, tongs, and other devices to avoid contact with hot water and instruments used.

5. Equipment

5.1 Electronic balance, ±1.0-mg sensitivity

5.2 Steam sterilizer, 121 °C-capability

5.3 Erlenmeyer flasks, 125-mL

5.4 Filter paper, Whatman 42, 150 mm

5.5 Pipette, electronic digital, 10,000 µL, with tips, 10,000 µL

5.6 Test tubes, 10-mL

5.7 Hot water bath, 60 °C capability

5.8 Cuvettes, plastic, 4.5-mL, 1-cm light path, Daigger Scientific

5.9 Spectrophotometer, UV-Visible, Varian, Cary 50 Conc, Varian Australia Pty Ltd.

5.10 Computer with Cary WinUV software, Varian Australia Pty Ltd., and printer

6. Reagents

6.1 Reverse osmosis deionized water (RODI), ASTM Type I grade of reagent water

6.2 0.5 *M* K_2SO_4 solution. In a 1-L volumetric, dissolve 87.135 g K_2SO_4 (dried for 2 h at 110 °C) in RODI water. Dilute to volume and invert to mix thoroughly.

6.3 Stock standard glucose solution (SSGS), 20.0 mg glucose L^{-1}. In 1-L of 0.5 *M* K_2SO_4 solution, dissolve 0.02 g glucose (dextrose). Dilute to volume and invert to thoroughly mix. Store in polyethylene containers. Make fresh weekly. Store in a refrigerator.

6.4 Solution 1: Add 4 g Na_2CO_3, 4 g sodium hexametaphosphate $[(NaPO_3)]_6$, and 0.2 g DL-aspartic acid in 100 mL RODI water. pH solution to 11.25 with NaOH.

6.5 Solution 2: Dissolve 0.48 g bicinchoninic acid in 12 mL RODI water (0.1 *M*).

6.6 Solution 3: Dissolve 1 g $CuSO_4$ in 25 mL RODI water (0.25 M).

6.7 Disodium bicinchoninic (BCA) reagent: Mix 100 mL Solution 1, 12 mL Solution 2, and 1.8 mL of Solution 3=BCA reagent. Store in polyethylene containers. Make fresh daily. Store in a refrigerator.

6.8 Standard glucose working solutions (SGWS), 10.0, 5.0, 2.5, 1.25, 0.75, and

0.375 mg glucose L^{-1}. In six test tubes, add 5 mL RODI water. Perform six serial dilutions. Begin as follows: add 5 mL of SSGS to Tube 1 and shake (10.0 mg glucose L^{-1}) and extract 5 mL from Tube 1, add to Tube 2, and shake (5.0 mg glucose L^{-1}). Proceed to make all six SGWS.

6.9 Standard glucose calibration solutions (SGCS). Add 2 mL of each SGWS to a separate test tube, followed by 2 mL BCA reagent. Blank = 2 mL RODI water and 2 mL BCA reagent.

7. Procedure

7.1 Weigh 10 g of <2-mm (sieved), air-dry soil to the nearest mg and place into a 125-mL Erlenmeyer flask. If soil is highly organic, weigh 2 g of fine-grind material to the nearest mg.

7.2 Add RODI water to soil at a 1:4 ratio (10 g to 40 mL water or 2 g soil to 8 mL water).

7.3 Autoclave 1 h at 121 °C and 15 psi. Cool and filter.

7.4 Pipette 2 mL of each sample extract, 0.5 mL K_2SO_4, and 2 mL disodium BCA reagent into test tubes.

7.5 Place all tubes (SGCS, blank, and samples) in hot water bath for 2 h at 60 °C.

7.6 Allow to cool and transfer sample extract and SGCS to cuvettes.

7.7 Set the spectrophotometer to read at 562 nm. Autozero with calibration blank.

7.8 Calibrate the instrument by using the SGCS. The data system will then associate the concentrations with the instrument responses for each SGCS. Rejection criterion for SPCS, if R^2 <0.99.

7.9 Run samples using calibration curve. Sample concentration is calculated from the regression equation.

7.10 If samples are outside calibration range, dilute sample extracts with extracting solution and re-analyze.

8. Calculations

Convert extract glucose equivalent (mg L^{-1}) to glucose equivalent-carbon in the soil (mg kg^{-1}) as follows:

Soil glucose-C (mg kg^{-1}) = [(A x B x C x R x 0.40 x 1000)/E]

where:

A = Sample reading (mg L^{-1})

B = Extract volume (L)

C = Dilution, if performed

R = Air-dry/oven-dry ratio (method 3D1)

0.40 = Mass fraction C in glucose

1000 = Conversion factor to kg-basis

E = Sample weight (g)

9. Report

Report data to the nearest 0.1 mg glucose equivalent-carbon kg^{-1} soil.

10. Precision and Accuracy

Precision and accuracy data are available from the SSL upon request.

11. References

Haynes, R.J., and G.S. Francis. 1993. Changes in microbial biomass C, soil carbohydrate composition and aggregate stability induced by growth of selected crop and forage species under field conditions. J. Soil Sci. 44:665–675.

Joergensen, R.G., T. Mueller, and V. Wolters.1996. Total carbohydrates of the soil microbial biomass in 0.5 M K_2SO_4 soil extracts. Soil Biol. Biochem. 28:9:1147–1153.

Sinner, M., and J. Puls. 1978. Non-corrosive dye reagent for detection of reducing sugars in borate complex ion-exchange chromatography. J. Chrom. 15.

Soil Analyses (6A)

Sample Preparation (1B3b2b1)

Acid Dissolution (6A3)

1 *N* HCl + $FeCl_2$ (6A3a)

CO_2 Analysis (6A3a1)

Gas Chromatography (6A3a1a)

Carbonates (6A3a1a1)

Air-Dry, <2 mm (6A3a1a1a1)

1. Application

Methods involving determination of CO_2 have usually been preferred for measuring soil carbonate (Loeppert and Suarez, 1996). CO_2 released can be measured gravimetrically (Allison, 1960; Allison and Moodie, 1965), titrimetrically (Bundy and Bremmer, 1972), manometrically (Martin and Reeve, 1955; Presley, 1975), volumetrically (Dreimanis, 1962), spectrophotometrically by infrared spectroscopy, or by gas chromatography (Loeppert and Suarez, 1996). The SSL routinely determines the amount of carbonate in the soil by treating the $CaCO_3$ with HCl, with the evolved CO_2 measured manometrically (methods 4E1a1a1a1-2

for <2-mm and 2- to 20-mm bases, respectively). The method herein describes soil carbonate by acid decomposition and CO_2 analysis by gas chromatography. This method is more commonly used in soil biochemical and biology studies, where organic C in soils with carbonates may be more precisely determined by subtracting the total carbonates (inorganic C) from total C (method 4H2a1).

2. Summary of Method

Soil carbonate is determined by chromatographic analysis of CO_2 evolved upon acidification of soil in a closed system of known headspace. Ferrous iron ($FeCl_2$) is added to the acid as an anti-oxidant, and the dilute acid solution (1*N* HCl) is chilled before addition to soil to minimize the decarboxylation of organic matter by the acid. Data are reported as mg CO_2-C per g of soil to the nearest 0.1 g (6A3a1a1). These data can be used to estimate soil organic carbon by subtracting (CO_2-C x 0.2727) from total carbon (4H2a1).

3. Interferences

It is essential that precautions be taken to ensure that there is no interference from organic matter oxidation (Loeppert and Suarez, 1996). This procedure may be more appropriate for soils with relatively low amounts of carbonates (<15%).

4. Safety

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses) when handling acids. Thoroughly wash hands after handling acids. Use the fume hood when diluting concentrated HCl. Use the safety showers and eyewash stations to dilute spilled acids. Use sodium bicarbonate and water to neutralize and dilute spilled acids.

5. Equipment

5.1 Canning jars, 1-qt (0.984-L), with lids fitted with gas-sampling septa

5.2 Syringe, 20-mL, with 18-gauge needle

5.3 Disposable syringe, 1-mL, for gas sampling

5.4 Needle, 18 or 20 gauge, for venting jars

5.5 Electronic balance, ±0.01-g sensitivity

5.6 Gas chromatograph (GC) with thermal conductivity detector (TCD)

5.7 Beaker, glass, 600-mL

5.8 Filter paper, Whatman 42, 150 mm

5.9 Stirrer

6. Reagents

6.1 Reverse osmosis deionized (RODI) water, ASTM Type I grade of reagent water

6.2 1*N* HCl with 3.1 g $FeCl_2$ added per 100 mL of solution, chilled to 4 to 5 °C. Prepare 500 mL of solution of as follows: weigh 15.5 g $FeCl_2$ into 600-mL beaker; add 20-mL RODI water; stir (medium speed) until all crystals have dissolved; filter solution to remove insoluble ferric iron particulates; transfer to 500-mL volumetric; add 41.7 mL concentrated HCl to aqueous $FeCl_2$; bring to volume with RODI water; and chill solution to 4 to 5 °C.

7. Procedure

7.1 Determine water content of soil sample so results may be expressed on an oven-dry soil basis. Refer to water retention methods (3C).

7.2 Weigh 5g of <2-mm (sieved), air-dry soil to the nearest 0.01 g into clean 1-qt jar.

7.3 Tightly seal jar with lid fitted with gas sampling septum. Also include one or more jars with no soil added to serve as reagent controls and CO_2 background indicators.

7.4 Add 20 ml of RODI water (room temperature) to jar through septum with 20-mL syringe, venting jar with 18 or 20 gauge needle.

7.5 Add 20 mL of chilled 1*N* HCl + $FeCl_2$ solution through septum as in Section 7.4 (do not vent), let stand 2 h, swirling soil-acid solution occasionally.

7.6 Take gas sample for gas chromatograph analysis using 1-mL syringe. Purge syringe several times before withdrawing final sample for analysis.

8. Calculations

Calculation of Soil Carbonate mass from CO_2% volumetric concentrations (Kettler and Doran, 1995).

8.1 Reaction equation:

$$CaCO_3 + 2HCl\ (aq) \rightarrow CO_2\uparrow + H_2O + CaCl_2\ (aq)$$

mg CO_2-C produced = mg CO_3−C dissolved by acid in soil

mg CO_2-C produced/OD = mg CO_3-C/OD

where:

OD = Oven-dry soil (g)

8.2 Net jar headspace:

Volume of Empty 1-qt jar = 978 cm^3 (measured by H_2O volume displacement).

Soil Solid Volume (cm^3) = [g Moist Soil / (1 + %H_2O/100)] / (Particle Density)

Soil Solid Volume (cm^3) = (5.00 g sample / (1 + %H_2O/100)) / (2.65g cm^{-3})

where:

2.65 = assumed particle density (g cm^{-3})

Net jar headspace (cm^3)

= Empty Jar − Soil Solid Volume − Soil H_2O Volume − Liquid Volume

= 978 cm^3 − (Soil Solid Volume, cm^3) − (g Oven-dry Soil/1 + % H_2O/100) − (20 cm^3 H_2O + 20 cm^3 Acid)

= 978 cm^3 − 1.89 cm^3 − 40 cm^3

= 936.1 cm^3 (936 to 935.4 cm^3 for 3 − 30% H_2O)

where:

5.00 = g soil oven-dry basis, assumed

8.3 Gaseous CO_2-Carbon produced:

This step is important for soils with >15% carbonates.

mg CO_2-Carbon produced by soil carbonate decomposition and detected as CO_2 in vapor space

= 4.594 mg CO_2-Carbon / atm x ((Mole % CO_{2s} x P_{ts}, atm) − (Mole % CO_{2b} x P_{tb}, atm))

where:

P_{tb} = Total pressure in blank jar by electronic manometer

P_{ts} = Total pressure in sample jar by electronic manometer

Mole % CO_{2b} = Mole % CO_2 in blank jar by GC

Mole % CO_{2s} = Mole % CO_2 in sample jar by GC

8.4 CO_2-Carbon produced but dissolved in solution:

mg CO_2-Carbon produced by soil carbonate decomposition but dissolved in solution

= (0.163 mg CO_2-C / atm) x ((Mole % CO_{2s} x P_{ts}, atm) − (Mole % CO_{2b} x P_{tb}, atm))

Total mg CO_3-Carbon / OD = Total mg CO_2-Carbon / OD

= {[(0.163 mg CO_2-C / atm) x ((Mole % CO_{2s} x P_{ts}, atm) − (Mole % CO_{2b} x P_{tb}, atm))] + [4.594 mg CO_2-Carbon / atm x ((Mole % CO_{2s} x P_{ts}, atm) − (Mole % CO_{2b} x P_{tb}, atm))]} / {FM/FMOD)}

= {[4.757 mg CO_2-C / FM / atm] x [(Mole % CO_{2s} x Pts, atm) − (Mole % CO_{2b} x P_{tb}, atm)]} x (FMOD)

where:

OD = Oven-dry soil (g)

FM = Field-moist soil (g)

FMOD = Field-moist soil/oven-dry ratio (g/g) (method 3D2)

8.5 Convert mg CO_2-C per g of soil to percent CO_2-C in soil as follows:

(mg CO_2-C/g soil) (1g/1000 mg) (100 g soil) = Percent CO_2-C in soil

9. Report

Report % CO_2-C in soil to the nearest 0.1%. These data can be used to estimate soil organic carbon by subtracting (CO_2-C x 0.2727) from total carbon (4H2a1).

10. Precision and Accuracy

Precision and accuracy data are available from the SSL upon request.

11. References

Allison, L.E. 1960. Wet combustion apparatus and procedure for organic and inorganic carbon in soil. Soil Sci. Soc. Am. Proc. 24:36–40.

Allison, L.E., and C.D. Moodie. 1965. Carbonate. p. 1379–1400. *In* C.A. Black, D.D. Evans, J.L. White, L.E. Ensminger, and F.E. Clark (eds.) Methods of soil analysis. Part 2. 2nd ed. Agron. Monogr. 9. ASA, CSSA, and SSSA, Madison, WI.

Bundy, L.G., and J.M. Bremmer. 1972. A simple titrimetric method for determination of inorganic carbon in soils. Soil Sci. Soc. Am. Proc. 36:273–275.

Dreimanis, A. 1962. Quantitative gasometric determination of calcite and dolomite by using Chittick apparatus. J. Sediment. Petrol. 32:520–529.

Kettler, T., and J. Doran. 1995. Determination of soil carbonate concentration by acid decomposition and GC CO_2 analysis. USDA–ARS, University of Nebraska, Lincoln (unpublished).

Loeppert, R.H., and D.L. Suarez. 1996. Carbonate and gypsum. *In* D.L. Sparks (ed.) Methods of soil analysis. Part 3. Chemical methods. ASA and SSSA, Madison, WI.

Martin, S.E., and R. Reeve. 1955. A rapid manometric method for determining soil carbonate. Soil Sci. 79:187–197.

Presley, B.J. 1975. A simple method for determining calcium carbonate in sediment samples. J. Sediment. Petrol. 45:745–746.

Particulate Organic Matter and C-Mineral (6A4)

Sample Preparation (1B3b2a1)
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, Analyzed (6A4a1a1-3a2)

1. Application

Particulate organic matter (POM) is a physical fraction of the soil >53 µm in diameter (Elliott and Cambardella, 1991; Cambardella and Elliott 1992; Follett and Pruessner, 1997). Some researchers combine this fraction with the fast or labile pool. Others have described this pool as slow, decomposable, or stabilized organic matter (Cambardella and Elliott, 1992). To avoid confusion, this fraction may best be described as representing an intermediate pool with regards to decomposition. This fraction is similar to various sieved and physical fractions such as the resistant plant material (RPM) (Jenkinson and Rayner, 1977), and size fractions (Gregorich et al., 1988), and variously determined light fractions of the soil organic matter (Strickland and Sollins, 1987; Hassink, 1995).

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 tillage plots (20 yr.). Measurable reductions are believed to occur in the range of 1 to 5 years (Cambardella and Elliott, 1992).

When paired samples are selected either in time or between two tillage treatments, a comparison can be made to determine the impact of the tillage practice. POM can be used in soil organic matter modeling, as a soil quality indicator and as an indicator of the SOM that can move into the active C pool.

Since the late 1970's several models have been developed to estimate the dynamics of organic matter in the soil. All of these models have at least two phases, slow and rapid. In measuring these two phases chemical fractionation (humic and fulvic acids) has been found to be less useful than physical fractionation (Hassink, 1995). Examples of some of these models can be found in Jenkinson and Rayner (1977), tests of the CENTURY Soil Organic Model (Parton et al., 1994; Metherell et al., 1993; and Montavalli et al., 1994). A minimum data set for soil organic carbon is proposed by Gregorich et al. (1994) that includes POM as one of the primary parameters.

2. Summary of Method

The procedural steps described herein encompasse the physical separation (1B3b2a) of the soil organic matter (<2 mm) into two fractions: (1) ≥53-µm, POM

and (2) <53 µm, C-Mineral (C-Min) (Cambardella and Elliot, 1992; Follett and Pruessner, 1997) and the analysis of these two fractions for total C, N, and S by methods 6A4a1a1-3, respectively. Typically, this procedure is determined on the A horizons (Soil Survey Staff, 1999) because detectable levels of both C and N are most likely to occur in this horizon.

3. Interferences

In some weathered soils there is approximately the same amount of C in both fractions. To date, no research has been done to establish the interpretation of this result. Charcoal in native sod that has been historically burned if residence time was to be determined from the two fractions, does not affect the POM determination and C and N analysis themselves.

4. Safety

Always wear safety glasses when working with glass containers.

5. Equipment

5.1 Pressure regulator for water, with stop cock attached to tubing

5.2 Sieve, 10 mesh, 2 mm

5.3 Sieve, 270 mesh, 53 µm

5.4 Mechanical reciprocating shaker, 200 oscillations min^{-1}, 1½ strokes, Eberbach 6000, Eberbach Corp., Ann Arbor, MI

5.5 Glass, Pyrex, pie or round cake pans

5.6 Evaporating crucibles

5.7 Drying oven (110 °C)

6. Reagents

6.1 Reverse osmosis deionized water (RODI), ASTM Type I grade of reagent water

7. Procedure

Physical Separation of Organic Matter (POM and C-Min)

7.1 Remove large pieces of organic matter, roots, plant residue, gravel, and wood material from an air-dry soil sample. Do not shake. Save the large fraction and weigh.

7.2 Weigh 10 g of <2-mm (sieved), air-dry soil to the nearest mg into a 125-mL Erlenmeyer flask. Add 30 mL of RODI water to sample.

7.3 If the soil has carbonates, take a sub-sample and measure the inorganic carbon following the gas chromatograph method (6A3a1a1).

7.4 Stopper sample tightly and shake for 15 h (overnight) at 200 oscillations min^{-1} at room temperature (20 °C ±2 °C).

7.5 Sieve the soil through a 53-µm sieve. The POM fraction will remain on top of the sieve and the C-min will be a slurry that is collected in a pie pan underneath the sieve. Use the regulator that is attached to the RODI water to rinse the POM with a steady gentle stream of water. Keep rinsing until the water that comes through the sieve is clear. Capture all the soil slurry and water (C-Min fraction) that passes the sieve.

7.6 Label and tare a glass pie pan and an evaporating crucible to the nearest 0.01 g.

7.7 Transfer the POM into an evaporating crucible by rinsing the sieve, including the sides, with a small amount of RODI water.

7.8 Transfer the C-Min slurry into a glass pie pan for drying. Rinse the contents of the pie pan into the labeled glass pie pan.

7.9 Dry the two fractions (POM, C-Min) in an oven at 110 °C. The C-Min fraction may require 48 h to dry, depending on how much water was used to rinse the sample.

7.10 Once the samples are dry, let them cool briefly and record the weight to the nearest 0.1 mg.

7.11 Transfer the entire contents for each fraction to an appropriately labeled scintillating vial.

Total Carbon, Nitrogen, and Sulfur Analysis

7.12 Determine total C, N, and S for POM and C-min fractions (6A4a1a1-3), using fine-grind samples (≈180 µm). Refer to 4H2a1-3 for the remaining procedural steps for 6A4a1a1-3.

8. Calculations

Calculate POM-C and C-Min using soil bulk density values determined by methods 4A or ASTM method D-2167 (American Society of Testing and Materials, 2004) and total C values determined by methods 6A4a1a1.

8.1 (%Total C of POM Fraction/100)x(POM (g)/10)xFMOD=POM-C g/g soil

where:

FMOD=Field-moist/oven-dry ratio (method 3D2)

8.2 (%Total C of C-Min Fraction/100)xC-Min (g)/10)xFMOD=C-Min g/g soil

8.3 (% Total C of POM fraction/100)x[POM (g)/10]xBulk Densityx100,000x Depth=POM-C kg ha^{-1} at given depth interval

8.4 (% Total C of C-Min fraction/100) x [C-Min (g) / 10] x Bulk Density x 100,000 x Depth = C-Min kg ha^{-1} at given interval depth.

Use the above equations for similar computations of N and S (6A4a1a2-3, respectively).

9. Report

Report POM-C and C-Min in kg ha^{-1} at a given depth interval (cm). Report separately similarly calculated values for N and S. Report the percent >2-mm fraction.

10. Precision and Accuracy

Precision and accuracy data are available from the SSL upon request.

11. References

American Society for Testing and Materials. 2004. Standard practice for density and unit weight of soil in place by the rubber balloon method. D 2167. Annual book of ASTM standards. Construction. Section 4. Soil and rock; dimension stone; geosynthesis. Vol. 04.08. ASTM, Philadelphia, PA.

Cambardella, C.A., and E.T. Elliott. 1992. Particulate soil organic-matter changes across a grassland cultivation sequence. Soil Sci. Soc. Am. J. 56:77–783.

Elliott, E.T., and C.A. Cambardella. 1991. Physical separation of soil organic matter. Agric. Ecosyst. Environ. 34:407–419.

Follett, R.F, and E. Pruessner. 1997. POM procedure. USDA–ARS, Ft. Collins, CO.

Gregorich, E.G., M.R. Carter, D.A. Angers, C.M. Monreal, and B.H. Ellert. 1994. Towards a minimum data set to assess soil organic matter quality in agricultural soil. Can. J. Soil Sci. 74:367–385.

Gregorich, E.G., R.G. Kachanoski, and R.P. Voroney. 1988. Ultrasonic dispersion of aggregates: Distribution of organic matter in size fractions. Can. J. Soil. Sci. 68:395–403.

Hassink, J. 1995. Decomposition rate constants of size and density fractions of soil organic matter. Soil Sci. Soc. Am. J. 59:1631–1635.

Jenkinson, D.S., and J.H. Rayner. 1977. The turnover of soil organic matter in some of the Rothamsted classical experiments. Soil Sci. 123:298–305.

Metherell, A.K., L.A. Harding, C.V. Cove, and W.J. Parton. 1993. CENTURY soil organic matter model environment, technical documentation agroecosystem, Version 4.0. Great Plains System Res. Unit Tech. Rep. No. 4, USDA–ARS, Ft. Collins, CO.

Montavalli, P.P., C.Q. Palm, W.J. Parton, E.T. Elliott, and S.D. Frey. 1994. Comparison of laboratory and modeling simulation methods for estimating soil carbon pools in tropical forest soils. Soil Biol. Biochem. 26:935–944.

Parton, W.J., D.S. Ojima, C.V. Cole, and D.S. Schimel. 1994. A general model for soil organic matter dynamics: Sensitivity to litter chemistry, texture and management. p. 147–167. *In* Quantitative modeling of soil forming processes, SSSA Spec. Publ. 39. SSSA, Madison, WI.

Soil Survey Staff. 1999. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys. USDA–NRCS Agric. Handb. 436. 2nd ed. U.S. Govt. Print. Office, Washington, DC.

Strickland, T.C., and P. Sollins. 1987. Improved method for separating light- and heavy-fraction organic material from soils. Soil Sci. Soc. Am. J. 51:1390–1393.

Fumigation Incubation (6B)

Sample Preparation (1B3b1a1)

Gas Chromatography (6B1)

CO_2 Analysis (6B1a)

Microbial Biomass (6B1a1)

Field-Moist, <2 mm (6B1a1a1)

2 *M* KCl Extraction (6B2)

Automatic Extractor (6B2a)

Ammonia—Salicylate (6B2a1)

Flow Injection, Automated Ion Analyzer (6B2a1a)

N as NH_3 (Mineralizable Nitrogen) (6B2a1a1)

Field-Moist, <2 mm Fumigated and <2 mm Non-Fumigated (6B2a1a1a1-2)

1. Application

Soil microorganisms are an important component of soil organic matter. One of their functions is to break down non-living organic matter in the soil. A variety of methods exist to measure the biomass of living soil microbes. The method described herein is by the chloroform fumigation incubation (Jenkinson and Powlson, 1976) with modifications, and CO_2 evolution measurement by gas chromatography. Mineralizable N may also be determined on microbial biomass.

2. Summary of Method

A freshly collected soil sample is weighed into two separate vials. One sample is fumigated using chloroform and the other is used as a control (non-fumigated). After fumigation both the fumigated and non-fumigated samples are brought up to 55% water filled pore space (WFPS) (Horwath and Paul, 1994). Both samples are placed in a sealed container and aerobically incubated for 20 days. During

this incubation period it is assumed that normal respiration occurs in the control sample container. The fumigated sample having a large carbon source for food, supplied from the dead microorganisms, has a higher CO_2 production. At the end of 10 days respiration readings are taken on both the control and the fumigated sample to determine the amount of CO_2 evolved by gas chromatography. The CO_2 level of the control sample is also measured at the end of 20 days. CO_2 produced by biomass flush (g CO_2-C/g of soil) and soil microbial biomass (kg C/ha for a given depth interval) are reported by method 6B1a1. Mineralizable N by 2 *M* KCl extraction may also be determined on microbial biomass using a flow injection automated ion analyzer by method 6B2a1a. Mineralizable N is reported as mg N kg^{-1} soil as NH_3.

3. Interferences

The determination of CO_2 evolution by gas chromatography gives a rapid and accurate measurement and can be used in acidic soils. However, this technique is prone to error in neutral and alkaline soils (Martens, 1987), as accumulation of carbonate species in the soil solution can lead to lowered CO_2 determinations (Horwath and Paul, 1994).

4. Safety

All fumigation work needs to be conducted in an adequate fume hood because chloroform has carcinogenic-volatile properties. Never determine residual chloroform by sense of smell. Make sure the vacuum pump is maintained to ensure proper operations.

5. Equipment

5.1 Face shield

5.2 Goggles

5.3 Rubber apron

5.4 Rubber gloves

5.5 Chloroform spill kit

5.6 Fume hood, 100-fpm face velocity

5.7 Vacuum chambers, fiberglass

5.8 Incubator, 25 °C

5.9 Vacuum pump, 26 and 14 in Hg, organic/oil free

5.10 Mason jars, 1-qt, with lids and septa

5.11 Vials, 60-mL glass, with snap caps, for samples

5.12 Beakers, 100-mL

5.13 Refrigerator, for sample and titrate storage

5.14 Sieve, 10 mesh, 2 mm

5.15 Electronic balance, ±0.01-g sensitivity

5.16 Electronic balance, ±1.0-mg sensitivity

5.17 Oven, 110 °C

5.18 Permanent marker

5.19 Paper towels

5.20 Tongs, 12 in

5.21 Mechanical vacuum extractor, 24-place, Sampletek, Mavco Industries, Lincoln, NE

5.22 Tubes, 60-mL polypropylene, for extraction tubes

5.23 Rubber tubing, 3.2 ID x 1.6 OD x 6.4 mm (⅛ ID x $^{1}/_{16}$ OD x 1 in) for connecting syringe barrels

5.24 Containers, polycon

5.25 Aluminum weighing pans, 60 mm diameter x 15 mm depth

5.26 Gas chromatograph (GC) with thermal conductivity detector (TCD)

5.27 GC syringes, 1-mL

6. Reagents

6.1 Reverse osmosis deionized (RODI), ASTM Type I grade of reagent water

6.2 Chloroform stabilized in amylene. Use purified chloroform within 3 weeks.

6.3 Helium, compressed gas

7. Procedure

7.1 Until sample preparation and analysis, keep soils moist and refrigerated.

7.2 Weigh soil to the nearest 0.01 g for bulk density determination. Remove a 15 to 20 g sample for water content. Sieve moist soil to <2 mm. Sub-sample (10 to 15 g) for post-sieve water content. Refrigerate samples until analyses can be performed. Dry post-sieve water content samples at 110 °C overnight. Weigh samples the following day.

7.3 Prepare 1 sample for the Fumigated Day 10 (F 10) and 1 for the Non-Fumigated Day 20 (NF 20). Prepare replicates for each sample.

7.4 Mark the volume on the glass sample container corresponding to 20 mL (or more if a larger quantity of soil is needed).

7.5 Label the non-fumigated container clearly with permanent marker.

7.6 Use etched containers for the fumigated set, as chloroform can dissolve written labels.

7.7 Weigh enough moist soil (nearest mg) to achieve approximately 25 g (or 50 g) oven-dry soil into 60-mL glass vial. Use soil moisture content conversion. Adjust soil, by gently tapping against the counter, so that it is leveled off at the bulk density line. Carefully add RODI water with a dropper to bring the moisture up to 55% WFPS, using the moisture content conversion. Make the surface as uniformly moist as possible.

7.8 Cap the vials and refrigerate samples overnight to equilibrate.

Fumigated Samples

7.9 Line the vacuum chambers with wet paper towels to prevent desiccation.

7.10 Place the vacuum chambers in the fume hood.

7.11 Place beaker with 30 to 40 mL of stabilized chloroform in the chambers. Evacuate at 14” Hg to drive off the amylene stabilizer. A volume change will be visible, approximately 5 to 10 mL.

7.12 Place the sample vials in the vacuum chambers.

7.13 Place the pure chloroform into the pan of the vacuum chambers.

7.14 Fumigate samples for 24 h.

7.15 Evacuate the fumigated samples 4 times for approximately 15 min at 27” Hg to drive off the chloroform.

Fumigated and Non-fumigated Samples

7.16 Add 5 to 10 mL of RODI water to the bottom of the mason jar to prevent desiccation.

7.17 Seal mason jars securely with rings and lids. Lids must be airtight during the incubation. Incubate samples at 25 °C for 10 days.

Day 10 Samples

7.18 Remove mason jars from incubator. Proceed to Section 7.25 for analysis.

7.19 Remove all F 10 samples from the mason jars.

7.20 Cap F 10 samples and store at 4 °C until they can be extracted for mineralizable N (2 *M* KCl). If a microbial inhibitor is used, samples can be stored in the refrigerator for up to 2 weeks before analysis. For longer periods they should be frozen. For extraction, proceed to Section 7.28.

7.21 Incubate NF 20 samples at 25 °C for 10 days. Make sure the mason jar lids are still sealing. If not, replace with new lids.

Day 20 Samples

7.22 Remove mason jars from incubator. Proceed to Section 7.25 for analysis.

7.23 Remove all NF 20 samples from the mason jars.

7.24 Cap samples and store at 4 °C until they can be extracted for mineralizable N (method 6B3a1a1). If a microbial inhibitor is used, samples can be stored in the refrigerator for up to 2 weeks before analysis. For longer periods they should be frozen. For extraction, proceed to Section 7.28.

Gas Chromatography

7.25 Measure the CO_2 accumulated in the headspace of the mason jars by gas chromatography.

7.26 Refer to manufacturer's manual for operation of the gas chromatograph.

7.27 Calibration curves and retention times for gas under analysis are established by analyzing the certified standard gas mixture (1% CO_2) by the procedure used for analysis of the sample. Flow rate is 30 mL min^{-1}. Monitor the baseline prior to analysis.

2 *M* KCl Extraction

7.28 Mix fumigated replicates together. Mix non-fumigated replicates together.

7.29 Weigh 5 g of moist soil to the nearest mg into 60-mL polypropylene extraction tubes. Tube will need to be tapped and rinsed with 2 *M* KCl in order to get the moist soil to bottom of tube.

7.30 Set up vacuum extractors. Add 25 mL of 2 *M* KCl to extraction tubes. Extract for 1 h.

7.31 Following extraction, transfer contents of tubes into polycon containers. Proceed with determining mineralizable N. Also analyze N in reagent RODI water as blanks. Refer to 4D10a1a1 for the remaining procedural steps for 6B2a1a1.

8. Calculations

8.1 Calculate the bulk density of 25 g of <2-mm, field-moist soil in a 100-mL beaker manually compressed to 20 cm^3 volume.

$$Db_1\ (g\ cm^{-3}) = 25\ g\ /(1 + H2O_f)/20\ cm^3$$

where:

Db_1 = Bulk density (g cm^{-3})

H_2O_f = Field water content (g g^{-1})

H_2O_f is determined by methods 4B.

8.2 Calculate the gravimetric water content [Gravimetric $H_2O_{0.55}$ (g/g)] required for soil to be at 55% water filled pore space (WFPS), using calculated Db_1 in Section 8.1 and an assumed particle density of 2.65 g cm^{-3}:

Gravimetric $H_2O_{0.55}$ (g/g) = {0.55 x [1 − (Db_1 / 2.65)]} / Db_1

where:

Gravimetric $H_2O_{0.55}$ (g/g) = 55% water filled pore space (WFPS)

2.65 = Assumed particle density (g cm^{-3})

8.3 Calculate the additional gravimetric water needed for soil to reach 55% WFPS:

H_2O_{add} = {[Gravimetric H_2O 0.55 (g/g)] − (H_2O_f)} x [W / (1 + H_2O_f)]

where:

W = Weight of soil (g)

H_2O_{add} = Amount of water to add to reach 55% WFPS (g)

8.4 Determine the CO_2-Carbon produced by biomass flush during 10 day incubation.

8.4.1 At 10 days, determine the mole % concentration of CO_2 in head space of jar by GC analysis.

8.4.2 Calculate the CO_2-Carbon produced by biomass flush as follows:

CO_2-Carbon produced by biomass flush, g BioCO_2-Carbon / g FM Soil =

[(mole %CO_2, 10 days, fumigated − mole %CO_2, 10 days, non-fumigated) x (0.47 g CO_2-C)] / W

where:

FM = Field-moist soil (g)

8.5 Determine the difference between fumigated CO_2-Carbon produced during the 10 to 20 day incubation period and the non-fumigated CO_2-Carbon produced during the same period.

8.5.1 At 20 days, determine the mole % concentration of CO_2 in head space of jar by GC analysis.

8.5.2 Calculate the (fumigated − non-fumigated) CO_2-Carbon produced during the 10 to 20 day incubation period as follows:

(fumigated − non-fumigated) CO_2-Carbon produced during the 10 to 20 day incubation period, g BioCO_2-Carbon / g FM Soil =

{[(mole %CO_2, 20 days, fumigated − mole %CO_2, 10 days, fumigated) − (mole % CO_2, 20 days, non-fumigated − mole %CO_2, 10 days, non-fumigated)] x (0.47 g CO_2-C)} / W

8.6 Calculate the Soil Biomass Flush (kg CO_2-C/ha), using the bulk density value (Db_2) determined by method 4A or ASTM method D-2167:

Soil biomass flush (kg CO_2-Carbon/ha) = (g $BioCO_2$-Carbon/g FM Soil) x (g FM Soil/g OD soil) x (Db_2: g OD soil/cm^3 FM Soil) x (1 kg CO_2-Carbon/1000 g CO_2-Carbon) x (100,000,000 cm^2/ha) x (layer thickness, cm)

8.7 Calculate Soil Microbial Biomass (kg C/ha for a given depth interval):

Soil Biomass Flush (kg C/ha)/0.41

0.41 = K_c, fraction of biomass C mineralized to CO_2 (Anderson and Domsch, 1978)

8.8 Calculate (fumigated – non-fumigated) mineralizable N (mg kg^{-1}):

Fumigated N – Non-fumigated N = {[(F_1-F_2) x A x B x E x 1000]/C} – {[(N_1-N_2) x D x F x E x 1000]}/G}

where:

F_1 = Analyte reading, fumigated (mg L^{-1})

F_2 = Blank reading, reagent RODI water, fumigated (mg L^{-1})

A = Extract volume, fumigated (L)

B = Dilution, fumigated (if performed)

C = Sample weight, fumigated (g)

N_1 = Analyte reading non-fumigated sample extract (mg L^{-1})

N_2 = Blank reading, reagent RODI water, non-fumigated (mg L^{-1})

D = Extract volume, non-fumigated (L)

F = Dilution, non-fumigated (if performed)

G = Sample weight, non-fumigated (g)

E = Field-moist/oven-dry ratio (method 3D2)

1000 = Conversion factor to kg-basis

9. Report

Report CO_2 produced by biomass flush (g CO_2-C/g of soil) and soil microbial biomass (kg C ha^{-1} for a given depth interval). Report the difference between mineralizable N of fumigated and non-fumigated to the nearest mg N kg^{-1} soil as NH_3.

10. Precision and Accuracy

Precision and accuracy data are available from the SSL upon request.

11. References

American Society for Testing and Materials. 2004. Standard practice for density and unit weight of soil in place by the rubber balloon method. D 2167. Annual book of ASTM standards. Construction. Section 4. Soil and rock; dimension stone; geosynthesis. Vol. 04.08. ASTM, Philadelphia, PA.

Anderson, J.P.E., and K.H. Domsch. 1978. Mineralization of bacteria and fungi in chloroform fumigated soils. Soil. Biol. Biochem. 10:207–213.

Horwath, W.R., and E.A. Paul. 1994. Microbial mass. p. 753–771. *In* R.W. Weaver, J.S. Angle, and P.S. Bottomley (eds.) Methods of soil analysis. Part 2. Microbiological and biochemical properties. ASA and SSSA, Madison, WI.

Jenkinson, D.S., and D.S. Powlson. 1976. The effects of biocidal treatments on metabolism in soil—V.A. method for measuring soil biomass. Soil Biol. Biochem. 8:209–213.

Kettler, T., and J. Doran. 1997. Procedure for determination of soil microbial biomass (gas chromatography method). USDA–ARS, University of Nebraska, Lincoln (unpublished).

Martens, R. 1987. Estimation of microbial biomass in soil by the respiration method: Importance of soil pH and flushing methods of the respired CO_2. Soil Biol. Biochem. 19:77–81.

Plant Analyses (6C)

Sample Preparation (1B3b3a1a1, 1B3b3b1a1)

Root Biomass (6C1)

Plant (Above-Ground) Biomass (6C2)

Plant Nutrition (6C3)

Total Analysis (6C3a)

Dry Combustion (6C3a1)

Thermal Conductivity Detector (6C3a1a)

Carbon, Nitrogen, and Sulfur (6C3a1a1-3)

Dry (50°C), Roots (6C3a1a1-3a1)

Dry (50°C), Plant Material (Above-Ground) (6C3a1a1-3a2)

1. Application

Root biomass in the upper 4 inches of the soil is an input value for the Revised Universal Soil Loss Equation (RUSLE) (Renard et al., 1997). The mass, size, and distribution of roots in the near surface are among the most important factors in determining the resistance of the topsoil to water and wind erosion. Root biomass is also one of the major carbon pools found in soil. Commonly, root mass and plant residue in the soil form between 3,000 (annual crop) and 15,000 (perennial grasses) lbs/ac/yr soil biomass (Harwood et al., 1998). Above-ground biomass

(production) represents annual yield and can be measured following the protocols found in the National Range and Pasture Handbook (USDA–NRCS, 1997). Root biomass represents biomass from more than 1 year.

The development of new roots and ultimately the decomposition of roots within the soil is a major contributor to the Soil Organic Carbon (SOC) pool. In this way, plant roots also contribute to the fertility of soils by slowly releasing macro- and micro-nutrients back into the soil.

Root biomass and SOC help bind the soil together by forming aggregates and granular structure. This improves the tilth as well as the erosion resistance of soil. Depending upon the root turnover rate (known for some species), climate, and residue decomposition rate (known for some areas, based on climate and soil moisture status) the amount of carbon stored in the soil can be determined from the root biomass, plant residue, and SOC.

Root biomass is frequently used to calculate root/shoot ratios in order to evaluate the health and vigor of plants, and determine the success of establishment of seeded plants at the 4-leaf stage.

Dried roots can be fine-grind, and total C, N, P, and S can be determined. The C/N ratio can also be determined, which is typically different from the C/N ratio of the above-ground plant material. Low levels of N in the soil will promote root growth over top growth (Bedunah and Sosebee, 1995). The C/N ratio of roots, plant residue in the soil, and SOC each contribute to the residue decomposition rate for soils. Low C/N values lead to more rapid decomposition, high C/N levels slow decomposition. The C/N ratio required for decomposition of plant residue, without a net tie-up of N, is approximately 25:1. Plant residue from young legumes commonly has a C/N ratio of 15:1. Plant residue from woody materials commonly is 400:1 (Harwood et al., 1998). The C/N ratio of soil microbes is quite variable but commonly falls between 15:1 and 3:1 (Paul and Clark, 1989).

Root biomass/horizon can be paired with the description of roots in each soil horizon (i.e. few fine, many very fine, etc.) in the pedon description and thus a qualitative estimate can be made of the mass in each size fraction of roots.

This automated method for determining root biomass also includes some plant residue. Woody material is removed and weighed separately.

Because root biomass determined in this manner includes plant residue, it can be used to estimate the soil plant residue pool in most models (Jenkinson and Rayner, 1977; Metherell et al., 1993).

2. Summary of Method

The procedural steps described herein encompass the physical separation of roots and plant residue from a soil sample using an automated root washer (1B3b3); these weights recorded for root (6C1) and plant biomass (6C2); and these fractions analyzed for total C, N, and S by methods 6C3a1a1-3, respectively.

3. Interferences

The soil must be dispersed for successful separation of the roots and plant residue from the soil sample. Tap water rather than distilled water should be used to help avoid puddling and dispersion problems.

4. Safety

Do not touch moving parts of the root washer when it is in operation. Avoid electrical shock by ensuring that the electrical cord is dry, and prevent the formation of pools of water near the cord.

5. Equipment

5.1 Automated root washer (after Brown and Thilenius, 1976)

- **5.1.1** Root cages, basket sieves, with No. 30 mesh and 0.5 mm-diameter openings
- **5.1.2** Garden hose
- **5.1.3** Sediment tank

5.2 Buckets

5.3 Analytical balance, ±0.01 g sensitivity

5.4 Drying oven (60 °C capability)

5.5 Weighing dishes

5.6 Scintillating vials

5.7 Tweezers

5.8 Drying trays

6. Reagents

6.1 Tap water

6.2 Algaecide, Bath Clear

7. Procedure

Sample Preparation

7.1 Weigh approximately 200 g of field-moist soil to the nearest 0.01 g and record the weight.

7.2 Pour all of the weighed soil into a root cage and cap it.

7.3 Immerse cage in tap water until soil disperses (overnight if samples are cloddy).

Root Washing

7.4 Make sure that machine is level and that the sediment tank is under the drain.

7.5 Load the root cages containing the soil and root slurry into the rotation bars. Be sure to load them evenly. If not using all of the rotation bar slots, load into every other slot.

7.6 Fill the washing tank with water to the top of the bottom cage.

7.7 Add 10 drops of algaecide to the washing tank. Attach machine to water source.

7.8 Turn on the water at the faucet then turn on the machine's spray nozzle. Do not start the machine with the lid open. Once the rotator has started, turn on spray nozzles.

7.9 Depending upon the number of samples, let the machine run from 40 to 90 min. (Ex: 12 samples usually take about 60 min.)

Clean Up and Maintenance

7.10 Upon completion of sample washing, shut down the sprayer first then the rotator. Drain the machine first by opening the bottom plug. Make sure the sediment tank is under the drain. After the machine is drained, let the water in the sediment tank settle. Replace plug in the machine.

7.11 Drain the sediment tank water off. Collect the sediment out of the machine and the sediment tank and properly dispose of it.

7.12 Flush out all of the sediment in the machine over the sediment tank. Repeat procedure until the machine is completely clean.

7.13 Clean the entire area. Run water down the drain for about 30 min after everything is clean.

Root/Plant Material Separation and Drying

7.14 Air-dry roots and plant material at room temperature overnight while still in the sieve cages.

7.15 Remove the roots/plant residue in the cage by tapping them. Brush out any roots/plant residue that clings to the side of the sieve cages.

7.16 Add water to a tray of roots/plant material. Float off as much of the organic matter as possible by adding water to a tray roots/plant residue. Much of the organic fraction will be less dense than the sand particles that are not removed during root washing. Pour floating matter into root cage to trap roots/plant residue; avoid introduction of inorganic portion into cage.

7.17 If roots/plant material remain in the inorganic fraction, use tweezers to remove as much of it as possible and return it to the cage.

7.18 Air dry at room temperature overnight all material in cage. Next day, tap and brush the air-dry material into a tray.

7.19 Remove the woody material, dry at 50 °C in an oven overnight, and record weight of woody material.

7.20 Separate plant residue from roots, dry at 50 °C in an oven overnight, and record weights of plant residue and roots.

7.21 Place the roots and plant residue into separate scintillation vials.

Total Carbon, Nitrogen, and Sulfur Analysis

7.22 Determine total C, N, and S for roots and plant material (6C3a1a1-3), using fine-grind samples (≈180 µm). Refer to 4H2a1-3 for the remaining procedural steps for 6C3a1a1-3.

Separating Roots and Organic Matter Residue (picking)

7.23 Following initial air-drying, use tweezers and separate organic matter residue from roots using tweezers. Roots are usually light colored, and organic residue is usually darker colored.

7.24 Place the organic residue and roots on separate tared watch glasses and re-dry and weigh.

7.25 Record each individual weight for plant residue and roots. Subtract the tare weights and record the total weight of air-dry roots and the total weight of air-dry plant residue. Report separately root biomass and plant residue rather than just roots including some organic residue.

8. Calculations

Calculate root biomass using soil bulk density values determined by methods (3B) described in this manual or ASTM method D-2167 (American Society for Testing and Materials, 2004).

Root biomass/ha for soil layer of given thickness (kg ha^{-1}) =

[Dry Roots (g)/Total sample weight (g) FM soil] x (Bulk density: g OD soil/ cm^3 FM soil) x (g FM soil/g OD soil) x (1 kg/1000 g) x (100,000,000 cm^2/ ha) x (Layer thickness, cm)

where:

OD = Oven-dry

FM = Field-moist

9. Report

Report root biomass as kg ha^{-1} at a given depth interval (cm). If plant residue was separated from roots, report each separately.

10. Precision and Accuracy

Precision and accuracy data are available from the SSL upon request.

11. References

American Society for Testing and Materials. 2004. Standard practice for density and unit weight of soil in place by the rubber balloon method. D 2167. Annual book of ASTM standards. Construction. Section 4. Soil and rock; dimension stone; geosynthesis. Vol. 04.08. ASTM, Philadelphia, PA.

Bedunah, D.J., and R.E. Sosebee (eds.). 1995. Wildland plants: Physiological ecology and developmental morphology. Soc. Range Mgt., Denver, CO.

Brown, G.R., and J.F. Thilenius. 1976. A low-cost machine for separation of roots from soil material. J. Range Mgt. 29:506–507.

Fribourg, H.A. 1953. A rapid method for washing roots. Agron. J. 45:334–335.

Harwood, R.R., M.A. Cavigelli, S.R. Deming, L.A. Frost, and L.K. Probyn (eds.). 1998. Michigan field crop ecology: Managing biological processes for productivity and environmental quality. Michigan State Univ. Ext. Bull. E-2646, 92 pp.

Jenkinson, D.S., and J.H. Rayner. 1977. The turnover of soil organic matter in some of the Rothamsted classical experiments. Soil Sci. 123:298–305.

Lauenroth, W.K., and W.C. Whitman. 1971. A rapid method for washing roots. J. Range Mgt. 24:308–309.

Metherell, A.K., L.A. Harding, C.V. Cove, and W.J. Parton. 1993. CENTURY soil organic matter model environment, technical documentation agroecosystem, Version 4.0. Great Plains System Res. Unit Tech. Rep. No. 4, USDA–ARS, Ft. Collins, CO.

Paul, E.A., and F.E. Clark. 1989. Soil microbiology and biochemistry. Academic Press, Inc., Harcourt Brace Jovanovich, Publ., San Diego, CA.

Renard, K.G., G.R. Foster, G.A. Weesies, D.K. McCool, and D.C. Yoder. 1997. Predicting soil erosion by water: A guide to conservation planning with the Revised Universal Soil Loss Equation (RUSLE). Agric. Handb. 703, USDA–ARS, U.S. Govt. Print Office, Washington, DC.

Sosebee, R.E. (ed.) 1977. Rangeland plant physiology. Range Sci. Series No. 4. Soc. Range Mgt., Denver, CO.

Thornley, J.H.M. 1995. Shoot:root allocation with respect to C, N and P: An investigation and comparison of resistance and teleonomic models. An. of Bot. 75:391–405.

USDA–NRCS, 1997. Inventory and monitoring grazing land resources. p. 4i – 4ex21. *In* National range and pasture handbook, Chapter 4. U.S. Govt. Print. Office, Washington DC.

MINERALOGY (7)

Instrumental Analyses (7A)

X-Ray Diffractometer (7A1)

Thin Film on Glass, Resin Pretreatment II (7A1a)

Mg Room Temperature, Mg Glycerol Solvated, K 300°, K 500° C (7A1a1)

1. Application

Clay fractions of soils are commonly composed of mixtures of one or more phyllosilicate minerals together with primary minerals inherited directly from the parent material (Olson et al., 1999). Positive identification of mineral species and quantitative estimation of their proportions in these polycomponent systems usually require the application of several complementary qualitative and quantitative analyses (Whittig and Allardice, 1986; Amonette and Zelazny, 1994; Wilson, 1994; Moore and Reynolds, 1997). One of the most useful methods to identify and to make semiquantitative estimates of the crystalline mineral components of soil is x-ray diffraction analysis (Hughes et al., 1994; Kahle et al., 2002). Quantification of a mineral by x-ray diffraction requires attention to many details, including 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). 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).

The operational strategy at the SSL and the preceding Lincoln SSL has been to base mineral quantification on first order peak intensities. Semi-quantitative 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 an in-house reference clay standard and subsequently soil samples. The intent is to keep interpretations consistent from sample to sample.

2. Summary of Method

Soils are dispersed and separated into fractions of interest. Sands and silts are mounted on glass slides as slurries, on a smear of Vaseline, or on double sticky tape for analysis. Clay suspensions are placed on glass slides to dry and to preferentially orient clay minerals. Most samples of soil clays contain fewer than 7 minerals that require identification. The soil clay minerals of greatest interest are phyllosilicates, e.g., kaolinite, mica (illite), smectite, vermiculite, hydroxy-interlayered vermiculite, smectite, hydroxy-interlayered smectite and chlorite.

Diffraction maxima (peaks) develop from the interaction of x-rays with planes of elements that repeat at a constant distance (d-spacing) through the crystal

structure. Generally, no two minerals have exactly the same d-spacings in three dimensions and the angles at which diffraction occurs are distinctive for a particular mineral (Whittig and Allardice, 1986; Moore and Reynolds, 1997). Phyllosilicates (or layer silicate minerals) have very similar structures except in the direction perpendicular to the layers (*c*-dimension). Several treatments are needed to sort out which minerals are present. Glycerol is added to expand smectites. Ionic saturation and/or heat treatments are used to collapse some 2:1 layer silicates and dehydroxylate kaolinite, gibbsite, and goethite, eliminating characteristic peaks.

The crystal "d" spacings of minerals, i.e., the interval between repeating planes of atoms, can be calculated by Bragg's Law as follows:

$$n\lambda = 2d \sin \theta$$

where:

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. The wavelength of radiation from an x-ray tube is constant and characteristic for the target metal in the tube. Copper radiation (CuKα) with a wavelength of 1.54 Å (0.154 nm) is used at the SSL. Because of the similar structure of layer silicates commonly present in soil clays, several treatments that characteristically affect the "d" spacings are necessary to identify the clay components. At the SSL, four treatments are used, i.e., Mg^{2+} (room temperature); Mg^{2+}-glycerol (room temperature); K^{+} (300 °C); and K^{+} (500 °C).

Standard tables to convert θ or 2θ 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). Through the years hardware has been updated and the recording of data has evolved from a strip chart recorder through several kinds of electronic software. X-ray by this method (7A1a1) is semiquantitative.

3. Interferences

Interstratification of phyllosilicate minerals causes problems in identification. These interstratified mixtures, differences in crystal size, purity, chemical composition, atomic unit cell positions, and background or matrix interferences affect quantification (Moore and Reynolds, 1997; Kahle et al., 2002). No pretreatments other than ionic saturation and dispersion with sodium hexametaphosphate are used for separation and isolation of the clay fraction in the routine procedure. Impurities, such as organic matter, carbonates, and iron oxides, may act as matrix interferences causing peak attenuation during x-ray analysis or may interfere with clay dispersion and separation. Pretreatments to

remove these impurities serve to concentrate the crystalline clay fraction and may increase accuracy, but also potentially result in degradation of certain mineral species (e.g., smectites) as well as loss of precision (Hughes et al., 1994).

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. Sedimentation of the clay slurry on a glass slide tends to cause differential settling by particle size (i.e., increasing the relative intensity of finer clay minerals).

Dried clay may peel from the XRD slide. One remedy is to rewet the peeled clay on the slide with 1 drop of glue-water mixture (1:7). Other remedies are:

a) Place double sticky tape on the slide prior to re-wetting the dried clay with the glue-water mixture.
b) Dilute the suspension if thick.
c) Crush with ethanol and dry, and then add water to make a slurry slide.
d) Roughen the slide surface with a fine-grit sandpaper.

An optimum amount of glycerol on the slides is required to solvate the clay, i.e., to expand smectites to 18 Å. X-ray analysis should be performed 1 to 2 days after glycerol addition. If excess glycerol is applied to the slide and free glycerol remains on the surface, XRD peaks are attenuated. Some suggestions to dry the slides and achieve optimum glycerol solvation are as follows:

a) Use a chamber such as a desiccator (with no desiccant) to dry slide, especially when the clay is thin.
b) If the center of slide is whitish and dry, usually with thick clay, brush slide with glycerol or add an additional drop of glycerol.

4. Safety

Operate the centrifuge with caution. Keep the centrifuge lid closed when in operation. Ensure that all rotors and tubes are seated firmly in proper location. Use tongs and appropriate thermal protection when operating the muffle furnace. The diffraction unit presents an electrical and radiation hazard. Analysts must receive radiation safety training before operating the equipment. Employees must wear a radiation film badge while in the room when the diffraction unit is in operation.

5. Equipment

5.1 Teaspoon (5 g)

5.2 Dispenser, 5 mL, for sodium hexametaphosphate solution

5.3 Centrifuge, International No. 2, with No. 240 head and carriers for centrifuge tubes, International Equip. Co., Boston, MA

5.4 Centrifuge tubes, plastic, 100 mL, on which 10-cm solution depth is marked

5.5 Rubber stoppers, No. 6, for centrifuge tubes

5.6 Mechanical reciprocating shaker, 100 oscillations min^{-1}, 1½ in strokes, Eberbach 6000, Eberbach Corp., Ann Arbor, MI

5.7 Plastic cups, 60 mL (2 fl. oz.) with lids

5.8 Label printer

5.9 Hypodermic syringes, plastic, 12 mL, with tip caps

5.10 Screen, 80 mesh, copper

5.11 Dropper bottle, plastic, 30 mL (1 fl. oz.), for a 1:7 glycerol:water mixture

5.12 Muffle furnace

5.13 X-ray diffractometer, Bruker 5000-Dmatic, with X-Y autosampler that accommodates 66 samples or standards, Bruker AXS Inc., Madison, WI

5.14 Computer, Diffrac^{plus} EVA software, release 2000, Bruker AXS Inc., Madison, WI, and printer

5.15 XRD slides, glass, 2.54 X 2.54 mm (frosted glass slides used for K-treated samples)

5.16 XRD sample preparation board, wood, with 32 places for glass XRD slides

5.17 Slide holder

5.18 Reference slides: quartz and clay from reference soil

6. Reagents

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

6.2 Sodium hexametaphosphate solution. Dissolve 35.7 g of sodium hexametaphosphate $(NaPO_3)_6$ and 7.94 g of sodium carbonate (Na_2CO_3) in 1 L RO water.

6.3 Potassium chloride (KCl), 1.0 *N*. Dissolve 74.60 g KCl in 1 L RO water or 671.40 g KCl in 9 L RO water.

6.4 Magnesium chloride ($MgCl_2$), 1.0 *N*. Dissolve 47.61 g $MgCl_2$ in 1 L RO water or 428.49 g $MgCl_2$ in 9 L RO water.

6.5 Glycerol:water mixture (1:7). Add 4 mL of glycerol to 28 mL RO water plus 2 drops of toluene.

6.6 Exchange resin, Rexyn 101 (H), analytical grade. Pretreatment of resin as follows:

6.6.1 Divide equally Rexyn 101 (H), approximately 250-g portions, into two 600-mL beakers labeled K and Mg and add appropriate salt solution (1.0 *N* KCl or 1.0 *N* $MgCl_2$). Cover resin with salt solution.

6.6.2 Stir, let settle for 10 min, decant clear solution, and add salt solution. Repeat 3 times. Leave resin covered in salt solution for 8 to 12 h.

6.6.3 Repeat step 6.6.2 on a second day. Resin is ready for syringes. Saturated resin not used initially for syringes can be saved for future use.

6.7 White glue, diluted 1:7 with RO water

7. Procedure

Preparation (Recharge) of Resin-Loaded Syringes

7.1 Place a small circle of 80-mesh screen in a 12-mL syringe and add 4 cm^3 of exchange resin from which salt solution has been drained. The procedure requires 2 Mg and 2 K slides for each sample, so two sets of syringes are prepared.

7.2 Saturate the resin in each of the syringes with 4 mL of the appropriate 1.0 *N* salt solution ($MgCl_2$ or KCl) and expel. Repeat saturation of resin. Individual steps follow.

7.3 Fill syringe completely with the salt solution and allow to equilibrate for 4 to 20 h.

7.4 Rinse syringe twice with 4 mL of RO water and rinse tip cap.

7.5 Completely fill syringe with RO water and allow to equilibrate for 4 to 20 h.

7.6 Rinse syringe twice with RO water.

7.7 Expel water, cap syringe, and store.

Preparation of Clay Suspension

7.8 Print run sheets using LIMS. Each run consists of 8 samples with 4 treatments for each sample.

7.9 Label each 100 ml plastic centrifuge tube with a sample number from the run sheet.

7.10 Place ≈5 g (1 tsp) of air-dry <2-mm soil in a 100-mL plastic centrifuge tube. If the sample appears to be primarily sand, use 10 g (2 tsp) of <2-mm soil to obtain sufficient clay.

7.11 Add 5 mL of sodium hexametaphosphate dispersion agent. If the soil contains gypsum or is primarily calcium carbonate, use 10 mL of sodium hexametaphosphate dispersing agent.

7.12 Fill tube to 9.5-cm height with RO water and close with a stopper.

7.13 Place the tubes in a mechanical shaker and shake overnight (at least 4 hours).

7.14 Remove stopper from tube and rinse stopper and sides of tube with enough water to bring the volume to the 10-cm mark.

7.15 Balance the pairs of tubes and place in centrifuge. Centrifuge at 750 rpm for 3.0 min.

7.16 If the clay is dispersed, carefully decant 30 mL of suspension into a labeled, 60-mL, plastic cup and cover with lid.

7.17 If the clay did not disperse after being shaken overnight, decant and discard the clear supernatant. Then add an additional 10 mL sodium hexametaphosphate and sufficient RO water to bring the level up to 9.5 cm depth. Repeat Sections 7.13 to 7.16.

7.18 Clay suspension is used for x-ray diffraction analysis. It can be dried and used for elemental or thermal analysis.

Thin Film on Glass, Resin Pretreatment

7.19 The SSL uses sample boards that hold 32 slides each, i.e., 8 samples x 4 treatments. Place run number on the sample board. Prepare the sample board with glass XRD slides to receive the following 4 treatments per clay suspension sample.

Mg^{2+}-room temperature

Mg^{2+}-glycerol (room temperature)

K^{+}-300 °C (heated 2 h)

K^{+}-500 °C (heated 2 h)

7.20 Use a hypodermic syringe to place 6 drops of the glycerol:water mixture (1:7) on each Mg^{2+}-glycerol slide

7.21 Draw 3 to 4 mL of the clay suspension into the Mg syringe and invert back and forth to facilitate cation exchange.

7.22 Dispense 3 drops to clear the tip.

7.23 Dispense ≈0.3 mL (6 to 10 drops) to cover the Mg and mg-glycerol XRD slides. Similarly, use the K syringes to apply clay suspension to the frosted glass K-300 and K-500 slides. Draw RO water into each syringe and expel 3 times to remove all of the clay suspension. Cap and store syringes. Recharge all syringes after 10 run boards.

7.24 When the clay suspension has dried, transfer the slides with the K^{+}-saturated clays to the muffle furnace. Heat for a minimum of 2 hours at 300 °C, remove the K-300 batch of slides. Set the temperature to 500 °C and heat slides for a minimum of 2 hours at 500 °C. After slides are cool, return them to the run board.

X-Ray Diffraction Operation

7.25 Complete x-ray analysis of the glycerol slide within 1 to 2 days after the slide dries. If this is not possible, add additional glycerol prior to run (e.g., add 6 drops of glycerol:water mixture to dry slide 24 h prior to x-ray analysis).

7.26 Place the tray with filled sample holders in the autosampler and execute the run. Use the following parameters:

CuKα radiation, λ=1.54 Å (0.154 nm)

Scan range=2° to 35°2θ

Generator settings=40 kv, 30 ma

Divergence slit=1°

Receiving slit=0.2 mm

Step size and scan speed vary depending on intensity of x-rays generated. Settings should be adjusted to maintain the same peak intensities on the standard reference clay and quartz standard over the long term regardless of tube intensities.

7.27 In the laboratory information system (LIMS), create a batch file. Data in file is transferred to a job program on the x-ray computer software for data analysis. These data include project and sample identification. Include both the quartz and soil standard with each run.

7.28 Activate job program for analysis. The job stores raw data on the hard disk under the subdirectory designated by year, project type, project name.

7.29 Prepare and print a 4-color graphics chart. The four colors are blue (Mg^{2+}); green (Mg^{2+}-glycerol); pink (K^{+} 300 °C); and red (K^{+} 500 °C). File hard copies of detected peaks and graphics chart in pasteboard binders by state, county, and chronology.

7.30 Compare quartz and soil standard patterns electronically with previous runs to ensure peak intensity and positions have remained constant.

Interpretation of X-Ray Diffraction Data

7.31 The angle in degrees two theta (2θ) measured in x-ray diffraction analyses is converted to angstroms (Å) using tables complied according to Bragg's Law. Refer to summary of method. Angstroms convert to nanometers (nm) by a factor of 0.1, e.g., 14 Å=1.4 nm.

7.32 Use the following x-ray diffraction criteria to identify some common crystalline minerals. The reported "d" values are for 00*l* basal spacings. The Miller index (*hkl*) specifies a plane or crystal face which has some orientation to the three crystallographic axes of a, b, and c. The Miller index (00*l*) indicates a crystal face that is perpendicular to the a and b

axes (Schulze, 1989). The following x-ray diffraction criteria also have some questions (Q) that may aid the analyst in interpreting the diffraction patterns. These questions are a suggested procedural approach to help the analyst identify the relative locations of a few peaks and to confirm key criteria. For a more complete list of d-spacings for confirmation or identification of a mineral consult the "Mineral Powder Diffraction File – Data Book" (JCPDS, 1980).

X-Ray Diffraction Criteria

7.32.1 Kaolinite and Halloysite

a. Crystal structure missing at 500 °C.

b. 7 Å (7.2 to 7.5 Å) with all other treatments.

Q. Is there a 7 Å peak? Is it destroyed at 500 °C? Kaolinite or Halloysite.

Q. Is the peak sharp and at ~ 7.1 Å (but absent at 500 °C)? Kaolinite.

Q. Is the peak broad and at 7.2 to 7.5 Å (but absent at 500 °C)? Halloysite.

7.32.2 Mica (Illite)

a. 10 Å with all treatments.

b. 10 Å with Mg^{2+}-saturation.

Q. Is there a 10 Å peak with Mg^{2+}-saturation? Mica (Illite).

7.32.3 Chlorite

a. Crystal structure of Fe-chlorites destroyed at 650 to 700 °C.

b. 14 Å with all other treatments.

c. 14 Å at 500 °C.

d. Generally also has strong 7 Å peak.

Q. Is there a 14 Å peak when heated to 500 °C? Chlorite.

7.32.4 Vermiculite

a. 14 Å with Mg^{2+}-saturation.

b. 14 Å with Mg^{2+}-glycerol solvation.

c. Nearly 10 Å with K^{+} saturation.

d. 10 Å when K^{+}-saturated and heated to 300 °C.

Q. Is there an enhanced 10 Å peak with K^{+}-saturation in comparison to Mg^{2+}saturation that cannot be attributed to smectite? Vermiculite.

7.32.5 Smectite

a. 14 Å with Mg^{2+}-saturation.

b. 12 to 12.5 Å with K^{+}- or Na^{+}-saturation.

c. 17 to 18 Å with Mg^{2+}-glycerol solvation.

d. 10 Å with K^{+}-saturation and heating to 300 °C.

Q. Is there a 17 to 18 Å peak upon solvation? Smectite.

7.32.6 Gibbsite

a. Peak at 4.83 to 4.85 Å with Mg^{2+} and Mg^{2+}-glycerol but destroyed when heated to 300 °C.

7.32.7 Goethite

a. Peak at 4.16 to 4.18 Å with Mg^{2+} and Mg^{2+}-glycerol but destroyed when heated to 300 °C.

7.32.8 Hydroxy-interlayed Vermiculite or Smectite

a. Failure to completely collapse to 10 Å of smectite or vermiculite when K^{+}-saturated and heated to 300 °C.

7.32.9 Quartz

a. Peaks at 4.27 Å and 3.34 Å with all treatments (only 3.34 if small amounts).

7.32.10 Lepidocrocite

a. Peak at 6.2 to 6.4 Å with Mg^{2+} and Mg^{2+}-glycerol but destroyed when heated to 300 °C.

7.32.11 Potassium Feldspar

a. Peak at 3.24 Å with all treatments.

7.32.12 Plagioclase Feldspar

a. Twin peaks between 3.16 and 3.21 with all treatments.

7.32.13 Calcite

a. Peak at 3.035 Å with all treatments.

7.32.14 Dolomite

a. Peak at 2.88 to 2.89 Å with all treatments.

7.32.15 Gypsum

a. Peak at 7.56 Å with Mg^{2+} and Mg^{2+}-glycerol, but destroyed when heated to 300 °C.

7.32.16 Mixed Layer Vermiculite-Mica

a. Randomly interstratified: Peak between 10 and 14 Å with Mg^{2+}

that does not expand with Mg^{2+}-glycerol; peak collapses to 10 Å with K^{+}-saturation and heating to 300 °C.

b. Regularly interstratified: A 24 Å peak (and higher orders); no change with Mg^{2+}-glycerol treatment; K^{+} saturation and heating collapses vermiculite and produces a 10 Å peak.

7.32.17 Mixed Layer Smectite-Mica

a. Randomly interstratified: Peak between 10 and 14 Å with Mg^{2+} that expands to 14–16 Å with Mg^{2+}-glycerol; Peak collapses to 10 Å with K^{+}-saturation and heating to 300 °C.

b. 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, then produces a 10 Å peak.

7.32.18 Mixed Layer Chlorite-Vermiculite

a. Randomly Interstratified: Peak at 14 Å with Mg^{2+} and Mg^{2+}-glycerol; Peak collapses incompletely to between 10 and 14 Å with K^{+}-saturation and heating.

b. Regularly interstratified: A 28 Å peak (and higher orders) with Mg-saturation; no expansion with Mg^{2+}-glycerol treatment; K^{+}-saturation and heating to 500 °C collapses vermiculite and a produces a 24 Å peak.

7.32.19 Mixed Layer Chlorite-Smectite

a. Randomly interstratified: Peak at 14 Å with Mg^{2+}-saturation; expands to higher spacings (≈16 Å) with Mg^{2+}-glycerol treatment; Peak collapses incompletely to between 10 and 14 Å with K^{+}-saturation and heating.

7.33 Use the x-ray diffraction criteria, i.e., diagnostic basal 00*l* spacings (Å), in Table 1 for identification and ready reference of some common crystalline minerals as affected by differentiating sample treatments.

7.34 Preferential orientation of clay mineral samples enhances diffraction from the basal (00*l*) 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:

7.34.1 Smectite (Mg^{2+}-glycerol):

a. 17 to 18 Å.

b. 8.5 to 9 Å (weak).

7.34.2 Chlorite, vermiculite, and smectite:

a. 14, 7, 4.7, and 3.5 Å.

b. 7, 4.7, and 3.5 Å weak for smectite.

(Note: High Fe substitution in the chlorite structure results in a decrease in the peak intensity of odd numbered orders (e.g., 14 and 4.7 Å) and increase in peak intensity of even number orders (7 and 3.5 Å)).

7.34.3 Mica:

a. 10, 5 (weak in biotites and moderate in muscovites), and 3.3 Å.

7.34.4 Kaolinite:

a. 7 and 3.5 Å.

7.35 The differentiation of kaolinite and halloysite in a sample can be aided by the use of formamide (Churchman et al., 1984). The intercalation and expansion of halloysite to a d-spacing of ≈10.4 Å is relatively rapid (20 to 30 min), whereas kaolinite expansion requires ≈4 h upon treatment. The procedure is as follows:

7.35.1 Lightly spray formamide as an aerosol on the dried Mg^{2+}-saturated slide.

7.35.2 Wait 15 min but not more than 1 h and x-ray approximately 7.6 to 13.5° 2θ (d = 11.6 to 6.55 Å).

7.35.3 Halloysite will expand to ≈10.4 Å, whereas kaolinite will remain unchanged.

7.35.4 Heating the sample to 110 °C for 15 min will collapse the halloysite to ≈7 Å.

7.35.5 The total amount of kaolinite and halloysite can be determined by thermal analysis. The intensity ratio of the 10.4 to 7.2 Å peaks of the formamide-treated sample can be used to determine the relative percentage of halloysite and kaolinite.

7.35.6 The total amount of kaolinite and halloysite can be determined by thermal analysis. The intensity ratio of the 10.4 to 7.2 Å peaks of the formamide-treated sample can be used to determine the relative percentage of halloysite and kaolinite.

8. Calculations

X-ray diffraction produces peaks on a chart that corresponds to 2θ angle on a goniometer. Standard tables to convert θ or 2θ 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 crystal "d" spacings of minerals, i.e., the interval between repeating planes of atoms, can be calculated by Bragg's Law. Refer to summary of method.

9. Report

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 s^{-1}, to assign each layer silicate mineral to one of the 5 semiquantitative classes.

Class	Peak height above background
	(counts sec^{-1})
5 (Very large)	>1800
4 (Large)	1120 to 1800
3 (Medium)	360 to 1120
2 (Small)	110 to 360
1 (Very small)	<110

Adjust class placement to reflect area under the curve if peak is broad relative to peak height or if thermal, elemental, clay activity data, or other evidence warrant class adjustment. If there are no peaks or no evidence of crystalline components, place the sample in NX class (noncrystalline). If there are only 1 to 3 very small (class 1) peaks, also indicate NX to infer a major noncrystalline component.

10. Precision and Accuracy

X-ray by method 7A1a1 is semi-quantitative. Precision and accuracy data are available from the SSL upon request.

11. References

Amonette, J.E., and L.W. Zelazny. 1994. Quantitative methods in soil mineralogy. Soil Sci. Soc. Am. Misc. Publ. SSSA. Madison, WI.

Brown, G. 1980. Appendix I (Tables for the determination of d in Å from 2θ for the Kα and Kβ radiations of copper, cobalt, and iron). p. 439–475. *In* G.W. Brindley and G. Brown (eds.) Crystal structures of clay minerals and their x-ray identification. Mineralogical Soc. Monograph No. 5. Mineralogical Soc. Great Britain.

Churchman, G.J., J.S. Whitton, G.G.C. Claridge, and B.K.G. Theng. 1984. Intercalation method using formamide for differentiating halloysite from kaolinite. Clays and Clay Minerals 32:241–248.

Hughes, R.E., D.M. Moore, and H.D. Glass. 1994. Qualitative and quantitative analysis of clay minerals in soils. p. 330–359. *In* J.E. Amonette and L.W. Zelazny (eds.) Quantitative methods in soil mineralogy. Soil Sci. Soc. Am. Misc. Publ. SSSA. Madison, WI.

JCPDS. 1980. Mineral powder diffraction file – Data book. International Centre for Diffraction Data, Swarthmore, PA.

Kahle, M., M. Kleber, and R. Jahn. 2002. Review of XRD-based quantitative analyses of clay minerals in soils: The suitability of mineral intensity factors. Geoderma 109:191–205.

Moore, D.M., and R.C. Reynolds, Jr. 1997. X-ray diffraction and the identification and analysis of clay minerals. Oxford Univ. Press. New York, NY.

Olson, C.G., M.L. Thompson, and M.A. Wilson. 1999. Section F. Soil Mineralogy, Chapter 2. Phyllosilicates. p. F-77 to F-123. *In* M.E. Sumner (ed.) Handbook of soil science. CRC Press, Boca Raton, FL.

Schulze, D.G. 1989. An introduction to soil mineralogy. p. 1–34. *In* J.B. Dixon and S.B. Weed (eds.) Minerals in soil environments. Soil Sci. Soc. Am. Book Series No. 1. SSSA, Madison, WI.

Switzer, G., J.M. Axelrod, M.L. Lindberg, and E.S. Larsen. 1948. Tables of d spacings for angle 2Θ. U.S. Dept. Interior. Geological Survey. Circular 29. Washington, DC.

Whittig, L.D., and W.R. Allardice. 1986. X-ray diffraction techniques. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:331–362.

Wilson, M.J. 1994. Clay mineralogy: Spectroscopic and chemical determinative methods. Chapman and Hall, NY.

Instrumental Analyses (7A)

Differential Scanning Calorimetry (7A4)

Thermal Analyzer (7A4a)

1. Application

Calorimetry measures specific heat or thermal capacity of a substance. Two separate types of differential scanning calorimetry (DSC) instruments have evolved over time. The term “DSC” is most appropriate for the power-compensated-type instrument in which the difference in the rate of heat flow between a sample and a reference pan is measured as materials are held isothermal to one another using separate furnaces (Karathanasis and Harris, 1994). The DSC therefore directly measures the magnitude of an energy change (ΔH, enthalpy or heat content) in a material undergoing an exothermic or endothermic reaction. Heat flow-type DSC instruments are more common and are similar in principal to differential thermal analyzers (DTA). The heat flow instruments have the sample and reference pans in a single furnace and monitor pan temperature from the conducting base. The difference in pan temperatures

(ΔT) results from clay mineral decomposition reactions in the sample as the furnace temperature is increased. The configuration of this instrument results in a signal that is independent of the thermal properties of the sample and ΔT can be converted to a calorimetric value via instrument calibration (Karathanasis and Harris, 1994). DSC is commonly used to quantify gibbsite ($Al(OH)_3$) and kaolinite ($Al_2Si_2O_5(OH)_4$) in soils and clays by measuring the magnitude of their dehydroxylation endotherms, which are between approximately 250 to 350 °C and 450 to 550 °C, respectively (Jackson, 1956; Mackenzie, 1970; Mackenzie and Berggen, 1970; Karathanasis and Hajek, 1982).

2. Summary of Method

An 8-mg sample of soil clay is weighed into an aluminum sample pan and placed in the DSC sample holder. The sample and reference pans are heated under flowing N_2 atmosphere from a temperature of 30 to 600 °C at a rate of 10 °C min^{-1}. Data are collected by the computer and a thermograph is plotted. Gibbsite and kaolinite are quantified by measuring the peak area of any endothermic reactions between 250 to 350 °C and 450 to 550 °C, respectively, and by calculating the ΔH of the reaction. These values are related to the measured enthalpies of standard mineral specimens (gibbsite and kaolinite). Percent kaolinite and gibbsite are reported by method 7A4a.

3. Interferences

Organic matter is objectionable because it produces irregular exothermic peaks in air or O_2, commonly between 300 to 500 °C, which may obscure important reactions from the inorganic components of interest (Schnitzer and Kodama, 1977). Analysis in an inert N_2 atmosphere helps to alleviate this problem although thermal decomposition of organic matter is still observed. Pretreatment with H_2O_2 may be necessary for soils with significant amounts of organic matter. Mineral salts that contain water of crystallization also may be interferences. Samples should be washed free of any soluble salts.

Use a representative soil sample as sample size is small (<10 mg). Avoid large aggregates in sample, the presence of which may cause thermal interferences because of differential kinetics of gas diffusion through the sample and physical movement of sample in a reaction.

The dehydroxylation of goethite is between 250 to 400 °C and may interfere with the identification and integration of the gibbsite endotherm (250 to 350 °C) (Mackenzie and Berggen, 1970). The dehydroxylation of illite is between 550 to 600 °C and partially overlaps the high end of the kaolinite endotherm (450 to 550 °C), resulting in possible peak integrations (Mackenzie and Caillere, 1975). The dehydroxylation of hydroxy-Al interlayers in hydroxy-Al interlayered vermiculite (HIV) is between 400 to 450 °C and may interfere with the low end of the kaolinite endotherm (450 to 550 °C), especially in the poorly crystalline kaolinites (Mackenzie and Caillere, 1975). Similarly, the dehydroxylation of nontronites,

Fe-rich dioctahedral smectites is between 450 to 500 °C and may interfere with kaolinite identification and measurement (Mackenzie and Caillere, 1975).

4. Safety

Secure high pressure N_2 tanks and handle with care. When changing the tanks, valves should be protected with covers. Do not heat aluminum sample pans >600 °C. Aluminum melts at 660 °C, and the sample pans alloy with and destroy the DSC cell. Always use high quality purge gases with the DSC. Minimum purity of 99.9% is recommended.

5. Equipment

5.1 Thermal analyzer, DSC 910S, TA Instruments, New Castle, DE

5.2 Thermal analyzer operating system software, Thermal Analyst 2100, Version 8.10B, TA Instruments, New Castle, DE

5.3 Data analysis software, TGA Standard Data Analysis Version 4.0, TA Instruments, New Castle, DE

5.4 Computer, IBM-PC 386, TA Instruments Operating System, Version 8.10B

5.5 Thermal analyzer instrument controller (MIM), TA Instruments, New Castle, DE

5.6 Autosampler, 920 Auto DSC, TA Instruments, New Castle, DE

5.7 Printer, Hewlett Packard, HP-7440, 8-pen plotter

5.8 Two-stage gas regulators, 50 psi maximum outlet pressure

5.9 Electronic balance, ±0.1-mg sensitivity, Mettler AE160

5.10 Forceps, flat-tipped

5.11 Weighing spatula

5.12 Desiccator

5.13 Mortar and pestle

5.14 Sieve, 80 mesh

5.15 N_2 gas, 99.99% purity

5.16 Kaolinite, standard, poorly crystalline, Georgia Kaolinite, Clay Minerals Society, Source Clay Minerals Project, sample KGa-2

5.17 Gibbsite, standard, Surinam Gibbsite, SSL 67L022

6. Reagents

6.1 Magnesium nitrate saturated solution [$Mg(NO_3)_2 \cdot 6H_2O$]

6.2 Ethanol

7. Procedure

Derive <2-µm Clay Fractions

7.1 Prepare Na-saturated clay as in method 7A1a1, preparation of clay suspension, sections 7.8 to 7.19.

7.2 Dry the clay suspension and transfer to mortar. Moisten sample with ethanol and grind with pestle to make an homogeneous slurry.

7.3 Air-dry sample using flowing air in hood. Lightly grind sample with pestle to make a homogeneous powder. Transfer to original container for storage until use.

7.4 Prior to analysis, sieve sample with 80-mesh screen. Equilibrate sample overnight over a saturated magnesium nitrate solution (55% relative humidity) in a glass desiccator.

DSC Operation

7.5 Set up the instrument and calibrate. Refer to the manufacturer's manual for operation of the DSC. Samples can be analyzed singly or with the autosampler for multiple samples.

7.6 Weigh ≈8 mg of sample, i.e., <80-mesh fine-earth (<2 mm) soil fraction or derived <2-µm clay fraction, into tared aluminum sample pan. Refer to section on derived <2-µm clay fractions, Steps 7.1 to 7.4.

7.7 Use flat-tipped forceps to remove aluminum sample pan from balance. Drop sample from a 4- to 5-mm height to uniformly distribute sample in pan. Return the sample pan with sample to the balance and record weight to nearest ±0.1 mg. This weight is entered into computer in appropriate menu.

7.8 Carefully place the aluminum sample pan in the center of DSC platinum sample side (front section) of sample holder.

7.9 Place empty aluminum sample pan in reference side (back section) of sample holder.

7.10 Cover the DSC cell.

7.11 The standard sample run heating program has a heating rate of 10 °C min^{-1}, a starting temperature of 30 °C, and an ending temperature of 600 °C.

7.12 Start the "Run" program.

7.13 When the run is complete, data are analyzed by entering the Data Analysis 2100 System and selecting the DSC Standard Data Analysis Program.

7.14 Display file and calculate joules g^{-1} for the mineral endotherm.

8. Calculations

The area under a curve representing an endothermic dehydroxylation reaction is proportional to the enthalpy (ΔH) of the reaction. The enthalpy is calculated with the DSC software per g of kaolinite or gibbsite (joules g^{-1}) as appropriate.

Analyze each of the standard clays on the DSC. Calculate the enthalpy per g for the endothermic reactions of the standard kaolinite and gibbsite (joules g^{-1}).

The purity of the standard clays is evaluated via TGA (7A2a). Adjust the DSC results of the standards using the purity measurements from TGA.

Determine the amount of kaolinite and gibbsite in soil samples by dividing the enthalpy of the sample (joules g^{-1}) by the enthalpy of the standard (joules g^{-1}). Multiply this result by 100 to express as a percentage.

9. Report

Report percent kaolinite and/or gibbsite to the nearest whole number.

10. Precision and Accuracy

Precision and accuracy data are available from the SSL upon request.

11. References

Jackson, M.L. 1956. Soil chemical analysis. Advanced course. Private publication, Madison, WI.

Karathanasis, A.D., and B.F. Hajek. 1982. Revised methods for rapid quantitative determination of minerals in soil clays. Soil Sci. Soc. Am. J. 46:419–425.

Karathanasis, A.D., and W.G. Harris. 1994. Quantitative thermal analysis of soil minerals. p. 360–411. *In* J.E. Amonette and L.W. Zelazny (eds.) Quantitative methods in soil mineralogy. Soil Sci. Soc. Am. Misc. Publ. SSSA, Madison, WI.

Mackenzie, R.C. 1970. Simple phyllosilicates based on gibbsite- and brucite-like sheets. p. 498–537. *In* R.C. Mackenzie (ed.) Differential thermal analysis. Vol. 1. Acad. Press, London.

Mackenzie, R.C., and G. Berggren. 1970. Oxides and hydroxides of higher-valency elements. p. 272–302. *In* R.C. Mackenzie (ed.) Differential thermal analysis. Acad. Press, NY.

Mackenzie, R.C., and S. Caillere. 1975. The thermal characteristics of soil minerals and the use of these characteristics in the qualitative and quantitative determination of clay minerals in soils. p. 529–571. *In* J.E. Gieseking (ed.) Soil components. Vol. 2. Inorganic components. Springer-Verlag, NY.

Mackenzie, R.C., and B.D. Mitchell. 1972. Soils. p. 267–297. *In* R.C. Mackenzie (ed.) Differential thermal analysis. Vol. 2. Acad. Press., London.

Rouston, R.C., J.A. Kittrick, and E.H. Hope. 1972. Interlayer hydration and the broadening of the 10A x-ray peak in illite. Soil Sci. 113:167–174.

Schnitzer, M., and H. Kodama. 1977. Reactions of minerals with soil humic substances. p. 741–770. *In* J.B. Dixon and S.B. Weed (eds.) Minerals in soil environments. 2nd ed. Soil Sci. Am. Book Series No. 1. ASA and SSSA, Madison, WI.

Tan, K.H., and B.F. Hajek. 1977. Thermal analysis of soils. p. 865–884. *In* J.B. Dixon and S.B. Weed (eds.) Minerals in soil environments. 2nd ed. Soil Sci. Am. Book Series No. 1. ASA and SSSA, Madison, WI.

Tan, K.H., B.F. Hajek, and I. Barshad. 1986. Thermal analysis techniques. p. 151–183. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical properties. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Optical Analyses (7B)

Platy Grains (7B2)

Static Tube Separation (7B2b)

1. Application

Static charge of mineral grains to glass and a magnetic separator are used to separate platy grains from non-platy grains in the 0.02–2 mm fraction of soil. The separates are weighed to determine the quantity of platy minerals. The platy separates are examined by optical microscope and analyzed by x-ray diffraction to determine the kinds of minerals present.

2. Summary of Method

A sample of <2-mm soil is prepared according to the procedure described in 7B2a. A small portion of sample is introduced into the top of an inclined glass tube mounted on a vibrator. As the tube is rotated and vibrated, the platy grains adhere to the tube and the non-platy grains (residue) roll or slide through. The residue is run through a magnetic separator to separate the coarser platy grains that did not adhere to the glass tube. Percent platy minerals of specific analyzed fraction are reported (7B2b).

3. Interferences

Large platy grains tend to slide through the tube into the residue, especially if the plates are stacked into a book.

4. Safety

No known hazards exist.

5. Equipment

5.1 Glass tube, 1.5 cm inside diameter, 30 cm long vibrating mechanism

5.2 Receptacles to hold grains

5.3 Funnel or glassine paper or aluminum weighing dish

5.4 Camel's hair brush

5.5 Gelatin capsules

5.6 Mechanical vibrator

6. Reagents

None.

7. Procedure

7.1 Prepare sample (disperse, fractionate, and dry sample as described in method 7B2a).

Static Charge Separation by Glass Tube

7.2 Set up vibrator as shown in figure 7B2b-1.

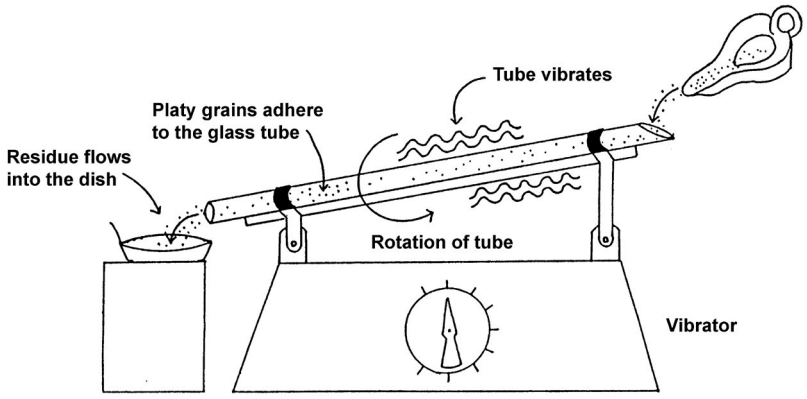


Figure 7B2b-1.—Apparatus for Static Tube Separation.

7.3 Weigh 0.1500 g of 0.02-2 mm material or particle-size separate onto a square of glassine paper and introduce into the upper end of the glass tube.

7.4 Turn on the vibrator until the material begins to flow. Rotate the tube slowly so the platy grains adhere to the tube wall. Adjust vibrator intensity and rotation to achieve a slow, smooth flow rate.

7.5 When rounded grains have passed through the tube, remove the tube and hold it vertically over a tared weighing dish. Tap the tube to remove

the platy grains. If grains remain, wash them out with RO water, dry, and weigh.

Note: The glass tube separation can be done by hand, without mechanical vibration, in the field office to obtain a fair approximation of the platy grain component.

8. Calculations

8.1 Percent platy grains = [100 x (weight of platy grains)] / (sample weight)

8.2 Percent residual grains = [100 x (weight of residual grains)] / (sample weight)

8.3 Recovery = (weight of platy and residual grains) / (sample weight)

9. Report

Report platy grains as a percent of the specific particle-size fraction analyzed, oven-dried soil weight.

10. Precision and Accuracy

Precision and accuracy data are not available for this method.

Optical Analyses (7B)
Platy Grains (7B2)
Froth Flotation (7B2c)

1. Application

This method used with coarse silt, very fine, fine, and medium sand fractions of soils with significant amounts of platy minerals (mica, vermiculite, chlorite, and their pseudomorphically altered weathering products). It provides weight percent data on each of the fractions. Combined use of froth flotation and magnetic separation improve separation of platy and non-platy grains to better estimate weight percentages of components.

2. Summary of Method

Platy minerals (muscovite, biotite, vermiculite, and kaolinite) are floated off over the top of a container in an agitated aqueous suspension by action of a complexer and frother, adapted from procedure provided by Louis Schlesinger of the Minerals Research Laboratory School of Engineering, North Carolina State University, in Asheville, NC. Percent platy minerals of specific analyzed fraction are reported (7B2c).

3. Interferences

There are no known interferences.

4. Safety

There are no known safety hazards.

5. Equipment

5.1 Modified 800 mL glass beaker for mixing container

5.2 Plastic bucket, 5 qt, for catch container

5.3 Mechanical mixer–1 laboratory reagent mixer or a magnetic bar stirrer

5.4 Manual mixer–1 glass rod pH meter

5.5 Oven, 110 °C

5.6 Wood tongue depressors or a similar spatula-like device

5.7 Syringe, 1 mL

5.8 Beaker, 800 mL aerator

5.9 Ring stand (to hold aerator assembly)

5.10 Funnel and stand to hold funnel 300-mesh sieve

5.11 Glass rod with rubber policeman

6. Reagents

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

6.2 Frother: Econofroth 910 frother, 100% solution (Mfg: Nottingham Company; P.O. Box 250049; Station N; 1303 Boyd Ave. NW; Atlanta, GA 303025; phone: 404-351-3501)

6.3 Promoter: Econofloat A-50 promoter, 5% solution (1 mL/20 mL or 50 mL/1000 mL); (Mfg: Nottingham Company)

6.4 NaOH (2.5% solution or 12.5 g per 500 g) 25 g/liter

6.5 H_2SO_4 , 0.9 *N* (2.5% solution or 12.5 g conc. H_2SO_4 per 500 g water)

6.6 Ethyl alcohol in wash bottle

7. Procedure

7.1 Prepare sample (disperse, fractionate, and dry sample as described in method 7B2a.)

7.2 Set up apparatus as shown in figure 7B2c-1.

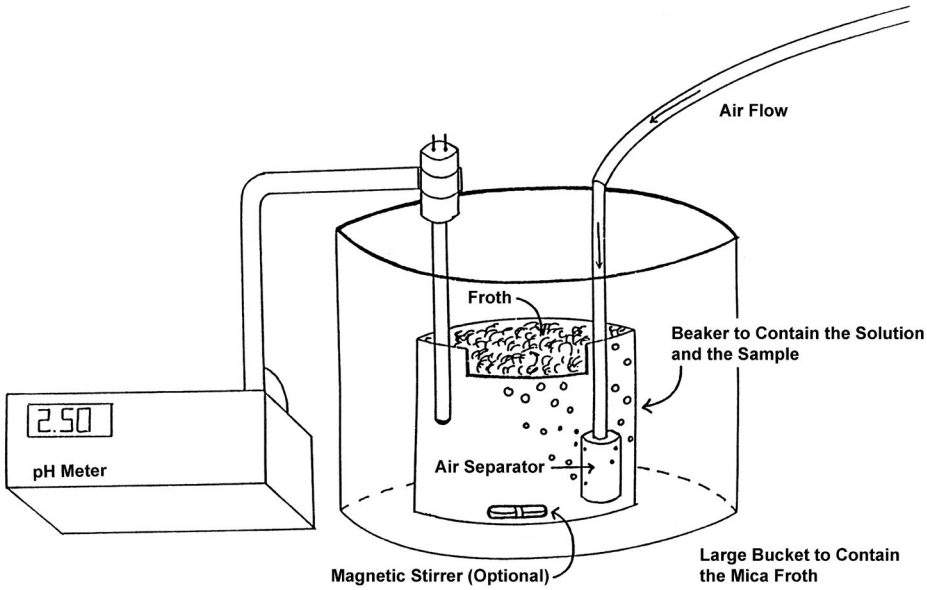


Figure 7B2c-1.—Apparatus for froth flotation.

7.3 Prepare 700 mL RO water, pH 2.5: Put 800-mL glass beaker on mechanical mixer and fill to 700 mL level. Adjust to pH 2.5 (not over 3.0) with 0.9 *N* H_2SO_4 solution and set the full beaker aside for use later.

7.4 Place 800 mL mixing container on mechanical mixer, and fill ¾ full with RO water.

7.5 Add 5 g of sample to water and start a strong mixing action.

7.6 Adjust pH of sample and water to 2.5 with 0.9 *N* H_2SO_4 solution.

7.7 Add 0.25ml of promoter.

7.8 Add 0.2ml of frother.

7.9 Continue to mix the sample solution for 2–5 minutes.

7.10 Check and readjust the pH level as necessary.

7.11 Place mixing container in plastic 5-qt catch bucket, lower aerator into solution, fill mixing container almost to top, using the water from section 7.3.

7.12 Turn off the mechanical mixer and turn on the air to the aerator to start the frothing action. The frothing foam should build to a point where the foam pours out of the modified mixing container. Add water from section 7.3 as needed to maintain foam overflow from the mixing container.

7.13 Use a glass stirring rod with a rubber policeman to mix the sample on the bottom of the mixing chamber in a grid like motion. As the platy minerals froth to the surface, use the wood tongue depressor to rake them over the side of the mixing chamber.

7.14 After 1–5 minutes the amount of platy minerals floating to the surface should diminish. At this time turn off the air, thoroughly remix the sample with the glass stirring rod, and repeat the procedure starting at section 7.12.

7.15 After 2–5 minutes during the second run through section 7.12, carefully inspect the foam to see if platy minerals are still frothing to the surface. Continue until little or no platy minerals are frothing to the surface.

7.16 Transfer contents of the catch bucket with ethyl alcohol to the 300-mesh sieve and rinse the sample.

7.17 Transfer the rinsed grains to an aluminum dish, dry in an oven at 110 °C, weigh and record the weight as platy grains.

7.18 Repeat steps 7.16 and 7.17 for the contents in the mixing container and record the weight as residual grains. *Note:* Delay weighing samples if magnetic separation (method 7B2a) will be done next.

8. Calculations

8.1 Percent platy grains = [100 x (weight of platy grains)] / (sample weight)

8.2 Percent residual grains = [100 x (weight of residual grains)] / (sample weight)

8.3 Recovery = (weight of platy and residual grains) / (sample weight)

9. Report

Report platy grains as a percent of the specific particle-size fraction analyzed, oven-dried soil weight.

10. Precision and Accuracy

Precision and accuracy data are not available for this method.

Table 1.—X-Ray Diffraction Parameters of Common Soil Minerals.

Mineral	Treatment						
	Na^+	Mg^{2+}	Mg^{2+}	K^+	K^+ 300 °C	K^+ 500 °C	K^+ 700 °C
	00l 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

Mineral	Treatment						
	Na^+	**Mg^{2+}**	**Mg^{2+}**	**K^+**	**K^+ 300 °C**	**K^+ 500 °C**	**K^+ 700 °C**
	00l diffraction spacing in angstroms						
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.

OBSOLETE METHODS SECTION III: SSIR NO. 42, SOIL SURVEY LABORATORY METHODS MANUAL, VERSION 3.0 (1996)

ION ANALYSES (5)

Cation Exchange Capacity (5A)
NH_4OAc, pH 7.0 (5A8)
Automatic Extractor (CEC-7)
Steam Distillation
Kjeltec Auto 1035 Analyzer (5A8c)

1. Application

The CEC determined with 1 *N* NH_4OAc buffered at pH 7.0 is a commonly used method and has become a standard reference to which other methods are compared (Peech et al., 1947). The advantages of using this method are that the extractant is highly buffered so that the extraction is performed at a constant, known pH (7.0) and that the NH_4^+ on the exchange complex is easily determined.

2. Summary of Method

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_4OAc and a mechanical vacuum extractor (Holmgren et al., 1977). 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. Steam distillation and titration are used to determine the NH_4^+ adsorbed on the soil exchange complex. The CEC by NH_4OAc, pH 7 is reported in meq 100 g^{-1} oven-dry soil in method 5A8c.

3. 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 and/or can contribute to erroneously high cation levels in the extract.

4. Safety

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses) when preparing reagents, especially concentrated acids and bases. Dispense concentrated acids and bases in a fume hood. Thoroughly wash hands after handling reagents. Use the safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate 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 is necessary.

Ethanol is flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the vacuum extractor and the Kjeltec Auto 1035 Analyzer.

5. Equipment

5.1 Mechanical vacuum extractor, 24 place, Centurion International, Inc., Lincoln, NE

5.2 Mechanical vacuum extractor, Mavco Sampletek, 5300 N. 57th St., Lincoln, NE

5.3 Syringes, polypropylene, disposable, 60 mL, for extraction vessel, extractant reservoir and tared extraction syringe

5.4 Rubber tubing, 3.2 ID x 6.4 OD x 25.4 mm (⅛ ID x ¼ OD x 1 in) for connecting syringe barrels

5.5 Polycons, Richards Mfg. Co.

5.6 Kjeltec Auto 1035/1038 Sampler System, Tecator, Perstorp Analytical Inc.

5.7 Digestion tubes, straight neck, 250 mL

5.8 Analytical filter pulp, ash-free, Schleicher and Schuell, No. 289

5.9 Plunger, modified. Remove rubber and cut plastic protrusion from plunger end.

5.10 Electronic balance, ±1-mg sensitivity

6. Reagents

6.1 Distilled deionized (DDI) water

6.2 Ammonium acetate solution (NH_4OAc), 1 *N*, pH 7.0. Add 1026 mL of glacial acetic acid (CH_3COOH) to 15 L DDI water. Add 1224 mL of concentrated ammonium hydroxide (NH_4OH). Mix and cool. Dilute with DDI water to 18 L and adjust to pH 7.0 with CH_3COOH or NH_4OH.

6.3 Ethanol (CH_3CH_2OH), 95%, U.S.P.

6.4 Nessler's reagent. Add 4.56 g of potassium iodide (KI) to 30 mL DDI water. Add 5.68 g of mercuric iodide (HgI_2). Stir until dissolved. Dissolve 10 g of sodium hydroxide (NaOH) in 200 mL of DDI water. Transfer NaOH solution to a 250-mL volumetric flask and slowly add K-Hg-I solution. Dilute to volume with DDI water and thoroughly mix. Solution should not contain a precipitate. Solution can be used immediately. Store in brown bottle to protect from light.

6.5 Sodium chloride (NaCl), reagent, crystal

6.6 Antifoam agent, slipicone release spray, Dow Chemical Corp. Alternatively, use n-octyl alcohol.

6.7 Boric acid, 4% (w:v), with bromcresol green-methyl red indicator (0.075 % bromcresol green and 0.05% methyl red), Chempure Brand

6.8 Hydrochloric acid (HCl), 0.05 *N*, standardized. Dilute 83 mL of concentrated HCl in 20 L of DDI water.

6.9 NaOH, 1 *M*. Add 500 mL of 50% NaOH solution to 8 L of DDI water. Dilute to 9 L with DDI water.

7. Procedure

Extraction of Bases

7.1 Prepare extraction vessel by tightly compressing a 1-g ball of filter pulp into the bottom of a syringe barrel with a modified plunger.

7.2 Weigh 2.50 g of <2-mm, air-dry soil and place in an extraction vessel. Weigh a smaller amount of sample, if the soil is highly organic. Prepare one quality control check sample per 48 samples.

7.3 Place extraction vessel on upper disk of the extractor and connect a tared extraction syringe. Use a 25.4-mm (1 in) length rubber tubing and insert the plunger in the slot of the stationary disk of the extractor.

7.4 Use a squeeze bottle to fill extraction vessel to the 20-mL mark with NH_4OAc solution (≈10 mL). Thoroughly wet the sample. Let stand for at least 20 min.

7.5 Put reservoir tube on top of the extraction vessel. Rapidly extract the NH_4OAc solution to a 0.5- to 1.0-cm height above sample. Turn off extractor. Add ≈45 mL of NH_4OAc solution to the reservoir tube. Set extractor for an overnight (12 to 16 h) extraction.

7.6 Next morning turn off the extractor. Pull the plunger of the syringe down. Do not pull plunger from the barrel of the syringe. Carefully remove the syringe containing the extract. Leave the rubber tubing on the extraction vessel. Weigh each syringe containing the NH_4OAc extract to the nearest 0.01 g.

7.7 Mix the extract in each syringe by manually shaking. Fill a polycon with extract solution and discard the excess. The solution in the polycon is reserved for analyses of extracted cations (methods 6N2, 6O2, 6P2, and 6Q2).

Removal of Excess Ammonium Acetate

7.8 Return the extractor to starting position. Attach syringe to the extraction vessel and rinse the sides of the extraction vessel with ethanol from a wash bottle. Fill the extraction vessel to the 20-mL mark with ethanol and let stand for 15 to 20 min.

7.9 Place reservoir tube on the extraction vessel. Rapidly extract the ethanol level to a 0.5- to 1.0-cm height above the sample. Turn off the extractor and add 55 to 60 mL of ethanol to the reservoir. Extract at a 45-min rate.

7.10 After the extractor has stopped, turn off the switch. Pull the plunger of the syringe down. Do not pull the plunger from the syringe barrel. Remove the syringe and discard the ethanol.

7.11 Repeat the ethanol wash.

7.12 After the second wash, collect a few drops of ethanol extract from the extraction vessel on a spot plate. Test for NH_4^+ by using Nessler's reagent. A yellow, red to reddish brown precipitate is a positive test. If the test is positive, repeat the ethanol wash and retest with Nessler's reagent. Repeat until a negative test is obtained.

Steam Distillation: Samples and Reagent Blanks

7.13 Remove the extraction vessel and transfer the sample to a 250-mL digestion tube. Add 6 to 7 g of NaCl to the digestion tube.

7.14 Perform the same transfer and addition of reagents for blanks as for samples.

7.15 Spray silicone antifoam agent (or 2 drops of n-octyl alcohol solution) into the digestion tubes for each of the samples and reagent blanks.

7.16 When using new reagents, e.g., boric acid, reagent blanks are distilled in 2 sets of 6, one set per Kjeltec machine. Each set of 6 is averaged and recorded on bench worksheet and manually set on each machine. During the steam distillation, the mean reagent blank titer is automatically subtracted from the sample titer.

7.17 On bench worksheet, record the normality of standardized acid, i.e., ≈0.05 *N* HCl.

7.18 Connect the tube to the distillation unit. Close the safety door. Distillation and titration are performed automatically. Record the titer in mL of titrant.

8. Calculations

CEC = [Titer x *N* x 100 x AD/OD] / [Sample Weight (g)]

where:

CEC = Cation Exchange Capacity (meq 100 g^{-1})

Titer = Titer of sample (mL)

N = Normality of HCl titrant

100 = Conversion factor to 100-g basis

AD/OD = Air-dry/oven-dry ratio (method 4B5)

9. Report

Report CEC-7 in units of meq 100 g^{-1} of oven-dry soil to the nearest 0.1 meq 100 g^{-1}.

10. Precision

Precision data are not available for this procedure.

11. References

Holmgren, G.G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Amer. 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. U.S. Dept. Agr. Circ. 757, 25 pp.

Cation Exchange Capacity (5A)
NH_4Cl (5A9)
Automatic Extractor
Steam Distillation (5A9c)
Kjeltec Auto 1035 Analyzer (5A9c)

1. Application

The CEC determined with a neutral unbuffered 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 value should be < CEC measured with a buffered solution at pH 7.0. The NH_4Cl CEC is ≈ equal to the NH_4OAc extractable bases plus the KCl extractable Al for noncalcareous soils.

2. Summary of Method

Displacement after washing is the basis for this procedure. The CEC is determined by saturating the exchange sites with an index cation ($NH4^+$); washing the soil free of excess saturated salt; displacing the index cation ($NH4^+$) adsorbed

by the soil; and measuring the amount of the index cation ($NH4^+$). A sample is leached using 1 *N* NH_4Cl and a mechanical vacuum extractor (Holmgren et al., 1977). 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. Steam distillation and titration are used to determine the NH_4^+ adsorbed on the soil exchange complex. The CEC by NH_4Cl is reported in meq 100 g^{-1} oven-dry soil in method 5A9c.

3. 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 and/or can contribute to erroneously high cation levels in the extract.

4. Safety

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses) when preparing reagents, especially concentrated acids and bases. Dispense concentrated acids and bases in a fume hood. 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 is necessary. Thoroughly wash hands after handling reagents. Use the safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids.

Ethanol is flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the vacuum extractor and the Kjeltec Auto 1030 Analyzer.

5. Equipment

5.1 Mechanical vacuum extractor, 24 place, Centurion International, Inc., Lincoln, NE

5.2 Mechanical vacuum extractor, Mavco Sampletek, 5300 N. 57th St., Lincoln, NE

5.3 Syringes, polypropylene, disposable, 60 mL, for extraction vessel, extractant reservoir, and tared extraction syringe

5.4 Rubber tubing, 3.2 ID x 6.4 OD x 25.4 mm (⅛ ID x ¼ OD x 1 in), for connecting syringe barrels

5.5 Polycons, Richards Mfg. Co.

5.6 Kjeltec Auto 1035/1038 Sampler System, Tecator, Perstorp Analytical Inc.

5.7 Digestion tubes, straight neck, 250 mL

5.8 Analytical filter pulp, ash-free, Schleicher and Schuell, No. 289

5.9 Plunger, modified. Remove rubber and cut plastic protrusion from plunger end.

5.10 Electronic balance, ±1-mg sensitivity

6. Reagents

6.1 Distilled deionized (DDI) water

6.2 Ammonium chloride solution (NH_4Cl), 1 *N*. Dissolve 535 g of NH_4Cl reagent in DDI water and dilute to 10 L.

6.3 Ethanol (CH_3CH_2OH), 95%, U.S.P.

6.4 Nessler's reagent. Add 4.56 g of potassium iodide (KI) to 30 mL DDI water. Add 5.68 g of mercuric iodide (HgI_2). Stir until dissolved. Dissolve 10 g of sodium hydroxide (NaOH) in 200 mL DDI water. Transfer NaOH solution to a 250-mL volumetric flask and slowly add K-Hg-I solution. Dilute to volume with DDI water and thoroughly mix. Solution should not contain a precipitate. Solution can be used immediately. Store the reagent in a brown bottle to protect from light.

6.5 Sodium chloride (NaCl), reagent, crystal

6.6 Antifoam agent, slipicone release spray, Dow Chemical Corp. Alternatively, use n-octyl alcohol.

6.7 Boric acid, 4% (w:v), with bromcresol green-methyl red indicator (0.075 % bromcresol green and 0.05% methyl red), Chempure Brand

6.8 Hydrochloric acid (HCl), 0.05 *N*, standardized. Dilute 83 mL of concentrated HCl in 16 L of DDI water.

6.9 NaOH, 1 *M*. Add 500 mL of 50% NaOH solution to 8 L of DDI water. Dilute to 9 L with DDI water.

7. Procedure

Extraction of Bases

7.1 Prepare extraction vessel by tightly compressing a 1-g ball of filter pulp into the bottom of a syringe barrel with a modified plunger.

7.2 Weigh 2.50 g of <2-mm, air-dry soil and place in an extraction vessel. Weigh a smaller amount of sample, if the soil is highly organic. Prepare one quality control check sample per 48 samples.

7.3 Place extraction vessel on upper disk of the extractor and connect a tared

extraction syringe. Use 25.4-mm (1 in) length rubber tubing and insert the plunger in the slot of the stationary disk of the extractor.

7.4 Use a squeeze bottle to fill extraction vessel to the 20-mL mark with NH_4Cl solution (≈10 mL). Thoroughly wet the sample. Let stand for at least 20 min.

7.5 Put reservoir tube on top of the extraction vessel. Rapidly extract the NH_4Cl solution to a 0.5- to 1.0-cm height above sample. Turn off extractor. Add ≈45 mL of NH_4Cl solution to the reservoir tube. Set extractor for an overnight (12 to 16 h) extraction.

7.6 Next morning turn off the extractor. Pull the plunger of the syringe down. Do not pull plunger from the barrel of the syringe. Carefully remove the syringe containing the extract. Leave the rubber tubing on the extraction vessel. Weigh each syringe containing the NH_4Cl extract to the nearest 0.01 g.

7.7 Mix the extract in each syringe by manually shaking. Fill a polycon with extract solution and discard the excess. The solution in the polycon is reserved for analyses of extracted cations (methods 6N2, 6O2, 6P2, and 6Q2).

Removal of Excess Ammonium Chloride

7.8 Return the extractor to starting position. Attach syringe to the extraction vessel and rinse the sides of the extraction vessel with ethanol from a wash bottle. Fill the extraction vessel to the 20-mL mark with ethanol and let stand for 15 to 20 min.

7.9 Place reservoir tube on the extraction vessel. Rapidly extract the ethanol level to a 0.5- to 1.0-cm height above the sample. Turn off the extractor and add 55 to 60 mL of ethanol to the reservoir. Extract at a 45-min rate.

7.10 After the extractor has stopped, turn off the switch. Pull the plunger of the syringe down. Do not pull the plunger from the syringe barrel. Remove the syringe and discard the ethanol.

7.11 Repeat the ethanol wash.

7.12 After the second wash, collect a few drops of ethanol extract from the extraction vessel on a spot plate. Test for NH_4^+ by using Nessler's reagent. A yellow, red to reddish brown precipitate is a positive test. If the test is positive, repeat the ethanol wash and retest with Nessler's reagent. Repeat until a negative test is obtained.

Steam Distillation: Samples and Reagent Blanks

7.13 Remove the extraction vessel and transfer the sample to a 250-mL digestion tube. Add 6 to 7 g of NaCl to the sample.

7.14 Perform the same transfer and addition of reagents for blanks as for samples.

7.15 Spray silicone antifoam agent (or 2 drops of n-octyl alcohol solution) into the digestion tubes for each of the samples and reagent blanks.

7.16 When using new reagents, e.g., boric acid, reagent blanks are distilled in 2 sets of 6, one set per Kjeltec machine. Each set of 6 is averaged and recorded on bench worksheet and manually set on each machine. During the steam distillation, the mean reagent blank titer is automatically subtracted from the sample titer.

7.17 On bench worksheet, record the normality of standardized acid, i.e., ≈0.05 *N* HCl.

7.18 Connect the tube to the distillation unit. Close the safety door. Distillation and titration are performed automatically. Record the titer in mL of titrant.

8. Calculations

CEC = [Titer x *N* x 100 x AD/OD] / [Sample Weight (g)]

where:

CEC = Cation Exchange Capacity (meq 100 g^{-1})

Titer = Titer of sample (mL)

N = Normality of HCl titrant

100 = Conversion factor to 100-g basis

AD/OD = Air-dry/oven-dry ratio (method 4B5)

9. Report

Report neutral salts CEC in units of meq 100 g^{-1} of oven-dry soil to the nearest 0.1 meq 100 g^{-1}.

10. Precision

Precision data are not available for this procedure.

11. References

Holmgren, G.G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Amer. 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. U.S. Dept. Agr. Circ. 757, 25 pp.

CHEMICAL ANALYSES (6)

Organic Carbon (6A)

Walkley-Black Modified Acid-Dichromate Organic Carbon (6A1)

$FeSO_4$ Titration, Automatic Titrator

Metrohm 686 Titroprocessor (6A1C)

1. Application

Organic C by the Walkley-Black method is a wet combustion technique to estimate organic C. A correction factor is used to convert the Walkley-Black value to an organic matter content. A common value for the factor is 1.724 based upon the assumption that soil organic matter contains 58% organic C. A review of the literature reveals that the factor is highly variable, not only among soils but also between horizons in the same soil (Broadbent, 1953). In addition, a recovery factor is used because the Walkley-Black method does not completely oxidize all the organic C.

2. Summary of Method

The SSL uses the Walkley-Black modified acid-dichromate $FeSO_4$ titration organic carbon procedure. A sample is oxidized with 1 *N* potassium dichromate and concentrated sulfuric acid (1:2 volume ratio). After 30 min, the reaction is halted by dilution with water. The excess dichromate is potentiometrically back-titrated with ferrous sulfate. A blank is carried throughout the procedure to standardize the ferrous sulfate. Percent organic C is reported on an oven-dry soil basis.

3. Interferences

Dichromate methods that do not use additional heating do not give complete oxidation of organic matter. Even with heating, the recovery may not be complete. Walkley and Black (1934) determined an average recovery factor of 76%. Other studies have found recovery factors ranging from 60% to 86%. Thus, an average correction factor yields erroneous values for many soils. The Walkley-Black method is only an approximate or semiquantitative estimate of organic C.

Maintain the ratio of dichromate solution to concentrated H_2SO_4 at 1:2 to help maintain uniform heating of the mixture.

The presence of significant amounts of chloride in the soil results in a positive error. If the chloride in the soil is known, use the following correction factor (Walkley, 1947) for the organic C.

$$\text{Organic C (\%)} = \text{Apparent soil C \%} - (\text{Soil } Cl^- \text{ \%})/12$$

The presence of significant amounts of ferrous ions results in a positive error (Walkley, 1947). The dichromate oxidizes ferrous to ferric iron.

$$Cr_2O_7^{2-} + 6\ Fe^{2+} + 14\ H^+ = 2\ Cr^{3+} + 6\ Fe^{3+} + 7\ H_2O$$

The presence of manganese dioxide results in a negative error (Walkley, 1947). When heated in an acidic medium, the higher oxides of manganese, e.g., MnO_2, compete with dichromate for oxidizable substances.

$$2\ MnO_2 + C^o + 4\ H^+ = CO_2 + 2\ Mn^{2+} + 2\ H_2O$$

All dichromate methods assume that the organic C in the soil has an average oxidation state of zero and an equivalent weight of 3 g per equivalent when reacting with dichromate. When the soil has carbonized material, e.g., charcoal, graphite, coal and soot, the Walkley-Black method gives low recovery of this material, i.e., recovery range is from 2 to 36%.

4. Safety

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses) when preparing acids and dichromate. Toxic chromyl chloride may be released from the sample, if high concentrations of chloride are present. Use the fume hood to contain the gases released by this procedure. Use the safety showers and eyewash stations to dilute spilled acids. Use sodium bicarbonate and water to neutralize and dilute spilled acids and dichromate. Follow the manufacturer's safety precautions when using the automatic titrator.

5. Equipment

5.1 Electronic balance, ±1-mg sensitivity

5.2 Titration beakers, borosilicate glass, 250 mL

5.3 Automatic dispenser, 5 to 20 mL, Oxford no. 470 or equivalent, for $K_2Cr_2O_7$, capable of volume adjustment to 10.00 ±0.01 mL, 0.5% reproducibility

5.4 Dispenser, Zippette 30 mL or equivalent, for concentrated H_2SO_4, Brinkmann Instruments, Inc.

5.5 Shaker, Eberbach 6000 power unit, fitted with spring holders for titration beakers, reciprocating speed of 60 to 260 epm, with 6040 utility box carrier and 6110 floor stand, Eberbach Corp., Ann Arbor, MI

5.6 Automatic titrator, Metrohm 686 Titroprocessor Series 04, 664 Control Unit, 674 Sample Changer Series 5, and 665 Dosimat Series 14, Metrohm Ltd., Brinkmann Instruments, Inc.

5.7 Platinum electrode, Metrohm part no. 6.0412.000

6. Reagents

6.1 Distilled deionized (DDI) water

6.2 Potassium dichromate, 1.000 *N*, primary standard. Dissolve 49.035 g of $K_2Cr_2O_7$ reagent, dried @ 105 °C, in 1-L volumetric flask with DDI water.

6.3 Sulfuric acid (H_2SO_4), concentrated, reagent

6.4 Ferrous sulfate, 1 *N*, acidic. Dissolve 1 kg of $FeSO_4 \cdot 7H_2O$ in 6 L of DDI water. Carefully add 640 mL of concentrated H_2SO_4 with stirring. Cool and dilute to 8 L with DDI water.

7. Procedure

Digestion of Organic C

7.1 Weigh 1.000 g air-dry soil and place in a titration beaker. If the sample contains >3% of organic C, use a smaller sample size. Refer to Table 1 for sample weight guide. If sample size is <0.5 g, use <80-mesh soil. If sample size is >0.5 g, use <2-mm soil.

7.2 With automatic dispenser, add 10.00 mL of $K_2Cr_2O_7$ solution to the titration beaker. Mix by swirling the sample.

7.3 Use the dispenser to carefully add 20 mL of concentrated H_2SO_4 to the beaker. Mix by swirling solution. Adjustment in the amount of $K_2Cr_2O_7$ added to sample requires appropriate adjustment in the amount of H_2SO_4 so that a 1:2 volume is maintained.

7.4 Place titration beaker on the reciprocating shaker and shake 1 min. If the dichromate-acid mixture turns a blue-green color, all the dichromate has been reduced. Add more dichromate and acid to maintain a 1:2 volume. Refer to Table 1 for dichromate:acid volumes.

Table 1.—Digestion of organic C. Guide for sample weight and dichromate:acid volumes.

OC	Sample	$K_2Cr_2O_7$	H_2SO_4
(%)	*(g)*	*(mL)*	*(mL)*
0-3	1.000	10.00	20
3-6	0.500	10.00	20
3-6	1.000	20.00	40
6-12	0.500	20.00	40
12-24	0.250	20.00	40
24-50	0.100	30.00	60

7.5 Place the beaker on a heat resistant surface for 30 min.

7.6 Add ≈180 mL DDI water to the beaker to stop the reaction.

Titration of Excess Dichromate

7.7 Titrate eight reagent blanks at the start of each batch to determine the normality of the ferrous sulfate. A blank is 10.00 mL $K_2Cr_2O_7$ plus H_2SO_4 without soil. The average titer is used for the blank titer value.

7.8 Place the appropriate blanks and samples in the sample holder magazines and place on the sample changer.

7.9 Refer to the manufacturer's instruction manual for operation of automatic titrator.

7.10 Set the endpoint to 700 mV. Set the controls of the 664 Control Unit to the appropriate settings.

7.11 Prime the burette with 50 mL of ferrous sulfate solution before starting the titrations.

7.12 When a long series of samples are being titrated, intersperse blank samples throughout the titrations. The blank titer drifts over time, mainly because of the temperature change of the solution. Any sample with a titer of less 1 milliliter and/or endpoint of less than 620 millivolts should be reanalyzed.

7.13 Press "Start" on the titrator.

8. Calculations

$$OC\ (\%) = [(Blank \times Volume) - (10 \times Titer) \times 3 \times 100 \times AD/OD] / [Blank \times Sample\ Weight\ (g) \times 0.77 \times 1000]$$

where:

OC (%) = Organic C (%)

Blank = Average titer of reagent blanks (mL)

Volume = Volume of 1 *N* $K_2Cr_2O_4$ (mL)

Titer = Titer of $FeSO_4$ (mL)

AD/OD = Air-dry/oven-dry ratio (method 4B5)

3 = Equivalents per C (assumed)

1000 = Meq eq^{-1}

100 = Convert to 100-g basis

0.77 = Assumed C oxidation factor

9. Report

Report organic C percentage to two decimal places, e.g., 0.95% OC, on an oven-dry basis.

10. Precision

Precision data are not available for this procedure. A quality control check sample is run in every batch of 20 samples. With 251 observations of the quality control check sample, the mean, standard deviation, and C.V. for organic carbon are 1.47, 0.025, and 1.7%, respectively.

11. References

Broadbent, F.E. 1953. The soil organic fraction. Adv. Agron. 5:153–183.

Walkley, A. 1947. A critical examination of a rapid method for determining organic carbon in soils: Effect of variations in digestion conditions and of inorganic soil constituents. Soil Sci. 63:251–263.

Walkley, A., and Black, I.A. 1934. An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. Soil Sci. 37:29–38.

Total Carbon (6A)
Dry Combustion (6A2)
LECO SC-444 Carbon Analyzer (6A2e)

1. Application

Total C in soils 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 found with carbonate minerals. The organic C in mineral soils generally ranges from 0 to 12 percent.

Total C is quantified by two basic methods, i.e., wet or dry combustion. The SSL uses dry combustion. 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. Organic C also can be determined directly (method 6A1c). The inorganic C should be equivalent to carbonate values measured by CO_2 evolution with strong acid (Nelson and Sommers, 1982).

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, 1975).

2. Summary of Method

A fine-ground (<80-mesh) soil sample is oxidized at high temperatures. The released gases are scrubbed, and the CO_2 in the combustion gases is measured by using an infrared detector. The microprocessor formulates the analytical results (C_i) by combining the outputs of the infrared detector and the system

ambient sensors with pre-programmed calibration, linearization, and weight compensation factors. Percent total C is reported on an oven-dry soil basis.

3. Interferences

This procedure simultaneously measures inorganic and organic C. A high rate of combustion can oversaturate the carbon detection cell. The rate of combustion can be retarded by adding a solid/powder combustion controller.

4. Safety

Wear protective clothing and safety glasses. Magnesium perchlorate may form explosive mixtures. Magnesium perchlorate may contain traces of perchloric acid, which remain from manufacturer's operations. This acid is anhydrous because of the strong desiccating capability of the salt. Avoid prolonged contact with oxidizable material or material capable of forming unstable perchlorate esters or salts. Remove magnesium perchlorate by using an excess of water to thoroughly dilute the material.

The use of high temperatures in the oxidation of samples requires that extreme caution be used to prevent burns and fires. Follow standard laboratory procedures when handling compressed gases. Oxygen is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the carbon analyzer.

5. Equipment

5.1 Carbon analyzer, Leco Model SC-444, Sulfur and Carbon Analyzers, Leco Corp., St. Joseph, MI

5.2 Combustion boats, part no. 529-203, Leco Corp., St. Joseph, MI

5.3 Single-stage regulator, oxygen service, part no. E11-W-N115Box, Air Products and Chemicals, Inc., Box 538, Allentown, PA 18105

5.4 Electronic balance, ±1-mg sensitivity

6. Reagents

6.1 Anhydrous magnesium perchlorate, granular

6.2 Glass wool

6.3 Compressed oxygen, >99.5% @ 30 psi

6.4 Calcium carbonate, $CaCO_3$, reagent grade.

6.5 Solid/Powder Combustion Controller, part no. 501-426, Leco Corp., St. Joseph, MI

6.6 Soil Calibration Sample, part no. 502-062, Leco Corp., St. Joseph, MI

7. Procedure

7.1 Use a fine-ground 80-mesh, air-dry soil.

7.2 Prepare instrument as outlined in the operator's instruction manual (Leco, 1994; Leco, 1993).

7.3 Methods are created with the method menu and stored in the instrument memory. System parameters are set as follows:

Furnace operating temperature: 1450 °C

Lance delay: 20 s

Analysis time settings: 70 to 180 s

Comparator level settings: 0.1%

7.4 Condition instrument by analyzing a few soil samples, until readings are stable.

7.5 Calibrate instrument by analyzing at least three replicates of each calibration standard. Use the soil calibration standard for samples with less than 3 to 4 percent total carbon and calcium carbonate for samples with more than 4 percent total carbon. Weigh standards in a range from 0.2 to 0.7 g.

7.6 Load samples on autoload rack, place in the analyzer, and press analyze key.

7.7 Weigh 0.2 to 0.5 g sample in a tared combustion boat.

7.8 Load samples on autoload rack, place in the analyzer, and press analyze key.

7.9 If results exceed calibration range, reduce weight of sample. If carbon detection cell is saturated, add approximately 1 g of solid/powder combustion controller to sample.

7.10 Repack the reagent (anhydrous magnesium perchlorate) tubes whenever the reagent becomes caked or moist or the warning alarm displays.

8. Calculations

$C\ (\%) = C_i \times AD/OD$

where:

C (%) = C (%), oven-dry basis

C_i = C (%) instrument

AD/OD = air-dry/oven-dry ratio (method 4B5)

9. Report

Report total C percentage on an oven-dry basis to the nearest 0.1%.

10. Precision

A quality control check sample is included in every batch of 10 samples. For 191 observations of calcium carbonate (actual total C = 12%), the mean, standard deviation, and C.V. for total carbon are 12.04, 0.31, and 2.5%, respectively. For 86 observations of soil calibration standard (reported total C = 0.77%), the mean, standard deviation, and C.V. for total carbon are 0.79, 0.02, and 2.2%, respectively.

11. References

Leco Corp. 1993. Sulfur and carbon in cements, soils, rock, ceramic and similar materials. Application Bulletin. Leco Corp., 3000 Lakeview Ave., St. Joseph, MI.

Leco Corp. 1994. Instruction manual. SC-444 Sulfur and carbon analyzers. Leco Corp., 3000 Lakeview Ave., St. Joseph, MI.

Nelson, D.W., and L.E. Sommers. 1982. Total carbon, organic carbon, and organic matter. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:539–579.

Soil Survey Staff. 1975. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys. USDA–SCS Agric. Handb. 436. U.S. Govt. Print. Office, Washington, DC.

Total Nitrogen (6B)
Dry Combustion (6B4)
LECO FP-428 Analyzer (6B4a)

1. Application

The total N content of the soil may range from <0.02% in subsoils, 2.5% in peats, and 0.06 to 0.5% in surface layers of many cultivated soils (Bremmer and Mulvaney, 1982). The total N data may 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 between 10 to 12. Variations in the C:N ratio may serve as an indicator of the amount of soil inorganic N. Uncultivated soils usually have higher C:N ratios than do cultivated soils.

Soils with 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). Since the organic C of many soils diminishes with depth while 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.

2. Summary of Method

A soil sample is combusted at high temperature with oxygen to release NO_x. The gases released are scrubbed to remove interferences (e.g., CO_2 and H_2O), and the NO_x is reduced to N_2. The N_2 is measured by thermal conductivity detection and reported as percent N.

3. Interferences

The total N that is measured by the combustion method does not distinguish among the types of N that are present in the soil. The purity of the helium and oxygen gases used in the instrument may affect the results of the analysis. The highest purity gases available are required to assure low detection limits and consistent results.

4. Safety

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (goggles or safety glasses) when handling hot crucibles. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary.

5. Equipment

5.1 Electronic balance, ±0.001-g sensitivity

6. Reagents

None.

7. Procedure

7.1 Weigh 0.200 g of 80-mesh, air-dry soil into a tin foil cup.

7.2 Close the tin foil cup by twisting the top closed as to fit the sample holder.

7.3 Place the enclosed sample in the sample holder.

7.4 When all the samples are in the sample holder, place the sample holder on the instrument.

7.5 Refer to manufacturer's manual for operation and calibration of the LECO FP-438 Analyzer.

7.6 On the bench worksheet, record the percent N for the samples.

8. Calculations

N (%) = Instrument Reading x AD/OD

where:

AD/OD = Air-dry/oven-dry ratio (method 4B5)

9. Report

Report total N as a dimensionless value to the nearest 0.001 unit on an oven-dry basis.

10. Precision

Precision data are not available for this procedure. For 105 observations of the quality control check sample for total N, the mean, standard deviation, and C.V. are 0.143, 0.004, and 2.7 percent, respectively.

11. References

Bremmer, J.M., and C.S. Mulvaney. 1982. Nitrogen—Total. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:595–624.

Nommik, H., and K. Vahtras. 1982. Retention and fixation of ammonium and ammonia in soils. *In* F.J. Stevenson (ed.) Nitrogen in agricultural soils. Agronomy 22:123–171.

Young, J.L., and R.W. Aldag. 1982. Inorganic forms of nitrogen in soil. *In* F.J. Stevenson (ed.) Nitrogen in agricultural soils. Agronomy 22:43–66.

Mineralizable Nitrogen (6B)

Steam Distillation (6B5)

Kjeltec Auto 1035 Sampler (6B5A)

1. Application

The most satisfactory methods currently available for obtaining an index for the availability of soil N are those involving the estimation of the N formed when soil is incubated under conditions which promote mineralization of organic N by soil microorganisms (Environmental Protection Agency, 1992). The method described herein for estimating mineralizable N is one of anaerobic incubation and is suitable for routine analysis of soils. This method involves estimation of the ammonium produced by a 1-week period of incubation of soil at 40 °C (Keeney and Bremner, 1966) under anaerobic conditions to provide an index of N availability.

2. Method Summary

An aliquot of air-dry homogenized soil is placed in a test tube with water, stoppered, and incubated at 40 °C for 1 week. The contents are transferred to a steam distillation, rinsed with 4 *N* KCl. The amount of ammonium-N is determined by steam distillation and titration for the KCl:soil mixture.

3. Interferences

There are no known interferences. The temperature and incubation period must remain constant for all samples. The test can be performed on field-moist or air-dry soil samples.

4. Safety

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses) when preparing reagents, especially concentrated acids and bases. Dispense concentrated acids and bases in a fume hood. Thoroughly wash hands after handling reagents. Use the safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids. Follow the manufacturer's safety precautions when using the incubator and Kjeltec Auto 1035 Analyzer.

5. Equipment

5.1 Electronic balance, ±1-mg sensitivity

5.2 Test tubes, 16-mm x 150-mm

5.3 PVC stoppers

5.4 Incubator, Model 10-140, Quality Lab Inc., Chicago, IL

5.5 Digestion tubes, straight neck, 250 mL

5.6 Kjeltec Auto 1035/1038 Sampler System, Tecator, Perstorp Analytical Inc.

6. Reagents

6.1 Distilled deionized (DDI) water

6.2 Potassium chloride (KCl), 4 *N*. Dissolve 298.24 g KCl in DDI water and dilute to 1-L volume.

6.3 Hydrochloric acid (HCl), 0.05 *N*, standardized. Dilute 83 mL of concentrated HCl in 20 L of DDI water.

6.4 Antifoam agent, slipicone release spray, Dow Chemical Corp. Alternatively, use n-octyl alcohol.

6.5 Boric acid, 4% (w:v), with bromcresol green-methyl red indicator (0.075 % bromcresol green and 0.05% methyl red), Chempure Brand

7. Procedure

Anaerobic Incubation of Soil Sample

7.1 Place 5.00 g of mineral soil (or 1.25 g of organic soil) into a 16-mm x 150-mm test tube. Record the soil sample weight to the nearest 0.00 g.

7.2 Add 12.5 ±1 mL of DDI water. Do not add ethanol to overcome any wetting difficulties as ethanol may act as an interference with microbial activity. Stopper the tube, shake, and place in a 40 °C constant-temperature incubator for 7 days. Refer to the manufacturer's instructions for set-up and operation of the incubator.

7.3 At the end of 7 days, remove the tube and shake for 15 s.

7.4 Transfer the contents of the test tube to a 250-mL digestion tube. Complete the transfer by rinsing the tube 3 times with 4 ml of 4 *N* KCl, using a total of 12.5 ±1 mL of the KCl.

Steam Distillation: Samples and Reagent Blanks

7.5 Remove the extraction vessel and transfer the sample to a 250-mL digestion tube.

7.6 Perform the same transfer and addition of reagents for blanks as for samples.

7.7 Spray silicone antifoam agent (or 2 drops of n-octyl alcohol solution) into the digestion tubes for each of the samples and reagent blanks.

7.8 When using new reagents, e.g., boric acid, reagent blanks are distilled in 2 sets of 6, one set per Kjeltec machine. Each set of 6 is averaged and recorded on bench worksheet and manually set on each machine. During the steam distillation, the mean reagent blank titer is automatically subtracted from the sample titer.

7.9 On bench worksheet, record the normality of standardized acid, i.e., ≈0.0500 *N* HCl.

7.10 Load samples in racks of 20. Distillation and titration are performed automatically. Record the titer in mL of titrant.

8. Calculations

$$N = (\text{Titer} \times N \times 100 \times \text{AD/OD}) / \text{Sample Weight (g)}$$

where:

N = Mineralizable N (meq 100 g^{-1})

Titer = Titer of sample (mL)

N = Normality of HCl titrant

100 = Conversion factor to 100-g basis

AD/OD = Air-dry/oven-dry ratio (method 4B5)

9. Report

Report mineralizable N in units of meq 100 g^{-1} of oven-dry soil to the nearest 0.001 meq 100 g^{-1}.

10. Precision

No precision data are available for this procedure.

11. References

Environmental Protection Agency. 1992. Handbook of laboratory methods for forest health monitoring. G.E. Byers, R.D. Van Remortel, T.E. Lewis, and M. Baldwin (eds.). Part III. Soil analytical laboratory. Section 10. Mineralizable N. U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Las Vegas, NV.

Keeney, D.R., and J.M. Bremner. 1966. Comparison and evaluation of laboratory methods of obtaining an index of soil nitrogen availability. Agron. J. 58:498–503.

Iron, Manganese, and Aluminum (6C, 6D, and 6G)

Dithionite-Citrate Extraction (6C2, 6D2, and 6G7)

Atomic Absorption Perkin-Elmer AA 5000 (6C2b, 6D2a, and 6G7a)

1. Application

Dithionite-citrate (CD) is used as a selective dissolution extractant for organically complexed Fe and Al, noncrystalline hydrous oxides of Fe and Al, and amorphous aluminosilicates (Wada, 1989). The CD solution is a poor extractant of crystalline hydrous oxides of Al, allophane, and imogolite. The CD solution does not extract opal, Si, or other constituents of crystalline silicate minerals (Wada, 1989). In *Soil Taxonomy*, the CD extractable Fe and Al are criteria for spodic placement (Soil Survey Staff, 1975).

2. Summary of Method

A soil sample is mixed with sodium dithionite, sodium citrate, and distilled deionized water, and shaken overnight. Superfloc 16 is added, and the mixture is made to volume. Solution is allowed to settle, and a clear extract is obtained. The CD extract is diluted with distilled deionized (DDI) water. The analytes are by an atomic absorption spectrophotometer (AA). The data are automatically recorded by a microcomputer and printer. The percent CD extractable Fe, Mn, and Al are reported in methods 6C2b, 6D2a, and 6G7a, respectively.

3. Interferences

There are four types of interferences (matrix, spectral, chemical, and ionization) in the AA analyses of these elements. These interferences vary in importance, depending upon the particular analyze selected.

The redo potential of the extractant is dependent upon the pH of the extracting solution and the soil system. Sodium citrate complexes the reduced Fe and usually buffers the system to a pH of 6.5 to 7.3. Some soils may lower the pH, resulting in the precipitation of Fe sulfides. The SSL has not had significant problems with this interference.

Filtered extracts can yield different recoveries of Fe, Mn, and Al, relative to unfiltered extracts.

4. Safety

Wear protective clothing (coats, aprons, sleeve guards, and gloves); eye protection (face shields, goggles, or safety glasses); and a breathing filter when handling dry sodium dithionite. Sodium dithionite may spontaneously ignite if allowed to become moist, even by atmospheric moisture. Keep dithionite in a fume hood.

Follow standard laboratory practices when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene gas is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the AA.

5. Equipment

5.1 Electronic balance, ±1-mg sensitivity

5.2 Filter paper, pre-pleated, 185-mm diameter, Schleicher and Schuell

5.3 Atomic absorption spectrophotometer (AA), model 5000, Perkin-Elmer Corp., Norwalk, CT

5.4 Automatic burner control, model 5000, Perkin-Elmer Corp., Norwalk, CT

5.5 Autosampler, AS-50, Perkin-Elmer Corp., Norwalk, CT

5.6 Dot matrix printer, P-132, Interdigital Data Systems, Inc.

5.7 Single-stage regulator, acetylene service, part number E11-0-N511A, Air Products and Chemicals, Inc., Box 538, Allentown, PA

5.8 Digital diluter/dispenser, Microlab 500, Hamilton Co., P.O. Box 10030, Reno, NV

5.9 Syringes, 10,000 and 1000 µL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV

5.10 Test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer, Curtin Matheson Scientific, Inc., Houston, TX

5.11 Containers, polypropylene

6. Reagents

6.1 Distilled deionized (DDI) water

6.2 Sodium dithionite ($Na_2S_2O_4$), purified powder

6.3 Sodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), crystal, reagent

6.4 Hydrochloric acid (HCl), concentrated 12 *N*

6.5 HCl, 1:1 HCl:DDI, 6 *N*. Carefully mix 1 part of concentrated HCl to 1 part DDI water.

6.6 HCl, 1% wt. Carefully dilute 25 mL of concentrated HCl to 1 L with DDI water.

6.7 Superfloc 16, 0.2% solution (w:v). Dissolve 2 g of Superfloc 16 in 1 liter of DDI water. Do not shake the mixture as this breaks the polymer chains of the Superfloc. Gently swirl the mixture occasionally over the several days that the solution requires to completely dissolve the Superfloc. Suggested source is American Cyanamid Co., P.O. Box 32787, Charlotte, NC.

6.8 Primary mixed standard, 4000 mg L^{-1} (4000 ppm) Fe, 600 mg L^{-1} (600 ppm) Mn, and 3000 mg L^{-1} (3000 ppm) Al. Dissolve 4.000 g of Fe wire, 0.6000 g of Mn metal powder, and 3.000 g of Al wire with 1:1 HCl in a glass beaker. When dissolved, transfer to a 1-L volumetric flask and make to volume with 1% HCl solution. Store in a polypropylene bottle.

6.9 High calibration standard, 240 mg/8 oz (1012 ppm) Fe; 36 mg/8 oz (152 ppm) Mn; and 180 mg/8 oz (759 ppm) Al. Pipette 60 mL of primary mixed standard into 8-oz bottle. Add 20 g of sodium citrate dihydrate, 1.24 mL of concentrated H_2SO_4, and 2 mL of Superfloc 16 solution. In standards, the H_2SO_4 substitutes for the dithionite. Fill to 8-oz volume with DDI water and mix thoroughly. After dissolution, transfer solution to a plastic bottle.

6.10 Low calibration standard, 120 mg/8 oz (506 ppm) Fe; 18 mg/8 oz (76 ppm) Mn; and 90 mg/8 oz (380 ppm) Al. Pipette 30 mL of primary mixed standard into 8-oz bottle. Add 20 g of sodium citrate dihydrate, 1.24 mL of concentrated H_2SO_4, and 2 mL of Superfloc 16 solution. In standards and reagent blanks, the H_2SO_4 substitutes for the dithionite. Fill to 8-oz volume with DDI water and mix thoroughly. After dissolution, transfer solution to a plastic bottle.

6.11 Calibration reagent blank solution. Add 20 g of sodium citrate dihydrate, 1.24 mL of concentrated H_2SO_4, and 2 mL of Superfloc 16 solution. In standards and reagent blanks, the H_2SO_4 substitutes for the dithionite. Fill to 8-oz volume with DDI water and mix thoroughly. After dissolution, transfer solution to a plastic bottle.

6.12 Acetylene gas, purity 99.6%

6.13 Compressed air with water and oil traps

7. Procedure

Extraction of Fe, Mn, and Al

7.1 Weigh 4.00 g of <2-mm, air-dry soil sample and place in an 8-oz nursing bottle.

7.2 Add 2 g of sodium dithionite and 20 to 25 g of sodium citrate dihydrate.

7.3 Add DDI water to 4-oz level on bottle and securely stopper bottle.

7.4 Shake overnight (12 to 16 h) in a reciprocating shaker. After shaking, use a dispenser to add 2 ml of Superfloc 16 solution.

7.5 Fill bottle to 8-oz volume with DDI water. Stopper and shake thoroughly for ~15 s.

7.6 Allow to settle for at least 3 days (3 to 5 days typical). The Fe, Mn, and Al are determined from a clear aliquot of solution.

Dilution of Sample Extracts and Standards

7.7 No ionization suppressant is required as the Na in the extractant is present in sufficient quantity. Set the digital diluter at 66 for diluent and 35 for CD extracts, calibration reagent blanks, and calibration standards for a 1:20 dilution as follows:

7.8 Dilute 1 part CD sample extract with 19 parts of DDI water (1:20 dilution).

7.9 Dilute 1 part calibration reagent blank with 19 parts of DDI water (1:20 dilution).

7.10 Dilute 1 part low calibration standard with 19 parts of DDI water (1:20 dilution).

7.11 Dilute 1 part high calibration standard with 19 parts of DDI water (1:20 dilution).

7.12 Dispense the reagent blanks and calibration standards in polycons from which the solutions are transferred to test tubes. Dispense the diluted sample solutions into test tubes which have been placed in the sample holders of the sample changer.

AA Calibration

7.13 Use the calibration reagent blank and high calibration standard to calibrate the AA. The AA program requires a blank and a standard, in that order, to establish a single point calibration curve for element determination. Perform one calibration, i.e., blank plus standard, for every 12 samples.

7.14 Use the low calibration standard (120 mg/8 oz Fe; 18 mg/8 oz Mn; and 90 mg/8 oz Al) as a check sample. Use high calibration standard for Fe check sample and low calibration standard for Mn and Al check sample.

AA Set-up and Operation

7.15 Refer to the manufacturer's manual for operation of the AA. The following are only very general guidelines for instrument conditions for the various analytes.

Element	Wave-length	Burner Head & Angle	Fuel/Oxidant
	(nm)		
Fe	248.5	5-cm, parallel	10 C_2H_2/25 Air
Al	309.35	5-cm, parallel	30 C_2H_2/17 N_2O
Mn	280.15	5-cm, parallel	10 C_2H_2/25 Air

Typical read delay is 6 s, and integration time is 8 s.

7.16 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

7.17 If sample exceeds calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record dilution. Remember to keep the matrix the same after dilution by diluting with DDI water (1:20 dilution).

7.18 The instrument readings are usually programmed to display analyte concentration in mg/8 oz.

8. Calculations

Fe (%) = (Fe x DR x 100 x AD/OD) / (Sample x 1000)

Fe_2O_3 (%) = (Fe x DR x 1.43 x 100 x AD/OD) / (Sample x 1000)

Mn (%) = (Mn x DR x 100 x AD/OD) / (Sample x 1000)

Al (%) = (Al x DR x 100 x AD/OD) / (Sample x 1000)

where:

Fe = mg/8 oz

Mn = mg/8 oz

Al = mg/8 oz

DR = Dilution Ratio

Sample = Sample weight (g)

1.43 = Conversion factor from Fe to Fe_2O_3

100 = Conversion factor to percent

AD/OD = Air-dry/oven-dry ratio (method 4B5)

1000 = Conversion factor (mg g^{-1})

9. Report

Report percent CD extractable Fe, Mn, and Al on oven-dry soil basis to the nearest whole number.

10. Precision

Precision data are not available for this procedure. A quality control check sample is run with every batch of samples. For the quality control check sample, the mean, standard deviation, and C.V. for Fe, Mn, and Al are as follows:

Element	Mean	n	Std. Dev.	C.V.
Fe	2.5	35	0.05	2.2%
Mn	0.01	19	0.00	0.0%
Al	0.26	33	0.01	5.4%

11. References

Soil Survey Staff. 1975. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys. USDA–SCS Agric. Handb. 436. U.S. Govt. Print. Office, Washington, DC.

Wada, K. 1989. Allophane and imogolite. *In* J.B. Dixon and S.B. Weed (eds.) Minerals in soil environments. 2nd ed. Soil Sci. Soc. Amer. No. 1. p. 1051–1087.

Iron, Manganese, and Aluminum (6C, 6D, and 6G)
Dithionite-Citrate Extraction (6C2, 6D2, and 6G7)
Atomic Absorption
Thermo Jarrell Ash, Smith-Hieftje 4000 (6C2c, 6D2b, and 6G7b)

1. Application

Dithionite-citrate (CD) is used as a selective dissolution extractant for organically complexed Fe and Al, noncrystalline hydrous oxides of Fe and Al, and amorphous aluminosilicates (Wada, 1989). The CD solution is a poor extractant of crystalline hydrous oxides of Al, allophane, and imogolite. The CD solution does not extract opal, Si, or other constituents of crystalline silicate minerals (Wada, 1989). In *Soil Taxonomy*, the CD extractable Fe and Al are criteria for spodic placement (Soil Survey Staff, 1975).

2. Summary of Method

A soil sample is mixed with sodium dithionite, sodium citrate, and distilled deionized water, and shaken overnight. Superfloc 16 is added, and the mixture is made to volume. Solution is allowed to settle, and a clear extract is obtained.

The CD extract is diluted with distilled deionized (DDI) water. The analytes are measured by an atomic absorption spectrophotometer (AA). The data are automatically recorded by a microcomputer and printer. The percent CD extractable Fe, Mn, and Al are reported in methods 6C2c, 6D2b, and 6G7b, respectively.

3. Interferences

There are four types of interferences (matrix, spectral, chemical, and ionization) in the AA analyses of these elements. These interferences vary in importance, depending upon the particular analyte selected.

The redox potential of the extractant is dependent upon the pH of the extracting solution and the soil system. Sodium citrate complexes the reduced Fe and usually buffers the system to a pH of 6.5 to 7.3. Some soils may lower the pH, resulting in the precipitation of Fe sulfides. The SSL has not had significant problems with this interference.

Filtered extracts can yield different recoveries of Fe, Mn, and Al, relative to unfiltered extracts.

4. Safety

Wear protective clothing (coats, aprons, sleeve guards, and gloves); eye protection (face shields, goggles, or safety glasses); and a breathing filter when handling dry sodium dithionite. Sodium dithionite may spontaneously ignite if allowed to become moist, even by atmospheric moisture. Keep dithionite in a fume hood.

Follow standard laboratory practices when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene gas is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the AA.

5. Equipment

5.1 Electronic balance, ±1-mg sensitivity

5.2 Filter paper, pre-pleated, 185-mm diameter, Schleicher and Schuell

5.3 Atomic absorption spectrophotometer (AA), Smith-Hieftje Model 4000, Thermo Jarrell Ash Corp., Franklin, MA

5.4 Autosampler, Model 150, Thermo Jarrell Ash Corp., Franklin, MA

5.5 ThermoSpec software, Version 3.01, Enable 4.0, DOS 5.0, Thermo Jarrell Ash Corp., Franklin, MA

5.6 Computer, CUi Advantage 486, Thermo Jarrell Ash Corp., Franklin, MA

5.7 Printer, NEC Pinwriter P3200

5.8 Single-stage regulator, acetylene service, part number E11-0-N511A, Air Products and Chemicals, Inc., Box 538, Allentown, PA

5.9 Digital diluter/dispenser, Microlab 500, Hamilton Co., P.O. Box 10030, Reno, NV

5.10 Syringes, 10,000 and 1000 µL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV

5.11 Test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer, Curtin Matheson Scientific, Inc., Houston, TX

5.12 Containers, polypropylene

6. Reagents

6.1 Distilled deionized (DDI) water

6.2 Sodium dithionite ($Na_2S_2O_4$), purified powder

6.3 Sodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), crystal, reagent

6.4 Hydrochloric acid (HCl), concentrated 12 *N*

6.5 HCl, 1:1 HCl:DDI, 6 *N*. Carefully mix 1 part of concentrated HCl to 1 part DDI water.

6.6 HCl, 1% wt. Carefully dilute 25 mL of concentrated HCl to 1 L with DDI water.

6.7 Superfloc 16, 0.2% solution (w:v). Dissolve 2 g of Superfloc 16 in 1 liter of DDI water. Do not shake the mixture as this breaks the polymer chains of the Superfloc. Gently swirl the mixture occasionally over the several days that the solution requires to completely dissolve the Superfloc. Suggested source is American Cyanamid Co., P.O. Box 32787, Charlotte, NC.

6.8 Primary mixed standard, 4000 mg L^{-1} (4000 ppm) Fe, 600 mg L^{-1} (600 ppm) Mn, and 3000 mg L^{-1} (3000 ppm) Al. Dissolve 4.000 g of Fe wire, 0.6000 g of Mn metal powder, and 3.000 g of Al wire with 1:1 HCl in a glass beaker. When dissolved, transfer to a 1-L volumetric flask and make to volume with 1% HCl solution. Store in a polypropylene bottle.

6.9 High calibration standard, 240 mg/8 oz (1012 ppm) Fe; 36 mg/8 oz (152 ppm) Mn; and 180 mg/8 oz (759 ppm) Al. Pipette 60 mL of primary mixed standard into 8-oz bottle. Add 20 g of sodium citrate dihydrate, 1.24 mL of concentrated H_2SO_4, and 2 mL of Superfloc 16 solution. In standards, the H_2SO_4 substitutes for the dithionite. Fill to 8-oz volume with DDI water and mix thoroughly. After dissolution, transfer solution to a plastic bottle.

6.10 Low calibration standard, 120 mg/8 oz (506 ppm) Fe; 18 mg/8 oz (76 ppm) Mn; and 90 mg/8 oz (380 ppm) Al. Pipette 30 mL of primary mixed standard into 8-oz bottle. Add 20 g of sodium citrate dihydrate, 1.24 mL of concentrated H_2SO_4, and 2 mL of Superfloc 16 solution. In standards and

reagent blanks, the H_2SO_4 substitutes for the dithionite. Fill to 8-oz volume with DDI water and mix thoroughly. After dissolution, transfer solution to a plastic bottle.

6.11 Calibration reagent blank solution. Add 20 g of sodium citrate dihydrate, 1.24 mL of concentrated H_2SO_4, and 2 mL of Superfloc 16 solution. In standards and reagent blanks, the H_2SO_4 substitutes for the dithionite. Fill to 8-oz volume with DDI water and mix thoroughly. After dissolution, transfer solution to a plastic bottle.

6.12 Acetylene gas, purity 99.6%

6.13 Compressed air with water and oil traps

7. Procedure

Extraction of Fe, Mn, and Al

7.1 Weigh 4.00 g of <2-mm, air-dry soil sample and place in an 8-oz nursing bottle.

7.2 Add 2 g of sodium dithionite and 20 to 25 g of sodium citrate dihydrate.

7.3 Add DDI water to 4-oz level on bottle and securely stopper bottle.

7.4 Shake overnight (12 to 16 h) in a reciprocating shaker. After shaking, use a dispenser to add 2 ml of Superfloc 16 solution.

7.5 Fill bottle to 8-oz volume with DDI water. Stopper and shake thoroughly for ~15 s.

7.6 Allow to settle for at least 3 days (3 to 5 days typical). The Fe, Mn, and Al are determined from a clear aliquot of solution.

Dilution of Sample Extracts and Standards

7.7 No ionization suppressant is required as the Na in the extractant is present in sufficient quantity. Set the digital diluter at 66 for diluent and 35 for CD extracts, calibration reagent blanks, and calibration standards for a 1:20 dilution as follows:

7.8 Dilute 1 part CD sample extract with 19 parts of DDI water (1:20 dilution).

7.9 Dilute 1 part calibration reagent blank with 19 parts of DDI water (1:20 dilution).

7.10 Dilute 1 part low calibration standard with 19 parts of DDI water (1:20 dilution).

7.11 Dilute 1 part high calibration standard with 19 parts of DDI water (1:20 dilution).

7.12 Dispense the reagent blanks and calibration standards in polycons from which the solutions are transferred to test tubes. Dispense the diluted

sample solutions into test tubes which have been placed in the sample holders of the sample changer.

AA Calibration

7.13 Use the calibration reagent blank and high calibration standard to calibrate the AA. The AA program requires a blank and a standard, in that order, to establish a single point calibration curve for element determination. Perform one calibration, i.e., blank plus standard, for every 12 samples.

7.14 Use the low calibration standard (120 mg/8 oz Fe; 18 mg/8 oz Mn; and 90 mg/8 oz Al) as a check sample. Use high calibration standard for Fe check sample and low calibration standard for Mn and Al check sample.

AA Set-up and Operation

7.15 Refer to manufacturer's manual for operation of the AA. The following are only very general guidelines for instrument conditions for the various analytes.

Element	Wave-length	Burner Head & Angle	Fuel/Oxidant
	(nm)		
Fe	248.5	5-cm, parallel	4 C_2H_2/16 Air
Al	309.35	5-cm, parallel	20 C_2H_2/10 N_2O
Mn	280.15	5-cm, parallel	4 C_2H_2/10 Air

Typical read delay is 6 s, and integration time is 8 s.

7.16 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

7.17 If sample exceeds calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record dilution. Remember to keep the matrix the same after dilution by diluting with DDI water (1:20 dilution).

7.18 The instrument readings are usually programmed to display analyte concentration in mg/8 oz.

8. Calculations

Fe (%) = (Fe x DR x 100 x AD/OD) / (Sample x 1000)

Fe_2O_3 (%) = (Fe x DR x 1.43 x 100 x AD/OD) / (Sample x 1000)

Mn (%) = (Mn x DR x 100 x AD/OD) / (Sample x 1000)

Al (%) = (Al x DR x 100 x AD/OD) / (Sample x 1000)

where:

Fe = mg/8 oz

Mn = mg/8 oz

Al = mg/8 oz

DR = Dilution Ratio

Sample = Sample weight (g)

1.43 = Conversion factor from Fe to Fe_2O_3

100 = Conversion factor to percent

AD/OD = Air-dry/oven-dry ratio (method 4B5)

1000 = Conversion factor (mg g^{-1})

9. Report

Report percent CD extractable Fe, Mn, and Al on oven-dry soil basis to the nearest whole number.

10. Precision

Precision data are not available for this procedure. A quality control check sample is run with every batch of samples.

11. References

Soil Survey Staff. 1975. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys. USDA–SCS Agric. Handb. 436. U.S. Govt. Print. Office, Washington, DC.

Wada, K. 1989. Allophane and imogolite. *In* J.B. Dixon and S.B. Weed (eds.) Minerals in soil environments. 2nd ed. Soil Sci. Soc. Amer. No. 1. p. 1051–1087.

Iron, Manganese, Aluminum, Calcium, Magnesium, Sodium, Potassium, Phosphorus, Silicon, Zirconium, Copper, Zinc, Titanium, Cadmium, Lead, Nickel, Chromium, and Cobalt

HF Plus Aqua Regia (HF + HNO_3 + HCl) Dissolution
Inductively Coupled Plasma Spectrometry
Thermo Jarrell Ash ICAP 61E Optima 3300 DV
(6C7b, 6D6a, 6G11b, 6N5b, 6O5b, 6P3b, 6Q3b, 6S6a, 6V1b, 8K1a, 8L1a, 8M1a, 8N1a, 8O1a, 8P1a, 8Q1a, and 8R1a)

1. Application

This procedure is an integral part of total analysis (7C4a) and represents the spectroscopic analysis of elements in the digestate.

2. Summary of Method

High and low calibration standards are prepared for Ca, K, Mg, Mn, Cu, Zn, Cd, Pb, Co (mixed standards CALO and CAHI); Al, Fe, Ti, Zr, Na, (mixed standards ALLO and ALHI); and Si, P, Se, As (mixed standards SILO and SIHI). A blank of HF, HNO_3, HCl, and H_3BO_3 is prepared. A Thermo Jarrell Ash ICAP 61E spectrometer is used for analysis. The concentration of Fe, Mn, Al, Ca, Mg, Na, K, P, Si, Zr, Cu, Zn, Ti, Cd, Pb, Cr, and Co are determined by ICP analysis by methods 6C7b, 6D6a, 6G11b, 6N5b, 6O5b, 6P3b, 6Q3b, 6S6a, 6V1b, 8K1a, 8L1a, 8M1a, 8N1a, 8O1a, 8P1a, 8Q1a, and 8R1a.

3. Interferences

None.

4. Safety

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Restrict the use of concentrated acids to the fume hood. Keep HF acid refrigerated and avoid contact with skin of all acids. Wash hands thoroughly after handling reagents.

5. Equipment

5.1 Volumetrics, 500-mL, polypropylene

5.2 Containers, 500-mL, polypropylene, with screw caps

5.3 Pipettors, electronic digital, Rainin Instrument Co., Woburn, MA, 2500 µL and 10 mL

5.4 Inductively coupled plasma spectrometer, ICAP-61E, Thermo Jarrell Ash Corp., Franklin, MA

5.5 RF generator, floor mounted power unit, 45 MHz free running, Perkin-Elmer Corp., Norwalk, CT

5.6 Computer, AT&T 386 Starstation, Model CPU-G72, and printer, NEC Pinwriter, P2200XE, Dot Matrix

5.7 ThermoSpec software, Thermo Jarrell Ash Corp., Franklin, MA

5.8 Line conditioner, Unity/1, Model UT8K, Best Power Technology, Inc., Necedah, WI

5.9 Compressed argon gas

5.10 Autosampler, Thermo Jarrell Ash Corp., Franklin, MA

5.11 High flow torch, Part No. 126440-01; Saffire (HF-resistant) tip, Part No. 127190-00; Polypropylene spray chamber, Part 131129-00, Thermo Jarrell Ash Corp., Franklin, MA

6. Reagents

6.1 Deionized distilled (DDI) water

6.2 Hydrofluoric acid (HF), 48%, low trace metal content

6.3 Concentrated hydrochloric acid (HCl), 12 *N*. Use instrumental grade which contains low levels of impurities.

6.4 Concentrated nitric acid (HNO_3), 16 *N*. Use instrumental grade which contains low levels of impurities.

6.5 Boric acid solution. Dissolve 25.0 g low trace metal, granular boric acid (H_3BO_3) in 1000 mL DDI water.

6.6 Standards, 1000 ppm, suitable for atomic absorption spectroscopy for all elements

7. Procedure

7.1 Instrument calibration standards for analysis are limited to specific combinations of elements because of chemical incompatibilities of certain elements. Specific combinations of elements in calibration standards are based on suggestion by Thermo Jarrell Ash (TJA), Inc. Each working standard is used in two concentrations, high and low. The concentrations of elements in the low standards (CALO, ALLO, and SILO) are 50 percent of the concentrations of elements in the low standards (CALO, ALLO, and SILO). Refer to Tables 1-3 for the amounts of primary standards (1000 ppm) to make 500-mL volume of the low and high calibration standards, at the specified concentrations, for ICP analysis.

Table 1.—Calibration standards for CALO and CAHI[1].

Element	Concen-tration	Concen-tration	Primary Std. Required For	Primary Std. Required For
	CALO	CAHI	CALO	CAHI
	(ppm)	*(ppm)*	*(mL)*	*(mL)*
Ca	75	150	37.5	75.0
K	25	50	12.5	25.0
Mg	20	40	10.0	20.0
Mn	10	20	5.0	10.0
Cu	5	10	2.5	5.0
Zn	5	10	2.5	5.0
Cd	5	10	2.5	5.0
Pb	5	10	2.5	5.0

[1]All calibration standards based on 500-ml final volume.

Table 2.—Calibration standards for ALLO and ALHI[1].

Element	Concen-tration	Concen-tration	Primary Std. Required For	Primary Std. Required For
	ALLO	AlHI	ALLO	AlHI
	(ppm)	*(ppm)*	*(mL)*	*(mL)*
Al	100	200	50.0	100.0
Fe	75	150	37.5	75.0
Ti	5	10	2.5	5.0
Zr	5	10	2.5	5.0
Na	25	50	12.5	25.0

[1]All calibration standards based on 500-ml final volume.

Table 3.—Calibration standards for SILO and SIHI[1].

Element	Concen-tration	Concen-tration	Primary Std. Required For	Primary Std. Required For
	SILO	SIHI	SILO	SIHI
	(ppm)	*(ppm)*	*(mL)*	*(mL)*
Si	225	450	112.5	225.0
P	5	10	2.5	5.0
Ti	5	10	2.5	5.0
Se	5	10	2.5	5.0
As	5	10	2.5	5.0

[1]All calibration standards based on 500-ml final volume.

7.2 To the calibration standards and a blank, also add the following chemicals: 25.0 mL HF; 3.75 mL HNO_3; 1.25 mL HCl; and 12.5 g granular Boric Acid. Make all standards and the blank to a final 500-mL volume with DDI water.

7.3 Use the TJA ICAP 61E spectrophotometer and analyze for the following elements: Fe, Mn, Al, Ca, Mg, Na, K, P, Si, Zr, Cu, Zn, As, Ti, Se, Cd, and Pb. No initial dilutions of samples are necessary prior to analysis. Use polypropylene spray chamber and HF-resistant torch on ICP. Check instrument alignment and gas pressures to obtain optimum readings with maximum signal to noise ratio. The torch tip used for HF digestions should not be run dry or used with RF powers exceeding 1350. The HF torch tip should only be used with high flow torch.

7.4 Use the HF blank standard solution to dilute those samples with concentrations greater than the high standard. Rerun all elements and use only the data needed from the diluted analysis.

7.5 Run the detection limits using the blank standard solution. These values establish the lower detection limits for each element. Analyzed values lower than the detection limits are set equal to zero.

7.6 When ICP analyses are completed, transfer data from the hard drive storage to a 3.5 inch floppy disk as an ASCII file via the "Report Writer" in the TJA software Thermospec, Version 5.06. These data are imported into a LOTUS 123, Version 3.1 spreadsheet for data analysis. Refer to method 7C4a.

8. Calculations

Refer to method 7C4a.

9. Report

Refer to method 7C4a.

10. Precision

No precision data are yet available for this procedure.

11. References

Refer to digestion procedure.

Organic Carbon, Iron, Manganese, and Aluminum (6A, 6C, 6D, and 6G)

Sodium Pyrophosphate Extraction (6A4)

CO_2 Evolution Gravimetric (6A4a)
Sodium Pyrophosphate Extraction (6C8, 6D4, and 6G10)
Atomic Absorption
Perkin-Elmer 5000 AA (6C8a, 6D4a, and 6G10a)

1. Application

Sodium pyrophosphate (0.1 *M* $Na_4P_2O_7$) is used as a selective dissolution extractant for organically complexed Fe and Al (Wada, 1989). The $Na_4P_2O_7$ solution is a poor extractant for allophane, imogolite, amorphous aluminosilicates, and noncrystalline hydrous oxides of Fe and Al. The $Na_4P_2O_7$ solution does not extract opal, crystalline silicates, layer silicates, and crystalline hydrous oxides of Fe and Al (Wada, 1989). In *Soil Taxonomy*, sodium pyrophosphate extractable organic C, Fe, and Al are criteria for spodic placement (Soil Survey Staff, 1975).

2. Summary of Method

The soil sample is mixed with 0.1 *M* $Na_4P_2O_7$ and shaken overnight. Superfloc 16 is added, and the mixture is made to volume. The solution is allowed to settle and a clear extract is obtained. The $Na_4P_2O_7$ extracted solution is diluted with distilled deionized (DDI) water. The diluted extract is aspirated into an atomic absorption spectrophotometer (AA). The analyte is measured by absorption of the light from a hollow cathode lamp. An automatic sample changer is used to aspirate a series of samples. The AA converts absorption to analyte concentration. Percent sodium pyrophosphate extractable Fe, Mn, and Al are reported in methods 6C8a, 6D4a, and 6G10a, respectively. The organic C in the sodium pyrophosphate extract is wet oxidized and gravimetrically measured in method 6A4a.

3. Interferences

There are four types of interferences (matrix, spectral, chemical, and ionization) in the AA analyses of these elements. These interferences vary in importance, depending upon the particular analyte selected.

The concentration of $Na_4P_2O_7$ solution must be close to 0.1 *M*. Variable amounts of Fe, Al, Mn, and organic C may be extracted by varying the pyrophosphate concentration.

4. Safety

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Restrict the use of concentrated HCl to a fume hood. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts.

Follow standard laboratory procedures when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the AA.

5. Equipment

5.1 Electronic balance, ±0.0001 g

5.2 Shaker, Eberbach 6000 power unit, reciprocating speed of 60 to 260 epm, with 6040 utility box carrier and 6110 floor stand, Eberbach Corp., Ann Arbor, MI

5.3 Nursing bottle, 240 mL (8 fl. oz.), graduated

5.4 Rubber stoppers, No. 2, to fit nursing bottles

5.5 Dispenser/diluters, Repipet, 0 to 10 mL, Labindustries, 1802 2nd St., Berkeley, CA

5.6 Atomic absorption spectrophotometer (AA), model 5000, Perkin-Elmer Corp., Norwalk, CT

5.7 Automatic burner control, model 5000, Perkin-Elmer Corp., Norwalk, CT

5.8 Autosampler, AS-50, Perkin-Elmer Corp., Norwalk, CT

5.9 Single-stage regulator, acetylene service, part number E11-0-N511A, Air Products and Chemicals, Inc., Box 538, Allentown, PA

5.10 Heated regulator, single-stage, nitrous oxide, stock number 808 8039, Airco Welding Products, P.O. Box 486, Union, NJ

5.11 Diluter/dispenser, Microlab 500, Catalogue No. 69052, Hamilton Co., Bonaduz, GR, Switzerland

5.12 Syringes, 10,000 and 1000 µL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV, 89510

5.13 Test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer, Curtin Matheson Scientific, Inc., Houston, TX

5.14 Absorption bulb, Nesbitt with stopper

5.15 Absorption bulb, Stetser-Norton

5.16 Flask, boiling, round bottom, short neck

5.17 Condenser, Allihn

5.18 Funnel, separatory, cylindrical, open top, with stopcock

5.19 Tube, drying, Schwartz

5.20 Containers, polypropylene

5.21 Dot matrix printer, P-132, Interdigital Data Systems, Inc.

6. Reagents

6.1 Distilled deionized (DDI) water

6.2 Hydrochloric acid (HCl), concentrated, 12 *N*

6.3 HCl, 1:1 HCl:DDI, 6 *N*. Carefully mix 1 part of concentrated HCl to 1 part DDI H_2O.

6.4 HCl, 1% wt. Carefully dilute 25 mL of concentrated HCl to 1 L with DDI H_2O.

6.5 Superfloc 16, 0.2% solution (w:v). Dissolve 2 g of Superfloc 16 in 1 liter of DDI H_2O. Do not shake the mixture as this breaks the polymer chains of the Superfloc. Gently swirl the mixture occasionally over the several days that the solution requires to completely dissolve the Superfloc. Suggested source is American Cyanamid Co., P.O. Box 32787, Charlotte, NC.

6.6 Sodium pyrophosphate solution, 0.1 *M*. Dissolve 800 g of $Na_4P_2O_7 \cdot H_2O$ in 16 L of DDI H_2O. Dilute to 18 L with DDI H_2O.

6.7 Primary mixed standard, 4000 mg L^{-1} (4000 ppm) Fe; 2000 mg L^{-1} (3000 ppm) Al; and 600 mg L^{-1} (600 ppm) Mn. Dissolve 4.000 g of Fe wire, 3.000 g of Al wire, and 0.600 g of Mn metal powder in 1:1 HCl:DDI in a glass beaker. When dissolved, transfer to a 1-L volumetric flask and fill with 1% HCl solution. Store in a polypropylene bottle.

6.8 High calibration mixed standards solution (HCMSS), 80 mg/8 oz (80 ppm) Fe; 12 mg/8 oz (12 ppm) Mn; and 60 mg/8 oz (60 ppm) Al. Pipette 20 mL of primary mixed standard into an 8-oz bottle. Add 10.55 g of $Na_4P_2O_7 \cdot H_2O$ and 3.5 mL of concentrated H_3PO_4. Dilute to 8 oz with DDI H_2O. Store in a polypropylene bottle.

6.9 Low calibration mixed standards solution (LCMSS), 40 mg/8 oz (40 ppm) Fe; 6 mg/8 oz (6 ppm) Mn; and 30 mg/8 oz (30 ppm) Al. Pipette 10 mL of primary mixed standard into an 8-oz bottle. Add 10.55 g of $Na_4P_2O_7 \cdot H_2O$ and 3.5 mL of concentrated H_3PO_4. Dilute to 8 oz with DDI H_2O. Store in a polypropylene bottle.

6.10 Calibration reagent blank solution (CRBS). Add 10.55 g of $Na_4P_2O_7 \cdot H_2O$ and 3.5 mL of concentrated H_3PO_4. Dilute to 8 oz with DDI H_2O. Store in a polypropylene bottle.

6.11 Potassium dichromate ($K_2Cr_2O_7$), reagent

6.12 Potassium iodide solution. Dissolve 100 g of KI in 100 mL of DDI H_2O.

6.13 Silver sulfate, saturated aqueous solution

6.14 Digestion acid mixture. Mix 600 mL of concentrated H_2SO_4 and 400 mL of 85% H_3PO_4.

6.15 Indicarb or Mikohlbite

6.16 Soda lime

6.17 Zinc granules, 300 mesh

6.18 Anhydrone

6.19 Acetylene gas, purity 99.6%

6.20 Nitrous oxide gas, compressed

6.21 Compressed air with water and oil traps

7. Procedure

Extraction of Fe, Mn, and Al

7.1 Weigh 2.00 g of <2-mm, air-dry soil sample and place in an 8-oz nursing bottle.

7.2 Add 0.1 *M* $Na_4P_2O_7$ solution to 7-oz level on bottle and securely stopper bottle.

7.3 Shake overnight (12 to 16 h) in a reciprocating shaker. After shaking, use a dispenser to add 4 mL of Superfloc 16 solution.

7.4 Fill bottle to 8-oz volume with $Na_4P_2O_7$ solution.

7.5 Stopper and shake vigorously for ≈15 s.

7.6 Allow to settle for at least 3 days (4 to 6 days typical). The Fe, Mn, and Al are determined from a clear aliquot of solution.

Dilution of Sample Extracts and Standards

7.7 No ionization suppressant is required as the Na in the extractant is present in sufficient quantity. Set the digital diluter on Hamilton diluter to 66 for diluent and 35 for sodium pyrophosphate sample extracts, calibration reagent blanks, and calibration standards for a 1:20 dilution as follows:

7.8 Dilute 1 part sample sodium pyrophosphate sample extract with 19 parts of DDI H_2O (1:20 dilution).

7.9 Dilute 1 part CRBS with 19 parts of DDI H_2O (1:20 dilution).

7.10 Dilute 1 part LCMSS with 19 parts of DDI H_2O (1:20 dilution).

7.11 Dilute 1 part HCMSS with 19 parts of DDI H_2O (1:20 dilution).

7.12 Dispense the diluted solutions into test tubes which have been placed in the sample holder of the sample changer.

AA Calibration

7.13 Use the calibration reagent blank and high calibration standard to calibrate the AA. The AA requires a blank and a standard, in that order, to establish a single point calibration curve for element determination. Perform one calibration, i.e., blank plus standard, for every 12 samples.

7.14 Use the low calibration standard as a check sample.

AA Set-up and Operation

7.15 Refer to the manufacturer's manual for operation of the Perkin-Elmer 5000 AA. The following are only very general guidelines for instrument conditions for the various analytes.

Analyte	Wave-length	Burner Head	Fuel/Oxidant
	(nm)		
Fe	248.8	5-cm parallel	10 C_2H_2/25 Air
Mn	280.1	5-cm parallel	10 C_2H_2/25 Air
Al	309.3	5-cm parallel	30 C_2H_2/17 Air

Typical read delay is 6 s, and the integration by peak area is 8 s.

7.16 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

7.17 If sample exceeds calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record dilution. Remember to keep matrix the same after dilution by diluting with DDI H_2O (1:20 dilution).

Organic C Determination

7.18 Pipette 100 mL of the extract into a 100-ml flask.

7.19 Evaporate the extract to near dryness using a 50 °C water bath and a gentle stream of clean, filtered air.

7.20 Construct the wet combustion apparatus. Refer to figure 6A4-1 of the apparatus for gravimetric organic C determination.

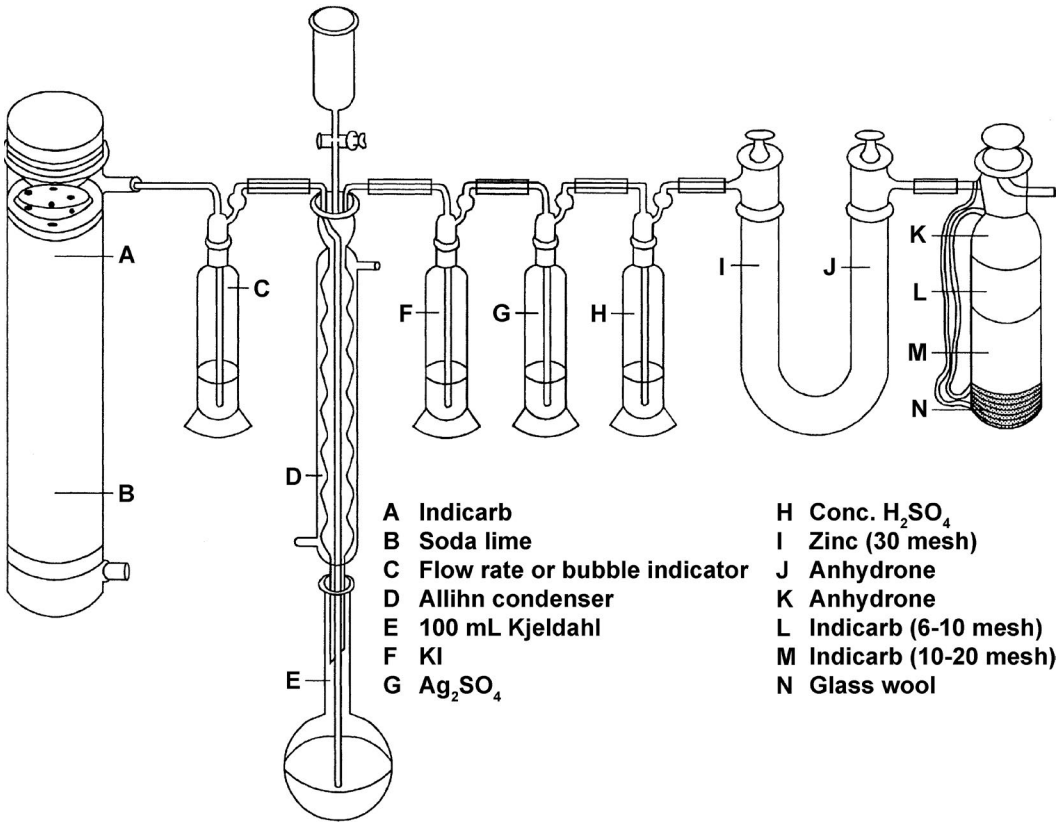


Figure 6A4-1.—Apparatus for gravimetric organic carbon determinations of 0.1 M sodium pyrophosphate extracts.

7.21 Add 1 to 2 g of potassium dichromate.

7.22 Wash the neck of the flask with 3 mL of DDI H_2O and connect to condenser.

7.23 Attach a weighed Nesbitt bulb to the system and open the valve at the top.

7.24 Pour 25 mL of digestion-acid mixture into the funnel. Add the mixture to the flask and immediately close the stopcock. Use the digestion-acid mixture to lubricate the stopcock.

7.25 The tip of the air-delivery tube should be ≈0.5 cm below the digestion-acid mixture. Adjust the flow of the "carrier stream" to maintain 1 to 2 bubble s^{-1} rate throughout the digestion. Apply suction on the outlet side of the Nesbitt bulb. Gentle air pressure and needle valve on the air pressure line aids flow adjustment.

7.26 With a gas flame or a variable power heating mantle, gently heat the flask until the mixture boils (≈3 to 4 min). Continue a gentle boiling for 10 min. Heating is too rapid if white fumes of SO_2 are visible above the second bulb of the reflux condenser.

7.27 Remove the heat and allow to aerate for 10 additional min at a rate of 6 to 8 bubbles s^{-1}.

7.28 Close the stopcock on the Nesbitt bulb, disconnect the bulb from the system, and weigh to the nearest 0.0001 g.

8. Calculations

Analyte (%) = (AA x DR x AD/OD x 100) / (Sample Weight (g) x 1000)

where:

Analyte = Fe, Mn, and Al

AA = Analyte concentration AA reading

DR = Dilution ratio of 1 if no additional dilution

Sample = Sample weight (g)

100 = Factor to convert to percent

1000 = Conversion factor (mg g^{-1})

AD/OD = Air-dry/oven-dry ratio

Organic C (%) = [(WtF − WtI) x 27.3 x Volume x AD/OD] / (Sample Weight (g) x 236.6)

where:

Wt_F = Nesbitt bulb weight after digestion (g)

Wt_I = Nesbitt bulb weight before digestion (g)

Volume = Volume of extract digested (mL)

AD/OD = Air-dry/oven-dry ratio (method 4B5)

27.3 = Conversion factor

236.6 = Total volume of extract (mL)

9. Report

Report percent sodium pyrophosphate extractable Fe, Mn, and Al on oven-dry soil basis to the nearest whole number.

10. Precision

Precision data are not available for this procedure.

11. References

Soil Survey Staff. 1975. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys. USDA–SCS Agric. Handb. 436. U.S. Govt. Print. Office, Washington, DC.

Wada, K. 1989. Allophane and imogolite. *In* J.B. Dixon and S.B. Weed (eds.) Minerals in soil environments. 2nd ed. Soil Sci. Soc. Amer. No. 1. p. 1051–1087.

Iron, Manganese, Aluminum, Silicon, and Phosphate (6C, 6D, 6G, 6V, 6S)

Ammonium Oxalate Extraction (6C9, 6D5, 6D6, 6G12, 6V2, 6S8)

Inductively Coupled Plasma Spectrometry

Thermo Jarrell Ash, ICAP 61E (6C9b, 6D5b, 6G12b, 6V2b, 6S8a)

Optical Density (8J) (of Ammonium Oxalate Extract)

1. Application

Oxalic acid-ammonium oxalate (acid oxalate) is used as a selective dissolution extractant for organically complexed Fe and Al, noncrystalline hydrous oxides of Fe and Al, allophane, and amorphous aluminosilicates (Wada, 1989). Acid oxalate is a poor extractant of imogolite and layer silicates and does not extract crystalline hydrous oxides of Fe and Al, opal, or crystalline silicate (Wada, 1989). A more reliable and accurate estimation of soil properties and a better understanding of the soil exchange complex is provided when acid oxalate extraction is used in conjunction with other selective dissolution procedures, thermal techniques, and chemical tests. In *Soil Taxonomy*, acid oxalate extractable Fe and Al are criteria for andic soil properties (Soil Survey Staff, 1999).

2. Summary of Method

A soil sample is extracted with a mechanical vacuum extractor (Holmgren et al., 1977) in a 0.2 *M* acid oxalate solution buffered at pH 3.0 under darkness. The acid oxalate extract is weighed. The acid oxalate extract is diluted with 0.002 *M* DDBSA. The analytes are measured by a inductively coupled plasma emission spectrophotometer (ICP). Data are automatically recorded by a microcomputer

and printer. The percent acid oxalate extractable Fe, Mn, Al, Si, and P are reported in methods 6C9b, 6D5b, 6G12b, 6V2b, and 6S8a respectively. In method 8J, the optical density of the extract is measured with a UV spectrophotometer at 430 nm.

3. Interferences

There are four types of interferences (matrix, spectral, chemical, and ionization) in the ICP analyses of these elements. These interferences vary in importance, depending upon the particular analyte chosen.

The acid oxalate buffer extraction is sensitive to light, especially UV light. The exclusion of light reduces the dissolution effect of crystalline oxides and clay minerals. If the sample contains large amounts of amorphous material (>2% Al), an alternate method should be used, i.e., shaking with 0.275 *M* acid oxalate, pH 3.25, 1:100 soil:extractant.

4. Safety

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Follow standard laboratory practices when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Follow the manufacturer's safety precautions when using the UV spectrophotometer and ICP.

5. Equipment

5.1 Electronic balance, ±1-mg sensitivity

5.2 Mechanical vacuum extractor, 24 place, Centurion International, Inc., Lincoln, NE

5.3 Mechanical vacuum extractor, Mavco Sampletek, 5300 N. 57th St., Lincoln, NE

5.4 Syringes, polypropylene, disposable, 60 mL, for extractant reservoir, extraction vessel, and tared extraction syringe

5.5 Rubber tubing, 3.2 ID x 6.4 OD x 25.4 mm, (⅛ ID x ¼ OD x 1 in) for connecting syringe barrels

5.6 Pre-pulped tubes

5.7 Extraction vessel, 60-mL, 10u polypropylene, part no. 6986-6010, Whatman Inc., 9 Bridewell Place, Clifton, NJ

5.8 Disposable glass tubes

5.9 UV-visible spectrophotometer, Carey-50, Varian Instruments

5.10 Cuvettes, disposable, polystyrene, 1-cm light path

5.11 Inductively coupled plasma spectrometer, ICAP 61E, Thermo Jarrell Ash Corp., Franklin, MA

5.12 Nebulizers, High-Solids, 41 psgi, Thermo Jarrell Ash Corp., Franklin, MA

5.13 RF generator, floor mounted power unit, Model 7/90, Thermo Jarrell Ash Corp., Franklin, MA

5.14 Computer, AT&T 386 Starstation, Model CPU-G72, and printer, NEC Pinwriter, P2200XE, Dot Matrix

5.15 ThermoSpec software, Thermo Jarrell Ash Corp., Franklin, MA

5.16 Line conditioner, Unity/I, Model UT8K, Best Power Technology, Inc., Necedah, WI

5.17 Single-stage regulator, high-purity, high-flow, argon, product no. E11-X-N145DHF, Air Products and Chemicals, Inc., Box 538, Allentown, PA

5.18 Autosampler, Thermo Jarrell Ash Corp., Franklin, MA

5.19 Digital diluter/dispenser, Microlab 500, Hamilton Co., P.O. Box 10030, Reno, NV

5.20 Syringes, 10,000 and 1000 µL, 1001 DX and 1010-TEL LL gastight, Hamilton Co., P.O. Box 10030, Reno, NV

5.21 Test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer, Curtin Matheson Scientific, Inc., Houston, TX

5.22 Containers, polypropylene

6. Reagents

6.1 Distilled deionized (DDI) water

6.2 Acid oxalate buffer solution, 0.2 *M*, pH 3.0. *Solution A* (base): Dissolve 284 g of $(NH_4)_2C_2O_4 \cdot 2H_2O$ in 10 L of DDI water. *Solution B* (acid): Dissolve 252 g of $H_2C_2O_4 \cdot H_2O$ in 10 L of DDI water. Mix 4 parts solution A with 3 parts solution B. Adjust acid oxalate solution pH by adding either acid or base solution. Store in a polypropylene bottle.

6.3 pH buffers, pH 4.00 and 7.00, for electrode calibration

6.4 Primary Fe standard, 1000 ppm. Certified Reference Solution, Fisher Chemical Scientific Co., Fairlawn, NJ.

6.5 Primary Al standard, 1000 ppm. Certified Reference Solution, Fisher Chemical Scientific Co., Fairlawn, NJ.

6.6 Primary Si standard, 1000 ppm. Certified Reference Solution, Fisher Chemical Scientific Co., Fairlawn, NJ.

6.7 Primary Mn standard, 1000 ppm. Certified Reference Solution, Fisher Chemical Scientific Co., Fairlawn, NJ.

6.8 Primary P standard, 1000 ppm. Certified Reference Solution, Fisher Chemical Scientific Co., Fairlawn, NJ.

6.9 Dodecylbenzenesulfonic acid (DDBSA), Tech 97%, 0.1 *M*. Dissolve 32.2 g DDBSA in 1-L DDI water.

6.10 DDBSA solution. Dilution solution for acid oxalate extracts. Add 40.0 mL of 0.1 *M* DDBSA and make to 2-L volume with DDI water (0.002 *M* DDBSA solution).

6.11 High calibration standard. Mix 60 mL of each primary standard (Si, Fe, and Al) with 10 mL of primary Mn standard and 20 mL of primary P standard in 1 L volumetric flask. Add 50 mL of 0.4 *M* acid oxalate solution and 16.0 mL of 0.1 *M* DDBSA and make to 1-L volume with DDI water. The elements are added in the order (Si, Fe, Al, Mn, P) to avoid element precipitation. Resulting solution contains 60 ppm each of Si, Fe, and Al, 10 ppm Mn, and 20 ppm P. Store in a polypropylene bottle.

6.12 Medium calibration standard. Mix 30 mL of each primary standard (Si, Fe, and Al) with 5 mL of primary Mn standard and 10 mL of primary P standard in 1 L volumetric flask. Add 50 mL of 0.4 *M* acid oxalate solution and 16.0 mL of 0.1 *M* DDBSA and make to 1-L volume with DDI water. Resulting solution contains 30 ppm each of Si, Fe, and Al, 5 ppm Mn, and 10 ppm P. Store in a polypropylene bottle.

6.13 Low calibration standard. Mix 10 mL of each primary standard (Si, Fe, and Al) with 2 mL of primary Mn standard, and 3 mL primary P standard in 1 L volumetric flask. Add 30 mL of 0.4 *M* acid oxalate solution and 16.0 mL of 0.1 *M* DDBSA and make to 1-L volume with DDI water. Resulting solution contains 10 ppm each of Si, Fe, and Al, 2 ppm Mn, and 3 ppm P. Store in a polypropylene bottle.

6.14 Calibration reagent blank solution. Add 50 mL of 0.4 *M* acid oxalate solution and 16.0 mL of 0.1 *M* DDBSA and make to 1-L volume with DDI water.

6.15 Argon gas, purity 99.9%

7. Procedure

Extraction of Fe, Mn, Al, Si, and P

7.1 Prepare disposable sample tubes.

7.2 Weigh 0.500 g of <2-mm, air-dry soil and place in sample tube. Prepare 2 reagent blanks (no sample in tube) per set of 48 samples.

7.3 Place the sample tube on the upper disk of the extractor and connect a tared extraction syringe. Use 25.4-mm (1-in) length rubber tubing to insert the handle of the plunger in the slot of the stationary extractor disk.

7.4 Use a dispenser to add 15.00 mL of acid oxalate buffer to the sample tube. Make sure that the sample is thoroughly wetted. During the addition, wash

sides of the tube and wet the sample. Shaking, swirling, or stirring may be required to wet organic samples. Allow sample to stand for at least 30 min.

7.5 Set extractor for 30-min extraction rate and extract until the acid oxalate buffer solution is at a 0.5 to 1.0-cm height above sample. Turn off extractor.

7.6 Put reservoir tube on top of the sample tube.

7.7 Add 35 mL of acid oxalate buffer to the reservoir tube.

7.8 Cover the extractor with a black plastic bag to exclude light. Adjust the extraction rate for a 12-h extraction.

7.9 After the extraction, shut off the extractor and pull plunger of syringe down. Do not remove the plunger from syringe barrel. Carefully remove the syringe with extract leaving the rubber tubing on the extraction vessel.

7.10 Weigh each syringe containing acid oxalate extract to the nearest 0.01 g.

7.11 Mix extract in each syringe by manually shaking. Fill a disposable tube with extract solution. This solution is reserved for determinations of Fe, Mn, Al, Si, and P. If optical density is to be measured, fill a disposable cuvette with extract solution. Discard excess solution.

Determination of Optical Density of Extract

7.12 Place 4 mL of acid oxalate extract in disposable cuvette.

7.13 Place 4 mL of acid oxalate reagent blank in disposable cuvette.

7.14 On Varian spectrophotometer, select a 430-nm wavelength. Select normal slit width and height. Refer to the manufacturer's manual for operation of the spectrophotometer.

7.15 Use the acid oxalate extract reagent blank to set spectrophotometer.

7.16 Record optical density of acid oxalate extract to nearest 0.000.

Dilution of Sample Extracts and Standards

7.17 Dilute acid oxalate extracts (1:10) with 0.002 *M* DDBSA solution. Add 1 part acid oxalate sample extract with 10 parts dilution solution.

7.18 Set the digital settings of the Hamilton diluter for a 1:10 dilution. Calibration reagent blanks and calibration standards are not diluted.

7.19 Dispense the diluted solutions into test tubes which have been placed in the sample holder of the sample changer.

ICP Calibration

7.20 Use a multipoint calibration for ICP analysis of acid oxalate extracts. The ICP calibrates the blank first, low standard, medium standard, followed by

the high standard. Prepare a quality control (QC) standard with analyte concentration between the high and low calibration standards. The ICP reads the QC after the high standard. If the QC falls within the range set by operator, the instrument proceeds to analyze the unknowns. If the QC is outside the range, the instrument restandardizes. The QC is analyzed approximately every 12 samples.

ICP Set-up and Operation

7.21 Refer to the manufacturer's manual for operation of the ICP. The following parameters are only very general guidelines for instrument conditions for the various analytes.

Parameter	Value
Gas Flow	
Torch Gas	High Flow
Auxiliary Gas Flow	Medium 1.0 LPM
Nebulizer Pressure	41 psi
Power	
Approximate RF Power	1150
Peristaltic Pump	
Analysis Pump Rate	150 RPM
Flush Pump Rate	200 RPM
Relaxation Time	10 s
Pumping Tube Type	Silicone-Orange-3stop
Argon Flow Rate	2.0 LPM
Purged Optical Pathway Enclosure Purge	2.0 SLPM Air

Nebulizer pressure depends on the type of nebulizer that is being used, i.e., low flow nebulizer requires a higher nebulizer pressure whereas a higher flow nebulizer requires a lower nebulizer pressure. To check for correct nebulizer pressure, aspirate with 1000.0 ppm yttrium. Adjust pressure to correct yttrium bullet.

7.22 Analyte data are reported at the following wavelengths.

Analyte	Wavelength
	(nm)
Fe	259.940
Al	167.081
Si	251.611
Mn	257.610
P	178.28

7.23 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings. The instrument readings are usually programmed in ppm.

7.24 If sample exceeds calibration standard, dilute the sample (1:5) with 0.4 *M* acid oxalate solution (matrix) and then dilute (1:10) with the DDBSA solution.

8. Calculations

8.1 Calculations (Fe, Al, Si)

Analyte (%) = [ICP x (Syr_{fin} − Syr_{init}) x D.R. x AD/OD] / [Sample Weight (g) x 10,000 x Density]

where:

ICP = ICP analyte concentration (ppm)

Syr_{fin} = Weight of syringe + extract (g)

Syr_{init} = Tare weight of syringe (g)

D.R. = Dilution ratio of samples over calibration range

Density = Density of acid oxalate solution (1.007)

AD/OD = Air-dry/oven-dry ratio (method 4B5)

8.2 Calculations (Mn, P)

Analyte (ppm) = [ICP x (Syr_{fin} − Syr_{init}) x D.R. x AD/OD] / [Sample Weight (g) x Density]

where:

ICP = ICP analyte concentration (ppm)

Syr_{fin} = Weight of syringe + extract (g)

Syr_{init} = Tare weight of syringe (g)

D.R. = Dilution ratio of samples over calibration range

Density = Density of acid oxalate solution (1.007)

AD/OD = Air-dry/oven-dry ratio (method 4B5)

9. Report

Report the percent acid oxalate extractable Fe, Al, and Si to the nearest 0.01%. Report the concentration of acid oxalate extractable Mn and P in ppm. Report the optical density of the acid oxalate extract to the nearest 0.001 unit.

10. Precision

Precision data are not available for this procedure.

11. References

Holmgren, G.G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Amer. J. 41:1207–1208.

Soil Survey Staff. 1999. Soil Taxonomy: A basic system of soil classification for making and interpreting soil surveys. 2nd ed. USDA–NRCS. Govt. Print. Office, Washington DC.

Wada, K. 1989. Allophane and imogolite. *In* J.B. Dixon and S.B. Weed (eds.) Minerals in soil environments. 2nd ed. Soil Sci. Soc. Amer. No. 1. p.1051–1087.

Manganese and Aluminum (6D and 6G)

KCl, Automatic Extractor (6D3 and 6G9)

Inductively Coupled Plasma Spectrometry, Thermo Jarrell Ash, ICAP 61E (6D3b and 6G9c)

1. Application

The Al extracted by 1 *N* KCl approximates exchangeable Al and is a measure of the “active” acidity present in soils with a 1:1 water pH <5.5. Above pH 5.5, precipitation of Al occurs during analysis. This method does not measure the acidity component of hydronium ions (H_3O^+). If Al is present in measurable amounts, the hydronium is a minor component of the active acidity. Because the 1 *N* KCl extractant is an unbuffered salt and usually affects the soil pH one unit or less, the extraction is determined at or near the soil pH. The KCl extractable Al is related to the immediate lime requirement and existing CEC of the soil. The “potential” acidity is better measured by the $BaCl_2$-TEA method (method 6H5a) (Thomas, 1982).

2. Summary of Method

A soil sample is leached with 1 *N* KCl using the mechanical vacuum extractor (Holmgren et al., 1977). The extract is weighed. The KCl extracted solution is diluted with distilled deionized water. The analytes are measured by inductively coupled plasma emission spectrophotometer (ICP). Data are automatically recorded by a microcomputer and printer. The Mn and Al are reported in mg kg^{-1} (ppm) and meq 100 g^{-1} oven-dry soil in methods 6D3b and 6G9c, respectively.

3. Interferences

There are four types of interferences (matrix, spectral, chemical, and ionization) in the ICP analyses of these cations. These interferences vary in importance, depending upon the particular analyte selected.

The soil:extractant ratio must remain constant. A soil:extractant ratio of 1:10 (w:v) for batch procedures is most commonly used. Using a leaching technique, a 1:20 (w:v) ratio gives comparable results. If the sample size is changed, the amount of extractable Al is changed. No other significant interferences have been identified for this procedure.

4. Safety

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Follow standard laboratory practices when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Follow the manufacturer's safety precautions when using the ICP.

5. Equipment

5.1 Electronic balance, ±1-mg sensitivity

5.2 Mechanical vacuum extractor, 24 place, Centurion International, Inc., Lincoln, NE

5.3 Mechanical vacuum extractor, Mavco Sampletek, 5300 N. 57th St., Lincoln, NE

5.4 Syringes, polypropylene, disposable, 60 mL, for extraction vessel, extractant reservoir and tared extraction syringe

5.5 Rubber tubing, 3.2 ID x 6.4 OD x 25.4 mm (⅛ ID x ¼ OD x 1 in), for connecting syringe barrels

5.6 Analytical filter pulp, ash-free, Schleicher and Schuell, No. 289

5.7 Plunger, modified. Remove rubber and cut plastic protrusion from plunger end.

5.8 Wash bottle, 20 mL, to dispense KCl

5.9 Polycons, Richards Mfg. Co.

5.10 Inductively coupled plasma spectrometer, ICAP 61E, Thermo Jarrell Ash Corp., Franklin, MA

5.11 RF generator, floor mounted power unit, Model 7/90, Thermo Jarrell Ash Corp., Franklin, MA

5.12 Computer, AT&T 386 Starstation, Model CPU-G72, and printer, NEC Pinwriter, P2200XE, Dot Matrix

5.13 ThermoSpec software, Thermo Jarrell Ash Corp., Franklin, MA

5.14 Line conditioner, Unity/I, Model UT8K, Best Power Technology, Inc., Necedah, WI

5.15 Single-stage regulator, high-purity, high-flow, argon, product no. E11-X-N145DHF, Air Products and Chemicals, Inc., Box 538, Allentown, PA

5.16 Autosampler, Thermo Jarrell Ash Corp., Franklin, MA

5.17 Nebulizers, Precision Glass, Type A, 2.3 mlpm, 35 psig, Precision Glass Co., 14775 Hinsdale Ave., Englewood, CO

5.18 Digital diluter/dispenser, Microlab 500, Hamilton Co., P.O. Box 10030, Reno, NV

5.19 Syringes, 10,000 and 1000 µL, 1001 DX and 1010-TEL LL gastight, Hamilton Co., P.O. Box 10030, Reno, NV

5.20 Test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer, Curtin Matheson Scientific, Inc., Houston, TX

5.21 Containers, polypropylene

6. Reagents

6.1 Distilled deionized (DDI) water

6.2 Potassium chloride solution (KCl), 1.0 *N*. Dissolve 1342 g of KCl reagent in 16 L DDI water. Allow solution to equilibrate to room temperature. Dilute to 18 L with DDI water. Use 1.0 *N* KCl for Al and Mn extraction.

6.3 Potassium chloride solution (KCl), 2.0 *N*. Dissolve 298.24 g of KCl reagent in 1.5 L DDI water. Allow solution to equilibrate to room temperature. Dilute to 2 L with DDI water. Use 2.0 *N* KCl for standards.

6.4 Primary Al standard, 1000 ppm (111 meq L^{-1}). Certified Reference Solution, Fisher Chemical Scientific Co., Fairlawn, NJ.

6.5 Primary Mn standard, 1000 ppm (250 meq L^{-1}). Certified Reference Solution, Fisher Chemical Scientific Co., Fairlawn, NJ.

6.6 High calibration Al and Mn standard, 10 meq L^{-1} and 8 ppm, respectively. Pipette 22.476 mL of primary Al standard into a 250-mL volumetric flask. Add 125.0 mL 2 *N* KCl solution to the flask and mix. Pipette 2.0 mL of primary Mn standard into flask and mix. Dilute to volume with DDI water.

6.7 Calibration reagent blank solution, 1.0 *N* KCl. Add 125 mL of 2.0 *N* KCl to a volumetric flask and make to 250-mL volume with DDI water. Store in polypropylene container.

6.8 Calibration Al and Mn check standard, 5 meq L^{-1} and 3.0 ppm, respectively. Pipette 11.24 mL of primary Al standard into a 250-mL volumetric flask. Add 125.0 mL 2 *N* KCl solution to the flask and mix. Pipette 0.75 mL of primary Mn standard into flask and mix. Dilute to volume with DDI water.

6.9 Dodecylbenzenesulfonic acid (DDBSA), tech 97%., 0.1 *M*. Dissolve 32.2 g DDBSA in 1-L DDI water.

6.10 DDBSA rinse solution. Dilute 40.0 mL 0.1 *M* DDBSA to 2-L volume with DDI water.

6.11 Argon gas, purity 99.9%

7. Procedure

Extraction of Al and Mn

7.1 Prepare extraction vessel by tightly compressing a 1-g ball of filter pulp into the bottom of a syringe barrel with a modified plunger.

7.2 Weigh exactly 2.50 g of <2-mm, air-dry soil and place in an extraction vessel. Prepare one quality control check sample per 48 samples.

7.3 Place the extraction vessel on the upper disk of the extractor and connect a tared extraction syringe. Use 25.4-mm (1-in) length rubber tubing to insert the handle of the plunger in the slot of the stationary extractor disk.

7.4 Use a squeeze bottle and fill extraction vessel to the 20-mL mark with 1.0 *N* KCl solution (≈10 mL). Make sure that the sample is thoroughly wetted. During the addition, wash sides of the tube and wet the sample. Shaking, swirling, or stirring may be required to wet organic samples. Allow sample to stand for at least 30 min.

7.5 Put reservoir tube on top of the extraction vessel. Set extractor for fast extraction rate and extract until the KCl solution is at a 0.5- to 1.0-cm height above sample. Turn off extractor.

7.6 Add 45 mL KCl solution to reservoir tube. Set extractor for 45-min extraction.

7.7 After the extraction, shut off extractor and pull plunger of syringe down. Do not remove the plunger from syringe barrel. Carefully remove the syringe with extract leaving the rubber tubing on the extraction vessel.

7.8 Weigh each syringe containing KCl extract to the nearest 0.01 g.

7.9 Mix extract in each syringe by manually shaking. Fill a polycon with extract solution and discard the excess. This solution is reserved for extractable Al and Mn analyses.

Dilution of Extracts and Standards

7.10 Set the digital settings at a 1:5 dilution for the KCl sample extracts, calibration reagent blanks, calibration standards, and calibration check standards as follows:

7.11 Dilute 1 part KCl sample extract with 4 parts of DDI water (1:5 dilution).

7.12 Dilute 1 part calibration reagent blank with 4 parts of DDI water (1:5 dilution).

7.13 Dilute 1 part calibration standard with 4 parts of DDI water (1:5 dilution).

7.14 Dilute 1 part calibration check standard with 4 parts of DDI water (1:5 dilution).

7.15 Dispense the diluted solutions into test tubes and place in the sample holder of the sample changer.

ICP Calibration

7.16 Use the calibration reagent blank (1.0 *N* KCl), high standard (10 meq L^{-1} Al and 8 ppm Mn), and the blank to calibrate the ICP.

7.17 Use the calibration check standard (5 meq L^{-1} Al and 3 ppm Mn) as a check sample. Perform a calibration check every 12 samples.

ICP Set-up and Operation

7.18 Refer to the manufacturer's manual for operation of the ICP. The following parameters are only very general guidelines for instrument conditions for the analytes.

Parameter	Value
Gas Flow	
Torch Gas	High Flow
Auxiliary Gas Flow	Medium 1.0 LPM
Nebulizer Pressure	32 PSI
RF Power	1150

Analyte	Wavelength	High/Low	Peak
	(nm)	*(Offset)*	*(Offset)*
Al	167.081	0/-21	-2
Mn	257.610	0/-1	0

7.19 Determine a set of 24 unknown samples for each successful calibration check.

7.20 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

7.21 If a sample exceeds the calibration standard, dilute the sample (1:5) as follows.

7.22 Analyze 4 quality control check samples for every 48 samples.

8. Calculations

8.1 The instrument readings are the analyte concentration (meq L^{-1} Al and ppm Mn) in undiluted extract. Use these values to calculate the analyte concentration on an oven-dry soil basis (meq 100 g^{-1}).

Analyte (meq 100 g^{-1}) = [ICP x ($Wt_{syr+ext}$ − Wt_{syr}) x D.R. x 100 x AD/OD] / [Sample Weight x 1.0412 x 1000]

where:

ICP = ICP analyte reading

$Wt_{syr+ext}$ = Weight of extraction syringe & extract (g)

Wt_{syr} = Weight of tared extraction syringe (g)

D.R. = Dilution ratio of samples over calibration range

1.0412 = Density of 1 *N* KCl @ 20 °C

1000 = g L^{-1}

100 = Conversion factor (100-g basis)

AD/OD = Air-dry/oven-dry ratio (method 4B5)

9. Report

Report KCl extractable Al and Mn in units of meq 100 g^{-1} of oven-dry soil to the nearest 0.01 meq 100 g^{-1}.

10. Precision

Precision data are not available for this procedure.

11. References

Holmgren, G.G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Amer. J. 41:1207–1208.

Thomas, G.W. 1982. Exchangeable cations. *In* A. Klute (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:159–165.

Manganese and Aluminum (6G)
KCl, Automatic Extractor (6G9)
Atomic Absorption
Thermo Jarrell Ash, Smith Hieftje 4000 (6D3c and 6G9d)

1. Application

The Al extracted by 1 *N* KCl approximates exchangeable Al and is a measure of the “active” acidity present in soils with a 1:1 water pH <5.5. Above pH 5.5,

precipitation of Al occurs during analysis. This method does not measure the acidity component of hydronium ions (H_3O^+). If Al is present in measurable amounts, the hydronium is a minor component of the active acidity. Because the 1 *N* KCl extractant is an unbuffered salt and usually affects the soil pH one unit or less, the extraction is determined at or near the soil pH. The KCl extractable Al is related to the immediate lime requirement and existing CEC of the soil. The "potential" acidity is better measured by the $BaCl_2$-TEA method (method 6H5a) (Thomas, 1982).

2. Summary of Method

A soil sample is leached with 1 *N* KCl using the mechanical vacuum extractor (Holmgren et al., 1977). The extract is weighed. The KCl extract is diluted with distilled deionized (DDI) water. The analytes are measured by an atomic absorption spectrophotometer. The data are automatically recorded by a microcomputer and printer. The Al and Mn are reported in meq 100 g^{-1} and mg kg^{-1} (ppm) oven-dry soil in method 6D3c and 6G9d.

3. Interferences

There are four types of interferences (matrix, spectral, chemical, and ionization) in the AA analyses of these cations. These interferences vary in importance, depending upon the particular analyte selected.

The soil:extractant ratio must remain constant. A soil:extractant ratio of 1:10 (w:v) for batch procedures is most commonly used. Using a leaching technique, a 1:20 (w:v) ratio gives comparable results. If the sample is changed, the amount of extractable Al is changed. No other significant interferences have been identified for this procedure.

4. Safety

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Restrict the use of concentrated HCl to a fume hood. Many metal salts are extremely toxic and may be fatal if ingested. Follow standard laboratory practices when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene gas is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the AA.

5. Equipment

5.1 Electronic balance, ±1-mg sensitivity

5.2 Mechanical vacuum extractor, 24 place, Centurion International, Inc., Lincoln, NE

5.3 Mechanical vacuum extractor, Mavco Sampletek, 5300 N. 57th St., Lincoln, NE

5.4 Syringes, polypropylene, disposable, 60 mL, for extraction vessel, extractant reservoir, and tared extraction syringe

5.5 Rubber tubing, 3.2 ID x 6.4 OD x 25.4 mm, (⅛ ID x ¼ OD x 1 in) for connecting syringe barrels

5.6 Analytical filter pulp, ash-free, Schleicher and Schuell, No. 289

5.7 Wash bottle, 20 mL, to dispense KCl

5.8 Polycons, Richards Mfg. Co.

5.9 Atomic absorption spectrophotometer (AA), Smith-Hieftje Model 4000, Thermo Jarrell Ash Corp., Franklin, MA

5.10 Autosampler, Model 150, Thermo Jarrell Ash Corp., Franklin, MA

5.11 ThermoSpec software, Version 3.01, Enable 4.0, DOS 5.0, Thermo Jarrell Ash Corp., Franklin, MA

5.12 Computer, CUi Advantage 486, Thermo Jarrell Ash Corp., Franklin, MA

5.13 Printer, NEC Pinwriter P3200

5.14 Single-stage regulator, acetylene service, part number E11-0-N511A, Air Products and Chemicals, Inc., Box 538, Allentown, PA

5.15 Digital diluter/dispenser, Microlab 500, Hamilton Co., P.O. Box 10030, Reno, NV

5.16 Syringes, 10,000 and 1000 µL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV

5.17 Test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer, Curtin Matheson Scientific, Inc., Houston, TX

5.18 Containers, polypropylene

6. Reagents

6.1 Distilled deionized (DDI) water

6.2 Potassium chloride solution (KCl), 1.0 *N*. Dissolve 1342 g of KCl reagent in 16 L DDI water. Allow solution to equilibrate to room temperature. Dilute to 18 L with DDI water. Use 1.0 *N* KCl solution for Al extraction.

6.3 Potassium chloride solution (KCl), 2.0 *N*. Dissolve 298.24 g of KCl reagent in 1.5 L DDI water. Allow solution to equilibrate to room temperature. Dilute to 2 L with DDI water. Use 2.0 *N* KCl solution for standards.

6.4 Primary Al standard, 1000 ppm. Certified Reference Solution, Fisher Chemical Scientific Co., Fairlawn, NJ.

6.5 Primary Mn standard, 1000 ppm. Certified Reference Solution, Fisher Chemical Scientific Co., Fairlawn, NJ.

6.6 High calibration Al (4 meq L^{-1}) and Mn (3 ppm) standard. Mix 9 mL of primary Al standard with 125 mL 2 *N* KCl. Add 0.75 mL of primary Mn standard and make to 250-mL volume with DDI water.

6.7 Low calibration Al (0.2 meq L^{-1}) and Mn (0.2 ppm) standard. Mix 1.8 mL of primary Al standard with 125 mL 2 *N* KCl. Add 0.05 mL of primary Mn standard and make to 250-mL volume with DDI water.

6.8 Calibration Al (2 meq L^{-1}) and Mn (1.5 ppm) check standard. Mix 4.5 mL of primary Al standard with 125 mL 2 *N* KCl. Add 0.375 mL of primary Mn standard and make to 250-mL volume with DDI water.

6.9 Calibration reagent blank solution, 1.0 *N* KCl. Add 125 mL of 2.0 *N* KCl to a volumetric flask and make to 250-mL volume with DDI water.

6.10 Nitrous oxide gas, compressed

6.11 Acetylene gas, compressed, purity 99.6%

6.12 Compressed air with water and oil traps

7. Procedure

Extraction of Al

7.1 Prepare extraction vessel by tightly compressing a 1-g ball of filter pulp into the bottom of a syringe barrel with a modified plunger.

7.2 Weigh exactly 2.50 g of <2-mm, air-dry soil and place in an extraction vessel. Prepare one quality control check sample per 48 samples.

7.3 Place the extraction vessel on the upper disk of the extractor and connect a tared extraction syringe. Use 25.4-mm (1-in) length rubber tubing to insert the handle of the plunger in the slot of the stationary extractor disk.

7.4 Use a squeeze bottle and fill extraction vessel to the 20-mL mark with 1.0 *N* KCl solution (≈10 mL). Make sure that the sample is thoroughly wetted. During the addition, wash sides of the tube and wet the sample. Shaking, swirling, or stirring may be required to wet organic samples. Allow sample to stand for at least 30 min.

7.5 Put reservoir tube on top of the extraction vessel. Set extractor for fast extraction rate and extract until the KCl solution is at a 0.5- to 1.0-cm height above sample. Turn off extractor.

7.6 Add 45 mL KCl solution to reservoir tube. Set extractor for 45-min extraction.

7.7 After the extraction, shut off extractor and pull plunger of syringe down. Do not remove the plunger from syringe barrel. Carefully remove the syringe with extract leaving the rubber tubing on the extraction vessel.

7.8 Weigh each syringe containing KCl extract to the nearest 0.01 g.

7.9 Mix extract in each syringe by manually shaking. Fill a polycon with extract solution and discard the excess. This solution is reserved for extractable Al and Mn analyses.

Dilution of Sample Extracts and Standards

7.10 No ionization suppressant is required as the K in the extractant is present in sufficient quantity. Set the digital settings at a 1:2 dilution for the KCl sample extracts, calibration reagent blanks, calibration standards, and calibration check standards as follows:

7.11 Dilute 1 part KCl sample extract with 1 part of DDI water (1:2 dilution).

7.12 Dilute 1 part calibration reagent blank with 1 part of DDI water (1:2 dilution).

7.13 Dilute 1 part calibration standard with 1 part of DDI water (1:2 dilution).

7.14 Dilute 1 part calibration check standard with 1 part of DDI water (1:2 dilution).

7.15 Dispense the diluted solutions into test tubes and place in the sample holder of the sample changer.

AA Calibration

7.16 Use the calibration reagent blank (1.0 *N* KCl), high standard (4 meq L^{-1} Al and 3 ppm Mn), and the low standard (2 meq L^{-1} Al and 1.5 ppm Mn) to calibrate the AA.

7.17 Use the calibration check standard (2 meq L^{-1} Al and 1.5 ppm Mn) as a check sample. Perform a calibration check every 12 samples.

AA Set-up and Operation

7.18 Refer to the manufacturer's manual for operation of the AA. The following parameters are only very general guidelines for instrument conditions for the analyte.

Element	Wave-length	Burner Head & Angle	Fuel/Oxidant
	(nm)		
Al	309.3	5-cm, parallel	20 C_2H_2/10 N_2O
Mn	280.1	5-cm, parallel	4 C_2H_2/16 Air

Typical read delay is 6 s, and integration by peak area is 8 s.

7.19 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

7.20 If a sample exceeds the calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record dilution. Remember to keep the matrix the same after dilution by diluting with DDI water (1:2 dilution).

7.21 Analyze one quality control check sample for every 48 samples.

8. Calculations

8.1 The instrument readings are the analyte concentration (meq L^{-1} Al) in undiluted extract. Use these values to calculate the analyte concentration on an oven-dry soil basis (meq 100 g^{-1}).

$$\text{Al (meq 100 g}^{-1}) = [\text{AAAl} \times (\text{Wt}_{\text{syr+ext}} - \text{Wt}_{\text{syr}}) \times \text{D.R.} \times 100 \times \text{AD/OD}] / [\text{Sample Weight (g)} \times 1.0412 \times 1000]$$

where:

AAAl = AA Al reading (meq L^{-1})

$Wt_{syr+ext}$ = Weight of extraction syringe and extract (g)

Wt_{syr} = Weight of tared extraction syringe (g)

D.R. = Dilution ratio for samples over calibration range

1.0412 = Density of 1 *N* KCl @ 20 °C

1000 = g L^{-1}

100 = Conversion factor (100-g basis)

AD/OD = Air-dry/oven-dry ratio (method 4B5)

9. Report

Report KCl extractable Al in units of meq 100 g^{-1} of oven-dry soil to the nearest 0.1 meq 100 g^{-1}.

10. Precision

Precision data are not available for this procedure. A quality control check sample is run with every batch of 48 samples.

11. References

Holmgren, G.G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Amer. J. 41:1207–1208.

Thomas, G.W. 1982. Exchangeable cations. *In* A. Klute (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:159–165.

Chloride, Sulfate, Nitrate, Fluoride, and Nitrite (6K, 6L, 6M, 6U, and 6W)

Saturation Extract (6K1, 6L1, 6M1, 6U1, and 6W1)

Chromatograph, Anion Suppressor

Dionex 2110i Ion Chromatograph (6K1d, 6L1d, 6M1d, 6U1b, and 6W1b)

1. Application

The soluble anions that are commonly determined in saline and alkali soils are carbonate, bicarbonate, sulfate, chloride, nitrate, nitrite, fluoride, phosphate, silicate, and borate (Khym, 1974; U.S. Salinity Laboratory Staff, 1954). Carbonate and bicarbonate are determined by titration. Phosphate, silicate, and borate usually are not determined because they are found only occasionally in measurable amounts in soils. Chloride, sulfate, nitrate, fluoride, and nitrite are measured in solution by chromatography. In saline and alkali soils, carbonate, bicarbonate, sulfate, and chloride are the anions that are found in the greatest abundance. In general, soluble sulfate is usually more abundant than soluble chloride.

2. Summary of Method

The saturation extract 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. A chart recording is made of the chromatograph. Standard anions are used to calibrate the system. A calibration curve is determined, and the anion concentrations are calculated. A computer program automates these actions. The saturated extract anions, Cl^-, SO_4^{2-}, NO_3^-, F^-, and NO_2^-, are reported in meq L^{-1} in methods 6K1d, 6L1d, 6M1d, 6U1b, and 6W1b, respectively.

3. Interferences

Some saturation extracts contain suspended solids. Filtering after dilution removes the particles. Saturation extracts of acid soils that contain Fe and/or Al may precipitate and clog the separator column. Saturation extracts of very high pH may contain organic material which may clog or poison the column. Low molecular weight organic anions will co-elute with inorganic anions from the column.

4. Safety

Wear protective clothing and safety glasses. When preparing reagents, exercise special care. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts. Follow the manufacturer's safety precautions when using the chromatograph.

5. Equipment

5.1 Ion chromatograph, Series 2110i, dual-channel system

5.2 Analytical column, AS4A 4mm P/N 37041, Dionex Corp., 1228 Titan Way, Sunnyvale, CA

5.3 Guard column, AG4A 4mm P/N 37042, Dionex Corp., 1228 Titan Way, Sunnyvale, CA

5.4 Analytical pumps, Dionex Corp., 1228 Titan Way, Sunnyvale, CA

5.5 Automated sampler, Dionex Corp., 1228 Titan Way, Sunnyvale, CA

5.6 Conductivity detectors, Dionex Corp., 1228 Titan Way, Sunnyvale, CA

5.7 Anion self-regenerating suppressor (ASRS-1) with controller (SRC-1), Dionex Corp., 1228 Titan Way, Sunnyvale, CA

5.8 Computer interfaces, Dionex Corp., 1228 Titan Way, Sunnyvale, CA

5.9 Computer software, A1-450 Chromatography Software Program Release 3.32, Microsoft Windows Operating Environment; Dionex Corp., 1228 Titan Way, Sunnyvale, CA

5.10 Computer, DFI

5.11 Printer, Epson, Fx-850

5.12 Poly-vials, 5 mL, P/N 038008, Dionex Corp., 1228 Titan Way, Sunnyvale, CA

5.13 Poly-vials, filter caps, 5 mL, P/N 038009, Dionex Corp., 1228 Titan Way, Sunnyvale, CA

5.14 Digital diluter/dispenser, Microlab 500, Hamilton C., P.O. Box 10030, Reno, NV

5.15 Syringes, gas tight, Hamilton 1001 DX and 1010-TEF LL, Hamilton Co., P.O. Box 10030, Reno, NV

5.16 Disposable 0.2-µm pore size, 25-mm filter assembly, Gelman Sciences, Inc., 674 South Wagner Road, Ann Arbor, MI 48106. Use for saturation extracts and standards.

5.17 Disposable 0.2-µm pore size, Ultipor N_{66} DFA3001NAEY, Pall Trinity Micro Corp., Cortland, NY. Use for filtering distilled deionized (DDI) water.

6. Reagents

6.1 Distilled deionized (DDI) filtered water

6.2 Sulfuric acid (H_2SO_4), concentrated, reagent

6.3 Toluene

6.4 Isopropanol to de-gas column

6.5 Stock $NaHCO_3$ solution, 0.480 *M*. Mix 40.34 g of dried $NaHCO_3$ with filtered DDI water and dilute to 1-L volume.

6.6 Stock Na_2CO_3 solution, 0.5040 *M*. Mix 53.42 g of dried Na_2CO_3 with filtered DDI water and dilute to 1-L volume.

6.7 Working eluent solution. Mix 100 mL of 0.5040 *M* $NaHCO_3$ and 100 mL of 0.4800 *M* Na_2CO_3 with filtered DDI water and dilute to 20-L volume. Add 8 drops of toluene to retard microbial growth.

6.8 Primary SO_4^{2-} standard, 0.5 *M* (1.0 *N*). Mix 17.7560 g of Na_2SO_4 with filtered DDI water and dilute to 250-mL volume.

6.9 Primary Cl^- standard, 1.0 *M* (1.0 *N*). Add 18.6392 g of KCl with filtered DDI water and dilute to 250-mL volume.

6.10 Primary F^- standard, 0.125 *M* (0.125 *N*). Add 1.3122 g of NaF with filtered DDI water and dilute to 250-mL volume.

6.11 Primary NO_3^- standard, 1.0 *M* (1.0 *N*). Add 25.2770 g of KNO_3 with filtered DDI water and dilute to 250-mL volume.

6.12 Primary mixed standard. Prepare 1 primary mixed standard by taking aliquots of each of the proceeding primary standards and diluting the combined aliquots to a 1-L volume with working eluent as follows:

Primary standards	Aliquot	Final volume w/ eluent	Concentration
	(mL)	*(mL)*	*(meq L^{-1})*
Na_2SO_4	50	1000	50
KCl	10	1000	10
NaF	100	1000	12.5
KNO_3	30	1000	30

Add eight drops of toluene to primary mixed standard to retard microbial growth and store in a glass container.

6.13 Mixed calibration standards. Prepare 4 mixed calibration standards (0.5, 1.0, 3.0, and 7.0 readings) by taking aliquots of primary mixed standard and diluting each aliquot to 100-mL volume with working eluent as follows:

Primary mixed standards	Final volume w/ eluent	Concentration			
		SO_4^{2-}	Cl^-	F^-	NO_3^-
(mL)	*(mL)*	*(meq L^{-1})*			
0.5	100	0.25	0.05	0.0625	0.15
1.0	100	0.50	0.10	0.125	0.30
3.0	100	1.5	0.30	0.375	0.90
7.0	100	3.5	0.70	0.875	2.1

6.14 $NaNO_2$, Baker reagent grade, 99.5% purity

6.15 Primary NO_2^- standard, 1 *N* (1000 meq L^{-1}). Mix 69.3568 g of reagent grade $NaNO_2$ with filtered DDI water and dilute to 1-L volume. Take 5 mL aliquot of primary NO_2^- standard and dilute with 500 mL of filtered DDI water (10 meq L^{-1}). Add eight drops of toluene to primary NO_2^- standard to retard microbial growth and store in a glass container.

6.16 NO_2^- calibration standards. Prepare 4 NO_2^- calibration standards (0.5, 1.0, 3.0, and 7.0 readings) by taking aliquots of primary NO_2^- standard (10 meq L^{-1}) and diluting each aliquot to 100-mL volume with working eluent as follows:

Primary standard meq L^{-1}	Final volume w/ eluent	NO_2- Concentration
(mL)	*(mL)*	*(meq L^{-1})*
0.5	100	0.5
1.0	100	1.0
3.0	100	3.0

7. Procedure

Dilution of Extracts

7.1 To estimate the total soluble anion concentration (meq L^{-1}), multiply the EC_s (method 8A3a) by 10. Subtract the CO_3^{2-} and HCO_3^- concentrations (methods 6I1b and 6J1b) from the total anion concentration. The remainder is the ≈ concentration (meq L^{-1}) of anions to be separated by ion chromatography.

$$\text{Anion concentration (meq } L^{-1}) = EC_s \times 10 - (HCO_3^- + CO_3^{2-})$$

Refer to Table 1 for dilution of saturation extract with the working eluent.

7.3 Place the diluted samples in the Poly-vials and cap with filter caps.

7.4 Place the mixed calibration standards in the Poly-vials.

Set-up and Operation of Ion Chromatograph (IC)

7.5 Because any number of factors may cause a change in IC operating conditions, only a general set-up of the Dionex 2110i ion chromatograph is presented. Individual analysts may modify some or all of the operating conditions to achieve satisfactory results. Typical operation parameters are as follows:

Parameter	Range
Conductivity cell range	3 µS cm^{-1} full scale to 100 µS cm^{-1}
Auto offset	"On"
Analytical pump flow rate	2.0 to 2.5 mL min^{-1}
Low pressure limit	100 psi
High pressure limit	1200 psi
Regenerant flow rate	3 to 4 mL min^{-1}
Injector loop	0.50 mL
Air pressure	3 to 8 psi

7.6 Load the sample holder cassettes with the capped samples, standards, and check samples.

7.7 Refer to the manufacturer's manual for the operation of chromatograph.

8. Calculations

Calibration Calculations

8.1 Use the peak height of each anion standard to either construct a calibrated curve to plot anion concentration or use a least squares analysis to calculate anion concentration. The analytes are reported in meq L^{-1}.

8.2 *Calibration Curve*: Plot the peak height against the meq L^{-1} of each anion standard on graph paper. Construct the calibration curve by finding the "best" line that fits the plotted standards.

8.3 *Linear Squares Analysis*: Use a least squares criterion, i.e. best moving average. Refer to a statistical analysis book for additional information on least squares analysis. An example for the anion Cl^- is as follows:

Cl^- concentration (meq L^{-1}) = Y = 0.1 1.5 4.0

Peak height = X = 8.43 170.0 441.5

Number of standards = n = 3

$\sum Y_i = 5.6$ $\sum X_i = 619.93$

$\sum Y_i/n = Y = 1.866$ $\sum X_i/n = X = 206.6433$
$\sum X_i Y_i = 2021.843$ $\sum X_i^2 = 223893.31$
$\sum X_i \sum Y_i = 3471.608$

$$b = \frac{\sum X_i Y_i - \sum X_i \sum Y_i/n}{\sum X_i^2 - (\sum X_i)^2/n} = \frac{2021.843 - 1157.2027}{223893.31 - 128104.4} = 0.0090265$$

b = slope of the line, i.e., the amount that Y changes when X changes by 1 unit.

The equation is as follows:

$Y = Y + b\,(X - X)$

$Y = 1.866 + 0.0090265\,(X) - 1.8653$

Analyte Calculation

8.4 *Calibration Curve*: Read the analyte concentration (meq L^{-1}) directly from the calibration curve.

Table 1.—Dilution factor for saturated paste soil extracts based on EC readings.

EC_s	Dilution Factor
(mmhos cm^{-1})	
0.00 to 0.55	4
0.56 to 0.65	5
0.66 to 0.75	6
0.76 to 0.85	7
0.86 to 0.95	8
0.96 to 1.05	9
1.06 to 1.20	10
1.21 to 1.40	15
1.41 to 1.50	25
1.51 to 1.60	30
1.61 to 1.80	40
1.81 to 2.00	50
2.01 to 2.30	60
2.31 to 2.60	70
2.61 to 3.10	80
3.11 to 3.55	90
3.56 to 4.05	100
4.06 to 4.60	120
4.61 to 5.20	140
5.21 to 5.85	150
5.86 to 6.55	160
6.56 to 7.30	180
7.31 to 8.00	200
8.01 to 9.00	225
9.01 to 10.00	240

EC_s	Dilution Factor
(mmhos cm^{-1})	
10.01 to 11.50	270
11.51 to 13.00	280
13.01 to 14.50	300
14.51 to 16.00	320
16.01 to 17.00	360
17.01 to 18.00	400
18.01 to 20.00	450
20.01 to 21.00	480
21.01 to 23.00	500
23.01 to 24.00	540
24.01 to 25.00	560
25.01 to 27.00	600
27.01 to 28.00	640
28.01 to 30.00	680
30.01 to 32.00	700
32.01 to 33.00	720
33.01 to 36.00	800
36.01 to 40.00	900
40.01 to 44.00	1,000

8.5 *Linear Regression*: Put the peak height in the preceding equation and solve for analyte concentration (meq L^{-1}). Thus, if sample extract has 204 peak height, the preceding equation is as follows:

$$Y = 1.866 + 0.0090265\ (204) - 1.8653 = 1.84 \text{ meq } L^{-1}$$

8.6 Repeat the calibration set and analyte calculation for each anion.

8.7 The chromatograph software automatically calculates the analyte concentrations and prints a report of the results.

9. Report

Report the saturation extract anions in units of meq L^{-1} to the nearest 0.1 meq L^{-1}.

10. Precision

Precision data are not available for this procedure.

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.) U.S. Dept. of Agric. Handb. 60. U.S. Govt. Print. Office, Washington, DC.

Calcium, Magnesium, Sodium, and Potassium (6N, 6O, 6P, and 6Q)
Saturation Extraction (6N1, 6O1, 6P1, and 6Q1)
Atomic Absorption
Perkin-Elmer AA 5000 (6N1b, 6O1b, 6P1b, and 6Q1b)

1. Application

The commonly determined soluble cations are Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}. In soils with a low saturation pH, measurable amounts of Fe and Al may be present. Determination of soluble cations is used to obtain the relations between total cation concentration and other properties of saline solutions such as electrical conductivity and osmotic pressure (U.S. Salinity Laboratory Staff, 1954). The relative concentrations of the various cations in the soil-water extracts also provide information on the composition of the exchangeable cations in the soil. Complete analyses of the soluble ions provide a means to determine total salt content of the soils and salt content at field-moisture conditions.

2. Summary of Method

The saturation extract from method 8A3a is diluted with an ionization suppressant ($LaCl_3$). The analytes are measured by an atomic absorption spectrophotometer (AA). The data are automatically recorded by a microcomputer and printer. The saturation extracted cations, Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}, are reported in meq L^{-1} in methods 6N1b, 6O1b, 6P1b, and 6Q1b, respectively.

3. Interferences

There are four types of interferences (matrix, spectral, chemical, and ionization) in the analysis of these cations. These interferences vary in importance, depending upon the particular analyte selected.

4. Safety

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Restrict the use of concentrated HCl to a fume hood. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts.

Follow standard laboratory procedures when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the AA.

5. Equipment

5.1 Electronic balance, ±1-mg sensitivity

5.2 Filter paper, pre-pleated, 185-mm diameter, Schleicher and Schuell

5.3 Atomic absorption spectrophotometer (AA), model 5000, Perkin-Elmer Corp., Norwalk, CT

5.4 Automatic burner control, model 5000, Perkin-Elmer Corp., Norwalk, CT

5.5 Autosampler, AS-50, Perkin-Elmer Corp., Norwalk, CT

5.6 Dot matrix printer, P-132, Interdigital Data Systems, Inc.

5.7 Single-stage regulator, acetylene service, part number E11-0-N511A, Air Products and Chemicals, Inc., Box 538, Allentown, PA

5.8 Digital diluter/dispenser, Microlab 500, Hamilton Co., P.O. Box 10030, Reno, NV

5.9 Syringes, 10,000 and 1000 µL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV

5.10 Test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer, Curtin Matheson Scientific, Inc., Houston, TX

5.11 Containers, polypropylene

6. Reagents

6.1 Distilled deionized (DDI) water

6.2 Hydrochloric acid (HCl), concentrated 12 *N*

6.3 HCl, 1:1 HCl:DDI, 6 *N*. Carefully mix 1 part of concentrated HCl to 1 part DDI water.

6.4 HCl, 1% wt. Carefully dilute 25 mL of concentrated HCl to 1 L with DDI water.

6.5 NH_4OH, reagent grade, sp gr 0.90

6.6 Glacial acetic acid, 99.5%

6.7 Primary stock mixed standards solution (PSMSS). Dissolve 0.8759 g of oven-dry reagent grade calcium carbonate ($CaCO_3$) in a minimum of volume of 1:1 HCl:DDI. Add 0.2127 g of clean Mg ribbon dissolved in 1:1 HCl. Add 1.0956 g of dry reagent grade sodium chloride (NaCl) and 0.1864

g of dry reagent grade KCl. Transfer to a 250-mL volumetric and bring to volume with 1% HCl solution. Resulting solution contains 70 meq L^{-1} (1403 ppm) Ca; 70 meq L^{-1} (851 ppm) Mg; 75 meq L^{-1} (1724 ppm) Na; 10 meq L^{-1} (391 ppm) K. Store in a polypropylene container.

6.8 NH_4OAc solution, 1.0 *N*, pH 7.0, reagent blank. Mix 57 mL of glacial acetic acid in 600 mL DDI water. While stirring, carefully add 68 mL concentrated of NH_4OH. Cool and adjust pH to 7.0 using NH_4OH or acetic acid. Dilute to 1 L with DDI water. The NH_4OAc solution is used for extraction of cations (method 5A8c).

6.9 Working stock mixed standards solution (WSMSS). Dilute 20 mL of the PSMSS with 80 mL DDI water (1:5). Resulting solution contains 14 meq L^{-1} (281 ppm) Ca; 14 meq L^{-1} (170 ppm) Mg; 15 meq L^{-1} (345 ppm) Na; 2 meq L^{-1} (78 ppm) K. Store in a polypropylene container.

6.10 Stock lanthanum ionization suppressant solution, 65,000 ppm. Wet 152.4 g of lanthanum oxide (La_2O_3) with 100 mL DDI water. Slowly and cautiously add 500 mL of 6 *N* HCl to dissolve the La_2O_3. Cooling the solution is necessary. Dilute to 2 L with DDI water. Filter solution. Store in polypropylene container.

6.11 Lanthanum ionization suppressant solution, 6500 ppm. Dilute 200 mL of stock lanthanum ionization suppressant solution with 1800 mL of DDI water (1:10). Store in polypropylene container.

6.12 Dilute calibration mixed standards solution (DCMSS). Dilute 1 part of the WSMSS with 39 parts of the lanthanum solution (1:40). Resulting solution contains 0.35 meq L^{-1} (7 ppm) Ca; 0.35 meq L^{-1} (4 ppm) Mg; 0.375 meq L^{-1} (9 ppm) Na; 0.05 meq L^{-1} (2 ppm) K. Store in polypropylene container.

6.13 Dilute calibration reagent blank solution (DCRBS). Dilute 1 part of DDI water with 39 parts of the lanthanum solution (1:40). Store in polypropylene container.

6.14 Compressed air with water and oil traps

6.15 Acetylene gas, purity 99.6%

7. Procedure

Dilution of Sample Extracts and Standards

7.1 The 10-mL syringe is for diluent (lanthanum ionization suppressant solution). The 1-mL syringe is for saturation sample extracts (method 8A3a), calibration reagent blanks, and calibration standards. Set the digital diluter at 1:40 dilution for saturation sample extracts, reagent blanks, and calibration standards as follows:

7.2 Dilute 1 part saturation sample extract with 39 parts of lanthanum ionization suppressant solution (1:40 dilution).

7.3 Dilute 1 part WSMSS with 39 parts of lanthanum ionization suppressant solution (1:40 dilution). This dilution is the DCMSS. Refer to reagents section.

7.4 Dilute 1 part DDI water with 39 parts of lanthanum ionization suppressant solution (1:40 dilution). This dilution is the DCRBS. Refer to reagents section.

7.5 Dispense the diluted solutions into test tubes which have been placed in the sample holders of the sample changer.

AA Calibration

7.6 Use the DCRBS and the DCMSS to calibrate the AA. The AA program requires a blank and a standard, in that order, to establish a single point calibration curve for element determination. Perform one calibration, i.e., blank plus standard, for every 12 samples.

AA Set-up and Operation

7.7 Refer to the manufacturer's manual for operation of the AA. The following are only very general guidelines for instrument conditions for the various analytes.

Analyte	Conc. meq/L	Burner & Angle	Wave-length	Slit	Fuel/Oxidant C_2H_2/Air
Ca	14.00	50 cm, @ 0°	422.7	0.7	10/25
Mg	14.00	50 cm, @ 30°	285.2	0.7	10/25
K	2.00	50 cm, @ 0°	766.5	1.4	10/25
Na	15.00	50 cm, @ 30°	589.0	0.4	10/25

7.8 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

7.9 If sample exceeds calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record dilution. Remember to keep the matrix the same after dilution by diluting with the lanthanum ionization suppressant solution (1:40 dilution).

7.10 Analyze one quality control check sample for every 48 samples.

7.11 The instrument readings are usually programmed in meq L^{-1}. Record analyte readings to 0.01 meq L^{-1}.

8. Calculations

8.1 The instrument readings are the analyte concentration (meq L^{-1} cation) in undiluted extract. Use these values and dilution ratio (if any) and calculate the analyte concentration in meq L^{-1} cation.

Analyte Concentration in Soil (meq L^{-1}) = Analyte AA reading (meq L^{-1}) x Dilution ratio (if any)

9. Report

Report the saturation extraction cations of Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} in units of meq L^{-1} to the nearest 0.1 meq L^{-1}.

10. Precision

Precision data are not available for this procedure.

11. References

U.S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. L.A. Richards (ed.) U.S. Dept. of Agric. Handb. 60. U.S. Govt. Print. Office, Washington, DC.

Calcium, Magnesium, Sodium, and Potassium (6N, 6O, 6P, and 6Q)
Saturation Extraction (6N1, 6O1, 6P1, and 6Q1)
Atomic Absorption

Thermo Jarrell Ash, Smith-Hieftje AA 4000 (6N1c, 6O1c, 6P1c, and 6Q1c)

1. Application

The commonly determined soluble cations are Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}. In soils with a low saturation pH, measurable amounts of Fe and Al may be present. Determination of soluble cations is used to obtain the relations between total cation concentration and other properties of saline solutions such as electrical conductivity and osmotic pressure (U.S. Salinity Laboratory Staff, 1954). The relative concentrations of the various cations in the soil-water extracts also provide information on the composition of the exchangeable cations in the soil. Complete analyses of the soluble ions provide a means to determine total salt content of the soils and salt content at field-moisture conditions.

2. Summary of Method

The saturation extract from method 8A3a is diluted with an ionization suppressant ($LaCl_3$). The analytes are measured by an atomic absorption spectrophotometer (AA). The data are automatically recorded by a microcomputer and printer. The saturation extracted cations, Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}, are reported in meq L^{-1} in methods 6N1c, 6O1c, 6P1c, and 6Q1c, respectively.

3. Interferences

There are four types of interferences (matrix, spectral, chemical, and ionization) in the analysis of these cations. These interferences vary in importance, depending upon the particular analyte selected.

4. Safety

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Restrict the use of concentrated HCl to a fume hood. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts.

Follow standard laboratory procedures when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the AA.

5. Equipment

5.1 Electronic balance, ±1-mg sensitivity

5.2 Filter paper, pre-pleated, 185-mm diameter, Schleicher and Schuell

5.3 Atomic absorption spectrophotometer (AA), Smith-Hieftje Model 4000, Thermo Jarrell Ash Corp., Franklin, MA

5.4 Autosampler, Model 150, Thermo Jarrell Ash Corp., Franklin, MA

5.5 ThermoSpec software, Version 3.01, Enable 4.0, DOS 5.0, Thermo Jarrell Ash Corp., Franklin, MA

5.6 Computer, CUi Advantage 486, Thermo Jarrell Ash Corp., Franklin, MA

5.7 Printer, NEC Pinwriter P3200

5.8 Single-stage regulator, acetylene service, part number E11-0-N511A, Air Products and Chemicals, Inc., Box 538, Allentown, PA

5.9 Digital diluter/dispenser, Microlab 500, Hamilton Co., P.O. Box 10030, Reno, NV

5.10 Syringes, 10,000 and 1000 µL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV

5.11 Test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer, Curtin Matheson Scientific, Inc., Houston, TX

5.12 Containers, polypropylene

6. Reagents

6.1 Distilled deionized (DDI) water

6.2 Hydrochloric acid (HCl), concentrated 12 *N*

6.3 HCl, 1:1 HCl:DDI, 6 *N*. Carefully mix 1 part of concentrated HCl to 1 part DDI water.

6.4 HCl, 1% wt. Carefully dilute 25 mL of concentrated HCl to 1 L with DDI water.

6.5 NH_4OH, reagent grade, sp gr 0.90

6.6 Glacial acetic acid, 99.5%

6.7 Primary stock mixed standards solution (PSMSS). Dissolve 0.8759 g of oven-dry reagent grade calcium carbonate ($CaCO_3$) in a minimum volume of 1:1 HCl:DDI. Add 0.2127 g of clean Mg ribbon dissolved in 1:1 HCl. Add 1.0956 g of dry reagent grade sodium chloride (NaCl) and 0.1864 g of dry reagent grade KCl. Transfer to a 250-mL volumetric and bring to volume with 1% HCl solution. Resulting solution contains 70 meq L^{-1} (1403 ppm) Ca; 70 meq L^{-1} (851 ppm) Mg; 75 meq L^{-1} (1724 ppm) Na; 10 meq L^{-1} (391 ppm) K. Store in a polypropylene container.

6.8 NH_4OAc solution, 1.0 *N*, pH 7.0, reagent blank. Mix 57 mL of glacial acetic acid in 600 mL DDI water. While stirring, carefully add 68 mL concentrated of NH_4OH. Cool and adjust pH to 7.0 using NH_4OH or acetic acid. Dilute to 1 L with DDI water. The NH_4OAc solution is used for extraction of cations (method 5A8c).

6.9 Working stock mixed standards solution (WSMSS). Dilute 20 mL of the PSMSS with 80 mL DDI water (1:5). Resulting solution contains 14 meq L^{-1} (281 ppm) Ca; 14 meq L^{-1} (170 ppm) Mg; 15 meq L^{-1} (345 ppm) Na; 2 meq L^{-1} (78 ppm) K. Store in a polypropylene container.

6.10 Stock lanthanum ionization suppressant solution, 65,000 ppm. Wet 152.4 g of lanthanum oxide (La_2O_3) with 100 mL DDI water. Slowly and cautiously add 500 mL of 6 *N* HCl to dissolve the La_2O_3. Cooling the solution is necessary. Dilute to 2 L with DDI water. Filter solution. Store in polypropylene container.

6.11 Lanthanum ionization suppressant solution, 6500 ppm. Dilute 200 mL of stock lanthanum ionization suppressant solution with 1800 mL of DDI water (1:10). Store in polypropylene container.

6.12 Dilute calibration mixed standards solution (DCMSS). Dilute 1 part of the WSMSS with 39 parts of the lanthanum solution (1:40). Resulting solution contains 0.35 meq L^{-1} (7 ppm) Ca; 0.35 meq L^{-1} (4 ppm) Mg; 0.375 meq L^{-1} (9 ppm) Na; 0.05 meq L^{-1} (2 ppm) K. Store in polypropylene container.

6.13 Dilute calibration reagent blank solution (DCRBS). Dilute 1 part of DDI water with 39 parts of the lanthanum solution (1:40). Store in polypropylene container.

6.14 Compressed air with water and oil traps

6.15 Acetylene gas, purity 99.6%

7. Procedure

Dilution of Sample Extracts and Standards

7.1 The 10-mL syringe is for diluent (lanthanum ionization suppressant solution). The 1-mL syringe is for saturation sample extracts (method 8A3a), calibration reagent blanks, and calibration standards. Set the digital diluter at 1:40 dilution for saturation sample extracts, reagent blanks, and calibration standards as follows:

7.2 Dilute 1 part saturation sample extract with 39 parts of lanthanum ionization suppressant solution (1:40 dilution).

7.3 Dilute 1 part WSMSS with 39 parts of lanthanum ionization suppressant solution (1:40 dilution). This dilution is the DCMSS. Refer to reagents section.

7.4 Dilute 1 part DDI water with 39 parts of lanthanum ionization suppressant solution (1:40 dilution). This dilution is the DCRBS. Refer to reagents section.

7.5 Dispense the diluted solutions into test tubes which have been placed in the sample holders of the sample changer.

AA Calibration

7.6 Use the DCRBS and the DCMSS to calibrate the AA. The AA program requires a blank and a standard, in that order, to establish a single point calibration curve for element determination. Perform one calibration, i.e., blank plus standard, for every 12 samples.

AA Set-up and Operation

7.7 Refer to the manufacturer's manual for operation of the AA. The following are only very general guidelines for instrument conditions for the various analytes.

Analyte	Conc. meq/L	Burner & Angle	Wave-length	Slit	Fuel/Oxidant C_2H_2/Air
Ca	14.00	50 cm, @ 0°	422.7	0.7	10/25
Mg	14.00	50 cm, @ 30°	285.2	0.7	10/25
K	2.00	50 cm, @ 0°	766.5	1.4	10/25
Na	15.00	50 cm, @ 30°	589.0	0.4	10/25

7.8 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

7.9 If sample exceeds calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record dilution. Remember to keep

the matrix the same after dilution by diluting with the lanthanum ionization suppressant solution (1:40 dilution).

7.10 Analyze one quality control check sample for every 48 samples.

7.11 The instrument readings are usually programmed in meq L^{-1}. Record analyte readings to 0.01 meq L^{-1}.

8. Calculations

8.1 The instrument readings are the analyte concentration (meq L^{-1} cation) in undiluted extract. Use these values and dilution ratio (if any) and calculate the analyte concentration in meq L^{-1} cation.

Analyte Concentration in Soil (meq L^{-1}) = Analyte AA reading (meq L^{-1}) x Dilution ratio (if any)

9. Report

Report the saturation extraction cations of Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} in units of meq L^{-1} to the nearest 0.1 meq L^{-1}.

10. Precision

Precision data are not available for this procedure.

11. References

U.S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. L.A. Richards (ed.) U.S. Dept. of Agric. Handb. 60. U.S. Govt. Print. Office, Washington, DC.

Calcium, Magnesium, Sodium, and Potassium (6N, 6O, 6P, and 6Q) NH_4OAC Extraction

(6N2, 6O2, 6P2, and 6Q2) Atomic Absorption

Perkin-Elmer AA 5000 (6N2e, 6O2d, 6P2b, and 6Q2b)

1. Application

The extractable bases (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) from the NH_4OAC extraction (method 5A8c) are generally assumed to be those exchangeable bases on the cation exchange sites of the soil. The abundance of these cations usually occurs in the sequence of $Ca^{2+} > Mg^{2+} > K^{+} > Na^{+}$. Deviation from this usual order signals that some factor or factors, e.g., free $CaCO_3$ or gypsum, serpentine (high Mg^{2+}), or natric material (high Na^{+}), have altered the soil chemistry. The most doubtful cation extractions with this method are Ca^{2+} in the presence of free $CaCO_3$ or gypsum and K^{+} in soils that are dominated by mica or vermiculite (Thomas, 1982).

2. Summary of Method

The NH_4OAc extract from method 5A8c is diluted with an ionization suppressant ($LaCl_3$). The analytes are measured by an atomic absorption spectrophotometer (AA). The analyte is measured by absorption of the light from a hollow cathode lamp. An automatic sample changer is used to aspirate a series of samples. The AA converts absorption to analyte concentration. The data are automatically recorded by a microcomputer and printer. The NH_4OAc extracted cations, Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}, are reported in meq 100 g^{-1} oven-dry soil in methods 6N2e, 6O2d, 6P2b, and 6Q2b, respectively.

3. Interferences

There are four types of interferences (matrix, spectral, chemical, and ionization) in the analyses of these cations. These interferences vary in importance, depending upon the particular analyte selected.

4. Safety

Wear protective clothing and safety glasses. When preparing reagents, exercise special care. Restrict the use of concentrated HCl to a fume hood. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts.

Follow standard laboratory procedures when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene gas is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the AA.

5. Equipment

5.1 Electronic balance, ±1-mg sensitivity

5.2 Filter paper, pre-pleated, 185-mm diameter, Schleicher and Schuell

5.3 Atomic absorption spectrophotometer (AA), model 5000, Perkin-Elmer Corp., Norwalk, CT

5.4 Automatic burner control, model 5000, Perkin-Elmer Corp., Norwalk, CT

5.5 Autosampler, AS-50, Perkin-Elmer Corp., Norwalk, CT

5.6 Dot matrix printer, P-132, Interdigital Data Systems, Inc.

5.7 Single-stage regulator, acetylene service, part number E11-0-N511A, Air Products and Chemicals, Inc., Box 538, Allentown, PA

5.8 Digital diluter/dispenser, Microlab 500, Hamilton Co., P.O. Box 10030, Reno, NV

5.9 Syringes, 10,000 and 1000 µL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV

5.10 Test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer, Curtin Matheson Scientific, Inc., Houston, TX

5.11 Containers, polypropylene

6. Reagents

6.1 Distilled deionized (DDI) water

6.2 Hydrochloric acid (HCl), concentrated 12 *N*

6.3 HCl, 1:1 HCl:DDI, 6 *N*. Carefully mix 1 part of concentrated HCl to 1 part DDI water.

6.4 HCl, 1% wt. Carefully dilute 25 mL of concentrated HCl to 1 L with DDI water.

6.5 NH_4OH, reagent-grade, sp gr 0.90

6.6 Glacial acetic acid, 99.5%

6.7 Primary stock mixed standards solution (PSMSS). Dissolve 0.8759 g of oven-dry reagent grade calcium carbonate ($CaCO_3$) in a minimum of volume of 1:1 concentrated HCl:DDI water. Add 0.2127 g of clean Mg ribbon dissolved in 1:1 HCl. Add 1.0956 g of dry reagent grade sodium chloride (NaCl) and 0.1864 g of dry reagent grade KCl. Transfer to a 250-mL volumetric and bring to volume with 1% HCl solution. Resulting solution contains 70 meq L^{-1} (1403 ppm) Ca; 70 meq L^{-1} (851 ppm) Mg; 75 meq L^{-1} (1724 ppm) Na; 10 meq L^{-1} (391 ppm) K. Store in a polypropylene container.

6.8 NH_4OAc solution, 1.0 *N*, pH 7.0, reagent blank. Mix 57 mL of glacial acetic acid in 600 mL of DDI water. While stirring, carefully add 68 mL of concentrated NH_4OH. Cool and adjust pH to 7.0 using NH_4OH or acetic acid. Dilute to 1 L with DDI water. The NH_4OAc solution is used for extraction of cations (method 5A8c).

6.9 Working stock mixed standards solution (WSMSS). Dilute 20 mL of the PSMSS with 80 mL DDI water (1:5). Resulting solution contains 14 meq L^{-1} (281 ppm) Ca; 14 meq L^{-1} (170 ppm) Mg; 15 meq L^{-1} (345 ppm) Na; 2 meq L^{-1} (78 ppm) K. Store in a polypropylene container.

6.10 Stock lanthanum ionization suppressant solution, 65,000 ppm. Wet 152.4 g lanthanum oxide (La_2O_3) with 100 mL DDI water. Slowly and cautiously add 500 mL of 6 *N* HCl to dissolve the La_2O_3. Cooling the solution is necessary. Dilute to 2 L with DDI water. Filter solution. Store in polypropylene container.

6.11 Lanthanum ionization suppressant solution, 6500 ppm. Dilute 200 mL of stock lanthanum ionization suppressant solution with 1800 mL of DDI water (1:10). Store in polypropylene container.

6.12 Dilute calibration mixed standards solution (DCMSS). Dilute 1 part of the WSMSS with 39 parts of the lanthanum solution (1:40). Resulting solution contains 0.35 meq L^{-1} (7 ppm) Ca; 0.35 meq L^{-1} (4 ppm) Mg; 0.375 meq L^{-1} (9 ppm) Na; 0.05 meq L^{-1} (2 ppm) K. Store in polypropylene container.

6.13 Dilute calibration reagent blank solution (DCRBS). Dilute 1 part of DDI water with 39 parts of the lanthanum solution (1:40). Store in polypropylene container.

6.14 Compressed air with water and oil traps

6.15 Acetylene gas, purity 99.6%

7. Procedure

Dilution of Sample Extracts and Standards

7.1 The 10-mL syringe is for diluent (lanthanum ionization suppressant solution). The 1-mL syringe is for NH_4OAc sample extracts (method 5A8c), calibration reagent blanks, and calibration standards. Set the digital diluter at a 1:40 dilution for the NH_4OAc sample extracts, reagent blanks, and calibration standards as follows:

7.2 Dilute 1 part NH_4OAc sample extract with 39 parts of lanthanum ionization suppressant solution (1:40 dilution).

7.3 Dilute 1 part WSMSS with 39 parts of lanthanum ionization suppressant solution (1:40 dilution). This is the DCMSS. Refer to reagents section.

7.4 Dilute 1 part DDI water with 39 parts of lanthanum ionization suppressant solution (1:40 dilution). This is the DCRBS. Refer to reagents section.

7.5 Dispense the diluted solutions into test tubes which have been placed in the sample holders of the sample changer.

AA Calibration

7.6 Use the DCRBS and the DCMSS to calibrate the AA. The AA program requires a blank and a standard, in that order, to establish a single point calibration curve for element determination. Perform one calibration, i.e., blank plus standard, for every 12 samples.

AA Set-up and Operation

7.7 Refer to the manufacturer's manual for operation of the AA. The following are only very general guidelines for instrument conditions for the various analytes.

Analyte	Conc. meq/L	Burner & Angle	Wave-length	Slit	Fuel/Oxidant C_2H_2/Air
Ca	14.00	50 cm, @ 0°	422.7	0.7	10/25
Mg	14.00	50 cm, @ 30°	285.2	0.7	10/25
K	2.00	50 cm, @ 0°	766.5	1.4	10/25
Na	15.00	50 cm, @ 30°	589.0	0.4	10/25

7.8 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

7.9 If sample exceeds calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record dilution. Remember to keep the matrix the same after dilution by diluting with the lanthanum ionization suppressant solution (1:40 dilution).

7.10 Analyze one quality control check sample for every 48 samples.

7.11 The instrument readings are usually programmed in meq L^{-1}. Record analyte readings to 0.01 meq L^{-1}.

8. Calculations

8.1 The instrument readings are the analyte concentration (meq L^{-1} cation) in undiluted extract. Use these values and calculate the analyte concentration on an oven-dry soil basis (meq 100 g^{-1}).

Analyte Concentration in Soil (meq 100 g^{-1}) = (A x B x C x E) / (10 x D)

where:

A = Analyte concentration in extract (meq L^{-1})

B = Extract volume (mL). Refer to method 5A8c.

= Weight of extract in syringe (g) / Density of 1 *N* NH_4OAc (1.0124 g cm^{-3})

C = Dilution ratio, if needed

D = Soil sample weight (g)

E = AD/OD ratio (method 4B5)

9. Report

Report the extractable Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} in units of meq 100 g^{-1} of oven-dry soil to the nearest 0.1 meq 100 g^{-1}.

10. Precision

Precision data are not available for this procedure. A quality control check sample is run with every batch of 48 samples. The number of observations,

mean, standard deviation, and C.V. for the quality control check sample are as follows:

Cation	n	Mean	Std. Dev.	C.V.
Ca	85	18.4	0.95	5.1%
Mg	84	7.5	0.23	3.1%
K	81	2.04	0.10	

11. References

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. Agronomy 9:159–165.

Calcium, Magnesium, Sodium, and Potassium (6N, 6O, 6P, and 6Q)
NH_4OAC Extraction (6N2, 6O2, 6P2, and 6Q2)
Atomic Absorption
Thermo Jarrell Ash, Smith-Hieftje 4000 (6N2f, 6O2e, 6P2c, and 6Q2c)

1. Application

The extractable bases (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) from the NH_4OAC extraction (method 5A8c) are generally assumed to be those exchangeable bases on the cation exchange sites of the soil. The abundance of these cations usually occurs in the sequence of $Ca^{2+} > Mg^{2+} > K^{+} > Na^{+}$. Deviation from this usual order signals that some factor or factors, e.g., free $CaCO_3$ or gypsum, serpentine (high Mg^{2+}), or natric material (high Na^{+}), have altered the soil chemistry. The most doubtful cation extractions with this method are Ca^{2+} in the presence of free $CaCO_3$ or gypsum and K^{+} in soils that are dominated by mica or vermiculite (Thomas, 1982).

2. Summary of Method

The NH_4OAc extract from method 5A8c is diluted with an ionization suppressant ($LaCl_3$). The analytes are measured by an atomic absorption spectrophotometer (AA). The data are automatically recorded by a microcomputer and printer. The NH_4OAc extracted cations, Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}, are reported in meq 100 g^{-1} oven-dry soil in methods 6N2f, 6O2e, 6P2c, and 6Q2c, respectively.

3. Interferences

There are four types of interferences (matrix, spectral, chemical, and ionization) in the analyses of these cations. These interferences vary in importance, depending upon the particular analyte selected.

4. Safety

Wear protective clothing and safety glasses. When preparing reagents, exercise special care. Restrict the use of concentrated HCl to a fume hood. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts.

Follow standard laboratory procedures when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene gas is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the AA.

5. Equipment

5.1 Electronic balance, ±1-mg sensitivity

5.2 Filter paper, pre-pleated, 185-mm diameter, Schleicher and Schuell

5.3 Atomic absorption spectrophotometer (AA), Smith-Hieftje Model 4000, Thermo Jarrell Ash Corp., Franklin, MA

5.4 Autosampler, Model 150, Thermo Jarrell Ash Corp., Franklin, MA

5.5 ThermoSpec software, Version 3.01, Enable 4.0, DOS 5.0, Thermo Jarrell Ash Corp., Franklin, MA

5.6 Computer, CUi Advantage 486, Thermo Jarrell Ash Corp., Franklin, MA

5.7 Printer, NEC Pinwriter P3200

5.8 Single-stage regulator, acetylene service, part number E11-0-N511A, Air Products and Chemicals, Inc., Box 538, Allentown, PA

5.9 Digital diluter/dispenser, Microlab 500, Hamilton Co., P.O. Box 10030, Reno, NV

5.10 Syringes, 10,000 and 1000 µL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV

5.11 Test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer, Curtin Matheson Scientific, Inc., Houston, TX

5.12 Containers, polypropylene

6. Reagents

6.1 Distilled deionized (DDI) water

6.2 Hydrochloric acid (HCl), concentrated 12 *N*

6.3 HCl, 1:1 HCl:DDI, 6 *N*. Carefully mix 1 part of concentrated HCl to 1 part DDI water.

6.4 HCl, 1% wt. Carefully dilute 25 mL of concentrated HCl to 1 L with DDI water.

6.5 NH_4OH, reagent-grade, sp gr 0.90

6.6 Glacial acetic acid, 99.5%

6.7 Primary stock mixed standards solution (PSMSS). Dissolve 0.8759 g of oven-dry reagent grade calcium carbonate ($CaCO_3$) in a minimum of volume of 1:1 concentrated HCl:DDI water. Add 0.2127 g of clean Mg ribbon dissolved in 1:1 HCl. Add 1.0956 g of dry reagent grade sodium chloride (NaCl) and 0.1864 g of dry reagent grade KCl. Transfer to a 250-mL volumetric and bring to volume with 1% HCl solution. Resulting solution contains 70 meq L^{-1} (1403 ppm) Ca; 70 meq L^{-1} (851 ppm) Mg; 75 meq L^{-1} (1724 ppm) Na; 10 meq L^{-1} (391 ppm) K. Store in a polypropylene container.

6.8 NH_4OAc solution, 1.0 *N*, pH 7.0, reagent blank. Mix 57 mL of glacial acetic acid in 600 mL of DDI water. While stirring, carefully add 68 mL of concentrated NH_4OH. Cool and adjust pH to 7.0 using NH_4OH or acetic acid. Dilute to 1 L with DDI water. The NH_4OAc solution is used for extraction of cations (method 5A8c).

6.9 Working stock mixed standards solution (WSMSS). Dilute 20 mL of the PSMSS with 80 mL DDI water (1:5). Resulting solution contains 14 meq L^{-1} (281 ppm) Ca; 14 meq L^{-1} (170 ppm) Mg; 15 meq L^{-1} (345 ppm) Na; 2 meq L^{-1} (78 ppm) K. Store in a polypropylene container.

6.10 Stock lanthanum ionization suppressant solution, 65,000 ppm. Wet 152.4 g lanthanum oxide (La_2O_3) with 100 mL DDI water. Slowly and cautiously add 500 mL of 6 *N* HCl to dissolve the La_2O_3. Cooling the solution is necessary. Dilute to 2 L with DDI water. Filter solution. Store in polypropylene container.

6.11 Lanthanum ionization suppressant solution, 6500 ppm. Dilute 200 mL of stock lanthanum ionization suppressant solution with 1800 mL of DDI water (1:10). Store in polypropylene container.

6.12 Dilute calibration mixed standards solution (DCMSS). Dilute 1 part of the WSMSS with 39 parts of the lanthanum solution (1:40). Resulting solution contains 0.35 meq L^{-1} (7 ppm) Ca; 0.35 meq L^{-1} (4 ppm) Mg; 0.375 meq L^{-1} (9 ppm) Na; 0.05 meq L^{-1} (2 ppm) K. Store in polypropylene container.

6.13 Dilute calibration reagent blank solution (DCRBS). Dilute 1 part of DDI water with 39 parts of the lanthanum solution (1:40). Store in polypropylene container.

6.14 Compressed air with water and oil traps

6.15 Acetylene gas, purity 99.6%

7. Procedure

Dilution of Sample Extracts and Standards

7.1 The 10-mL syringe is for diluent (lanthanum ionization suppressant solution). The 1-mL syringe is for NH_4OAc sample extracts (method 5A8c), calibration reagent blanks, and calibration standards. Set the digital diluter at a 1:40 dilution for the NH_4OAc sample extracts, reagent blanks, and calibration standards as follows:

7.2 Dilute 1 part NH_4OAc sample extract with 39 parts of lanthanum ionization suppressant solution (1:40 dilution).

7.3 Dilute 1 part WSMSS with 39 parts of lanthanum ionization suppressant solution (1:40 dilution). This is the DCMSS. Refer to reagents section.

7.4 Dilute 1 part DDI water with 39 parts of lanthanum ionization suppressant solution (1:40 dilution). This is the DCRBS. Refer to reagents section.

7.5 Dispense the diluted solutions into test tubes which have been placed in the sample holders of the sample changer.

AA Calibration

7.6 Use the DCRBS and the DCMSS to calibrate the AA. The AA program requires a blank and a standard, in that order, to establish a single point calibration curve for element determination. Perform one calibration, i.e., blank plus standard, for every 12 samples.

AA Set-up and Operation

7.7 Refer to the manufacturer's manual for operation of the AA. The following are only very general guidelines for instrument conditions for the various analytes.

Analyte	Conc. meq/L	Burner & Angle	Wave-length	Slit	Fuel/Oxidant C_2H_2/Air
Ca	14.00	50 cm, @ 0°	422.7	0.7	10/25
Mg	14.00	50 cm, @ 30°	285.2	0.7	10/25
K	2.00	50 cm, @ 0°	766.5	1.4	10/25
Na	15.00	50 cm, @ 30°	589.0	0.4	10/25

7.8 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

7.9 If sample exceeds calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record dilution. Remember to keep the matrix the same after dilution by diluting with the lanthanum ionization suppressant solution (1:40 dilution).

7.10 Analyze one quality control check sample for every 48 samples.

7.11 The instrument readings are usually programmed in meq L^{-1}. Record analyte readings to 0.01 meq L^{-1}.

8. Calculations

8.1 The instrument readings are the analyte concentration (meq L^{-1} cation) in undiluted extract. Use these values and calculate the analyte concentration on an oven-dry soil basis (meq 100 g^{-1}).

Analyte Concentration in Soil (meq 100 g^{-1}) = (A x B x C x E) / (10 x D)

where:

A = Analyte concentration in extract (meq L^{-1})

B = Extract volume (mL). Refer to method 5A8c.

= Weight of extract in syringe (g) / Density of 1 *N* NH_4OAc (1.0124 g cm^{-3})

C = Dilution ratio, if needed

D = Soil sample weight (g)

E = AD/OD ratio (method 4B5)

9. Report

Report the extractable Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} in units of meq 100 g^{-1} of oven-dry soil to the nearest 0.1 meq 100 g^{-1}.

10. Precision

Precision data are not available for this procedure. A quality control check sample is run with every batch of 48 samples.

11. References

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. Agronomy 9:159–165.

Total Sulfur (6R)

SO_2 Evolution, Infrared (6R3)

LECO SC-444 Sulfur Analyzer (6R3c)

1. Application

Organic and inorganic S forms are found in soils, with the organic S fraction accounting for >95% of the total S in most soils from humid and semi-humid (Tabatabai, 1982). 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%.

In well-drained, well-aerated soils, most of the inorganic S normally occurs as sulfate. In marine tidal flats, other anaerobic marine sediments, and mine spoils, there are usually large amounts of reduced S compounds which 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.

The typical use of total S is as an index of the total reserves of this element, which may be converted to plant available S. The SSL uses the combustion technique (LECO sulfur analyzer) for analysis of total S (method 6R3b). 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 and other carbonates, ammonium chloride and other chlorides, potassium phosphate and 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, 1982). Extraction reagents for organic S include hydrogen peroxide, sodium bicarbonate, sodium hydroxide, sodium oxalate, sodium peroxide, and sodium pyrophosphate. There are other methods available for determination of soil S, especially for total S and SO_4^{2}-S. The investigator may refer to the review by Beaton et al. (1968).

2. Summary of Method

A fine-ground (<80-mesh) soil sample is oxidized at high temperature. The gases released are scrubbed, and the SO_2 in the combustion gases are measured using an infrared detector. Percent S is reported on an oven-dry soil basis.

3. Interferences

No significant interferences are known to affect the oxidizable S measurement.

4. Safety

Wear protective clothing and safety glasses. Magnesium perchlorate may form explosive mixtures. Magnesium perchlorate may contain traces of perchloric acid, which remain from manufacturer's operations. This acid is anhydrous because of the strong desiccating capability of the salt. Avoid prolonged contact with oxidizable material or material capable of forming unstable perchlorate esters or salts. Remove magnesium perchlorate by using an excess of water to thoroughly dilute the material.

The use of high temperatures in the oxidation of samples requires that extreme caution be used to prevent burns and fires. Follow standard laboratory procedures when handling compressed gases. Oxygen is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire

blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the sulfur analyzer.

5. Equipment

5.1 Sulfur analyzer, Leco Model SC-444, Sulfur and Carbon Analyzers, Leco Corp., St. Joseph, MI

5.2 Combustion boats, part no. 529-203, Leco Corp., St. Joseph, MI

5.3 Single-stage regulator, Oxygen Service, Part No. E11-W-N115BOX, Air Products and Chemicals, Inc., Box 538, Allentown, PA 18105

5.4 Electronic balance, ±1-mg sensitivity

6. Reagents

6.1 Anhydrone, anhydrous magnesium perchlorate, granular

6.2 Glass wool

6.3 Compressed oxygen, >99.5% @ 30 psi

6.4 Calcium carbonate, $CaCO_3$, reagent grade

6.5 Solid/Powder Combustion Controller, part no. 501-426, Leco Corp., St. Joseph, MI

6.6 Soil Calibration Sample, part no. 502-062, Leco Corp., St. Joseph, MI

6.7 Sulfur Calibration Sample, part no. 502-648, Leco Corp., St. Joseph, MI

7. Procedure

7.1 Use a fine-ground 80-mesh, air-dry soil.

7.2 Prepare instrument as outlined in the operator's instruction manual (Leco, 1994; Leco, 1993).

7.3 Methods are created with the method menu and stored in the instrument memory. System parameters are set as follows:

Furnace operating temperature: 1450 °C

Lance delay: 20 s

Analysis time settings: 120 to 300 s

Comparator level settings: 0.3%

7.4 Condition instrument by analyzing a few soil samples, until readings are stable.

7.5 Calibrate instrument by analyzing at least three replicates of each calibration standard. Use the soil calibration standard for samples with less than 0.01 percent TS and the sulfur standard for samples with more than 0.01 percent TS. Weigh standards in a range from 0.2 to 0.5 g.

7.6 Load samples on autoload rack, place in the analyzer, and press analyze key.

7.7 Weigh 0.2 to 0.5 g sample in a tared combustion boat. Add approximately 1 g of solid/powder combustion controller to sample.

7.8 Load samples on autoload rack, place in the analyzer, and press analyze key.

7.9 Repack the reagent (anhydrous magnesium perchlorate) tubes whenever the reagent becomes caked or moist or the warning alarm displays.

8. Calculations

$S\ (\%) = S_i \times AD/OD$

where:

S (%) = S (%) on oven-dry basis

S_i = S (%) instrument

AD/OD = air-dry/oven-dry ratio (method 4B5)

9. Report

Report total S as a percentage of oven-dry weight to the nearest 0.1%.

10. Precision

Precision data are not available for this procedure. A quality control check sample is run in every batch of 12 samples. A blank (crucible only) and a rerun of one of the 12 samples (unknowns) also are run in every batch. For 27 observations of the quality control check sample, the mean, standard deviation, and C.V. for total S are 0.57, 0.02, and 4.3%, respectively.

11. References

Beaton, James D., G.R. Burns, and J. Platou. 1968. Determination of sulfur in soils and plant material. Tech. Bull. No. 14. The Sulfur Inst., 1725 K Street, N.W., Washington, D.C. 20006.

Leco Corp. 1993. Sulfur and carbon in cements, soils, rock, ceramic and similar materials. Application Bulletin. Leco Corp., 3000 Lakeview Ave., St. Joseph, MI.

Leco Corp. 1994. Instruction manual. SC-444 Sulfur and Carbon Analyzers. Leco Corp., 3000 Lakeview Ave., St. Joseph, MI.

Tabatabai, M.A. 1982. Sulfur. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:501–538.

Bray P-1 Absorbed Phosphorus (6S)
Bausch and Lomb, Spectrophotometer 20 (6S3)

1. Application

The Bray P-1 procedure is widely used as an index of available P in the soil. The selectivity of the Bray extractant is designed to remove the easily acid-soluble P, largely calcium phosphates, and a portion of the phosphates of Al and Fe (Bray and Kurtz, 1945; Olsen and Sommers, 1982). In general, this method has been most successful on acid soils (Bray and Kurtz, 1945; Olsen and Sommers, 1982).

2. Summary of Method

A 1-g soil sample is shaken with 10 mL of extracting solution for 15 min at 100 oscillations per min^{-1}. The solution is filtered. A 2-mL aliquot is transferred to a colorimetric tube to which 8-mL of ascorbic acid molybdate solution are added. The percent transmittance of the solution is read using a spectrophotometer. The Bray P-1 is reported in mg kg^{-1} (ppm) P.

3. Interferences

Many procedures may be used to determine P. Studies have shown that incomplete or excessive extraction of P to be the most significant contributor to inter-laboratory variation. The Bray P-1 procedure is sensitive to the soil/extractant ratio, shaking rate, and time. This extraction uses the ascorbic acid-potassium antimonyl-tartrate-molybdate method. The Fiske-Subbarrow method is less sensitive but has a wider range before dilution is required (North Central Regional Publication No. 221, 1988). For calcareous soils, the Olsen method is preferred. An alternative procedure for calcareous soils is to use the Bray P-1 extracting solution at a 1:50 soil:solution ratio. This procedure has been shown to be satisfactory for some calcareous soils (North Central Regional Publication No. 221, 1988; Smith et al., 1957).

4. Safety

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses). When preparing reagents, exercise special care. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts. Restrict the use of concentrated H_2SO_4 and HCl to a fume hood. Use safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids.

5. Equipment

5.1 Electronic balance, ±0.01-g sensitivity

5.2 Shaker, Eberbach 6000 power unit, reciprocating speed of 60 to 260 oscillations min^{-1}, with 6040 utility box carrier and 6110 floor stand, Eberbach Corp., Ann Arbor, MI

5.3 Spectrophotometer 20, Bausch and Lomb

5.4 Pipettors, electronic digital, Rainin Instrument Co., Woburn, MA, 2500 µL and 10 mL

5.5 Cuvettes, glass, 10 mL, 1-cm light path

5.6 Funnel, 60° angle, long stem, 50-mm diameter

5.7 Filter paper, quantitative, Whatman grade 2, 9-cm diameter

5.8 Erlenmeyer flasks, 50 mL

5.9 Centrifuge, high-speed, International Equipment Co., IECB-22M

6. Reagents

6.1 Distilled deionized (DDI) water

6.2 Hydrochloric acid (HCl), concentrated, 12 *N*

6.3 HCl, 1 *N*. Carefully add 83.33 mL of concentrated HCl to DDI water and dilute to 1-L volume.

6.4 Sulfuric acid (H_2SO_4), concentrated, 36 *N*

6.5 Bray No. 1 extracting solution, 0.025 *N* HCl and 0.03 *N* NH_4F. Dissolve 8.88 g of NH_4F in 4 L DDI H_2O. Add 200 mL of 1.0 *N* HCl and dilute to 8 L with DDI water. The solution pH should be 2.6 ±0.5. Store in a polyethylene bottle.

6.6 Stock standard P solution (SSPS), 100 ppm P. Add 0.2197 g of KH_2PO_4 in 25 mL of DDI water. Dilute to a final volume of 500 mL with extracting solution. Store in a refrigerator. Solution is stable to 1 yr.

6.7 Sulfuric-tartrate-molybdate solution (STMS). Dissolve 60 g of ammonium molybdate tetrahydrate $[(NH_4)_6Mo_7O_{24}•4H_2O]$ in 200 mL of boiling DDI water. Allow to cool to room temperature. Dissolve 1.455 g of antimony potassium tartrate (potassium antimonyl tartrate hemihydrate $K(SbO)C_4H_4O_6•½H_2O$) in the ammonium molybdate solution. Slowly and carefully add 700 mL of concentrated H_2SO_4. Cool and dilute to 1 L with DDI water. Store in the dark in the refrigerator.

6.8 Ascorbic acid solution. Dissolve 33.0 g of ascorbic acid in DDI water and dilute to 250 mL with DDI water. Store in the dark in the refrigerator.

6.9 Working ascorbic acid molybdate solution (WAMS). Prepare fresh each day. Mix 25 mL of STMS solution with 800 mL of DDI water. Add 10 mL of ascorbic acid solution and dilute to 1 L with DDI water.

6.10 Standard P calibration solutions (SPCS), 0.2, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, and 8.0 ppm. Dilute the SSPS with the extracting solution as

follows: 0.2 ppm=0.5:250; 0.5 ppm=0.5:100; 1.0 ppm=1:100; 2.0 ppm=2:100; 3.0 ppm=3:100; 4.0 ppm=4:100; 5.0 ppm=5:100; 6.0 ppm=6:100; 7:0 ppm=7:100; 8.0 ppm=8:100.

7. Procedure

7.1 Weigh 1.00 g of air-dry soil into a 50-mL Erlenmeyer flask.

7.2 Dispense 10.0 mL of extracting solution to flask.

7.3 Securely place the flask in the shaker. Shake for 15 min at 100 oscillations min^{-1} at room temperature (20 °C).

7.4 Remove the sample from the shaker. Decant, filter, and collect extract.

7.5 Centrifuging or repeated filtering may be necessary to obtain clear extracts. Decant into 13-mL centrifuge tube and centrifuge at 10,000 RPM for 10 min.

7.6 Use the pipettor to transfer a 2-mL aliquot of the sample to a cuvette. Also transfer a 2-mL aliquot of each SPCS to a cuvette. Use a clean pipette tip for each sample and SPCS.

7.7 Dispense 8 mL of the WAMS to sample aliquot and to each SPCS (1:5 dilution).

7.8 The color reaction requires a minimum of 20 min before analyst records readings.

7.9 Set the spectrophotometer (red bulb) to read at 882 nm.

7.10 Set the 100% transmittance against the blank which has 8 mL of the WAMS solution and 2 mL of extracting solution.

8. Calculations

8.1 Transmittance of a solution is the fraction of incident radiation transmitted by the solution, i.e., $T=P/P_o$, and is often expressed as a percentage, i.e., $\%T=P/P_o x100$. The absorbance of a solution is directly proportional to concentration and is defined by the equation, $A=-\log_{10} T$. These relationships are derived from Beer's law.

Calibration Calculations

8.2 Use transmission of each SPCS to either construct a calibrated curve to plot P or use a least squares analysis to calculate P. The P is reported in ppm.

8.3 *Calibration Curve*: Plot the transmittance against the ppm P of each SPCS on semilog graph paper or convert to absorbances and plot on linear graph paper. Construct the calibration curve by finding the "best" line that fits the plotted SPCS.

8.4 *Linear Squares Analysis*: Use a least squares criterion, i.e. best moving average. Refer to a statistical analysis book for additional information on least squares analysis. To facilitate data manipulation in a least squares analysis, the following standard curve is developed using the concentration of SPCS as a f[ln(%T)]. Final calculated analyte concentration with either $\log_{10}$ or ln base would be the same. Using the following example, calculate analyte concentration with P (ppm) in extract=Y variable and percent transmittance (% T)=the X variable. The X variable is the natural logarithm of T.

P	T
(ppm)	*(%)*
0	100
2	77
4	59
6	45
8	33
0	24

Number of standards=n=6

$\sum Y_i = 30$ $\quad\quad$ $\sum X_i = 23.5077$

$\sum Y_i/n = Y = 5$ $\quad\quad$ $\sum X_i/n = X = 3.9180$

$\sum X_i Y_i = 107.5902$ $\quad\quad$ $\sum X_i^2 = 93.5185$

$\sum X_i \sum Y_i = 705.231$

$$b = \frac{\sum X_i Y_i - \sum X_i \sum Y_i/n}{\sum X_i^2 - (\sum X_i)^2/n} = \frac{107.5902 - 117.5385}{93.5185 - 92.102} = -7.023$$

b = slope of the line, i.e., the amount that Y changes when X changes by 1 unit.

The equation is as follows:

$Y = Y + b\,(X - X)$

$Y = 5 - 7.023\,(\ln(X) - 3.9180)$

Analyte Calculation

8.5 *Calibration Curve*: Read the P (ppm) directly from the calibration curve.

8.6 *Least Squares Analysis*: Put the ln(%T) in the preceding equation and solve for ppm P. Thus, if sample extract has 84% transmission, the preceding equation is as follows:

$$Y = 5 - 7.023 \ln(84) + 27.516 = 1.40 \text{ ppm}$$

8.7 Convert the extract P (ppm) to soil P (ppm or lbs/A) as follows:

$$\text{Soil P (ppm)} = \text{Extract P (ppm)} \times 10$$

$$\text{Soil P (lbs/A)} = \text{Extract P (ppm)} \times 20$$

9. Report

Report the soil Bray P-1 mg kg^{-1} (ppm) to the nearest whole number.

10. Precision

Precision data are not available for this procedure.

11. References

Bray, R.H., and L.T. Kurtz. 1945. Determination of total, organic, and available forms of phosphorus in soils. Soil Sci. 59:39–45.

North Central Regional Publication No. 221. 1988. Recommended chemical soil test procedures for the North Central region. Agric. Exp. Stn. of IL, IN, IA, KS, MI, MN, MS, NE, ND, OH, SD, WI, and USDA cooperating.

Olsen, S.R., and L.E. Sommers. 1982. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:403–430.

Smith, F.W., B.G. Ellis, and J. Grava. 1957. Use of acid-fluoride solutions for the extraction of available phosphorus in calcareous soils and in soils to which rock phosphate has been added. Soil Sci. Soc. Am. Proc. 21:400–404.

New Zealand P Retention (6S)

UV-Visible Spectrophotometer (6S4)

Beckmann DU-7 (6S4b)

1. Application

In *Soil Taxonomy*, the P retention of soil material is a criterion for andic soil properties (Soil Survey Staff, 1990). Andisols and other soils that contain large amounts of allophane and other amorphous minerals have capacities for binding P (Gebhardt and Coleman, 1984). The factors that affect soil P retention are not well understood. However, allophane and imogolite have been considered as major materials that contribute to P retention in Andisols (Wada, 1985). Phosphate retention is also called P absorption, sorption, or fixation.

2. Summary of Method

A 5-g soil sample is shaken in a 1000-ppm P solution for 24 h. The mixture is centrifuged at 2000 rpm for 15 min. An aliquot of the supernatant is transferred to a colorimetric tube to which nitric vanadomolybdate acid reagent (NVAR) is added. The percent transmittance of the solution is read using a spectrophotometer. The New Zealand P retention is reported as percent P retained.

3. Interferences

No significant problems are known to affect the P retention measurement.

4. Safety

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses). When preparing reagents, exercise special care. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts. Restrict the use of concentrated HNO_3 to a fume hood. Use safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids.

5. Equipment

5.1 Electronic balance, ±0.01-g sensitivity

5.2 Shaker, Eberbach 6000 power unit, reciprocating speed of 60 to 260 epm, with 6040 utility box carrier and 6110 floor stand, Eberbach Corp., Ann Arbor, MI

5.3 Digital diluter/dispenser, Microlab 500, Hamilton Co., P.O. Box 10030, Reno, NV

5.4 Syringes, 10,000 and 1000 µL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV

5.5 Diluter/dispenser, 25 mL

5.6 UV-Visible Spectrophotometer, DU-7, Beckmann Instruments, Inc.

5.7 Cuvettes, Labcraft Brand, disposable, polystyrene, square-bottom, 4.5 mL, 12.5 mm x 12.5 mm x 46 mm, Curtin Matheson Scientific, Inc., Houston, TX

5.8 Centrifuge, International No. 2, Model V, with no. 250 A head, International Equip. Co., Boston, MA

5.9 Trunions, International no. 320, International Equip. Co., Boston, MA

5.10 Centrifuge tubes, 50 mL, Oak-Ridge, polyallomer, Nalgene 3119, Nalge Co., Box 20365, Rochester, NY

5.11 Plastic cups, 2 fl. oz.

5.12 Pipets, volumetric, class A, glass, various sizes of 1 to 20 mL

6. Reagents

6.1 Distilled deionized (DDI) water

6.2 Nitric acid (HNO_3), concentrated, 16 *N*

6.3 P retention solution, 1000 ppm P. Dissolve 35.2 g of KH_2PO_4 and 217.6 g of sodium acetate ($Na_2C_2H_3O_2 \cdot 3H_2O$) in DDI water. Add 92 mL of glacial acetic acid. Dilute to 8 L with DDI water in a volumetric flask. The solution pH should range between 4.55 and 4.65.

6.4 Molybdate solution. Dissolve 16 g of ammonium molybdate (VI) [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] in 50 °C DDI water. Allow the solution to cool to room temperature and dilute to 1 L with DDI water.

6.5 Nitric acid solution. Carefully and slowly dilute 100 mL of concentrated HNO_3 to 1 L of DDI water. Add the acid to the water.

6.6 Nitric vanadomolybdate acid reagent (NVAR), vanadate solution. Dissolve 0.8 g of NH_4VO_3 in 500 mL of boiling DDI water. Allow the solution to cool to room temperature. Carefully and slowly add 6 mL of concentrated HNO_3. Dilute to 1 L with DDI water. Mix the nitric acid solution with the vanadate solution and then add the molybdate solution. Mix well.

6.7 Stock P standard solution (SPSS), 4000 ppm P. Dissolve 17.6 g KH_2PO_4 in DDI water. Dilute to 1 L with DDI water.

6.8 Standard P calibration P solutions (SPCS), 100, 80, 60, 40, 20, and 0% P retained. Dilute the SPSS with a solution that contains 32.8 g of sodium acetate (CH_3COONa) and 23 mL of glacial acetic acid diluted to 2 L with DDI water as follows: 100% = DDI water (0 ppm); 80% = 1:20 (200 ppm); 60% = 1:10 (400 ppm); 40% = 3:20 (600 ppm); 20% = 1:5 (800 ppm); and 0% = 1:4 (1000 ppm). The percent amount refers to percent P retention.

7. Procedure

7.1 Weigh 5.00 g of air-dry soil into a 50-mL centrifuge tube.

7.2 Use the dispenser to add 25.0 mL of P-retention solution to centrifuge tube.

7.3 Cap centrifuge tube and place in shaker and shake for 24 h at room temperature (20 °C).

7.4 Add 2 to 3 drops of Superfloc, 0.02% w/v to each tube.

7.5 Centrifuge sample at 2000 rpm for 15 min. Filter using a Milipore filter, if necessary.

7.6 Pour sample supernatant into plastic cup.

7.7 Use the digital diluter to add the nitric vanadomolybdate acid reagent (NVAR) to each sample supernatant and to each SPCS. To fill a 4.5-mL cuvette, use a dilution of 1:20 sample dilution.

7.8 The color reaction requires a minimum of 30 min before the analyst records readings.

7.9 Set the spectrophotometer to read at 466 nm. Autozero using the DDI water (blank). A blank has all reagents contained in the sample extract except the soil.

7.10 Record the percent transmittance to the nearest 0.01 unit for the sample extract and each SPCS.

8. Calculations

8.1 Transmittance of a solution is the fraction of incident radiation transmitted by the solution, i.e., $T = P/P_o$, and is often expressed as a percentage, i.e., $T = P/P_o \times 100$. The absorbance of a solution is directly proportional to concentration and is defined by the equation, $A = -\log_{10} T$. These relationships are derived from Beer's law.

Calibration Calculations

8.2 Use the transmittance of each SPCS to either construct a calibrated curve to plot P or use a least squares analysis to calculate P. The P is reported in percent retained.

8.3 *Calibration Curve*: Plot the transmittances against the ppm P of each SPCS on semilog graph paper or convert to absorbances and plot on linear graph paper. Construct the calibration curve by finding the "best" line that fits the plotted SPCS.

8.4 *Least Squares Analysis*: Use a least squares criterion, i.e. best moving average. Refer to a statistical analysis book for additional information on least squares analysis. To facilitate data manipulation in a least squares analysis, the following standard curve is developed using the concentration of SPCS as a f[ln(%T)]. Final calculated analyte concentration with either $\log_{10}$ or ln base would be the same. Refer to method 6S3b for an example of least squares analysis.

Analyte Calculation

8.5 *Calibration Curve*: Read the percent P directly from the calibration curve.

8.6 *Least Squares Analysis*: Refer to method 6S3 for an example of least squares analysis.

9. Report

Report the percent New Zealand P retention to the nearest whole number.

10. Precision

Precision data are not available for this procedure.

11. References

Gebhardt, H., and N.T. Coleman. 1984. Anion adsorption of allophanic tropical soils: III. Phosphate adsorption. p. 237–248. *In* K.H. Tan (ed.) Andosols. Benchmark papers in soil science series. Van Nostrand Reinhold, Co., Melbourne, Canada.

Soil Survey Staff. 1990. Keys to soil taxonomy. 4th ed. SMSS technical monograph no. 6. Blacksburg, VA.

Wada, K. 1985. The distinctive properties of Andosols. p. 173–229. *In* B.A. Stewart (ed.) Adv. Soil Sci. Springer-Verlag, NY.

Citric Acid Extractable Phosphorus (6S)
Beckmann DU-7, UV-Visible Spectrophotometer (6S5)

1. Application

In *Soil Taxonomy*, citric acid soluble P_2O_5 is a criterion for distinguishing between mollic (<250 ppm P_2O_5) and anthropic epipedons (>250 ppm P_2O_5) (Soil Survey Staff, 1975). Additional data on anthropic epipedons from several parts of the world may permit improvements in this definition (Soil Survey Staff, 1994). The method 6S5 is used by N.A.A.S. (England and Wales) and is based on the method developed by Dyer (1894).

2. Summary of Method

A sample is checked for $CaCO_3$ equivalent. Sufficient citric acid is added to sample to neutralize the $CaCO_3$ plus bring the solution concentration of citric acid to 1%. A 1:10 soil:solution is maintained for all samples. The sample is shaken for 16 h and filtered. Ammonium molybdate and stannous chloride are added. The percent transmittance of the solution is read using a spectrophotometer. The 1% citric acid extractable P_2O_5 is reported in mg kg^{-1} (ppm).

3. Interferences

Unreacted carbonates interfere with the extraction of P_2O_5. Sufficient citric acid is added to sample to neutralize the $CaCO_3$. However, a high citrate level in 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.

Positive interferences in the analytical determination of P_2O_5 are silica and arsenic, if the sample is heated. Negative interferences in the P_2O_5 determination are arsenate, fluoride, thorium, bismuth, sulfide, thiosulfate, thiocyanate, or excess

molybdate. A concentration of Fe >1000 ppm interferes with P_2O_5 determination. Refer to Snell and Snell (1949) and Metson (1956) for additional information on interferences in the citric acid extraction of P_2O_5.

4. Safety

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses) when preparing reagents, especially concentrated acids and bases. Dispense concentrated acids and bases in fume hood. Use the safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids. Follow standard laboratory procedures.

5. Equipment

5.1 Electronic balance, ±0.01-g sensitivity

5.2 Shaker, Eberbach 6000 power unit, reciprocating speed of 60 to 260 oscillations min^{-1}, with 6040 utility box carrier and 6110 floor stand, Eberbach Corp., Ann Arbor, MI

5.3 Digital diluter/dispenser, product no. 100004, with hand probe and actuator, product no. 230700, Hamilton Co., P.O. Box 10030, Reno, NV

5.4 Syringes, 10,000 and 1000 µL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV

5.5 Centrifuge tubes, 50 mL, Oak-Ridge, polyallomer, Nalgene 3119, Nalge Co., Box 20365, Rochester, NY

5.6 Filter paper, quantitative, Whatman grade 2, 9-cm diameter

5.7 Funnel, 60° angle, long stem, 50-mm diameter

5.8 Erlenmeyer flasks, 50 ml

5.9 Bottles with gas release caps

5.10 Pipettors, electronic digital, Rainin Instrument Co., Woburn, MA, 2500 µL and 10 mL Digital Pipette, 10-ml

5.11 UV-visible spectrophotometer, DU-7, Beckmann Instruments, Inc.

5.12 Cuvettes, Labcraft Brand, disposable, polystyrene, square-bottom, 4.5 mL, 12.5 mm x 12.5 mm x 46 mm, Curtin Matheson Scientific, Inc., Houston, TX

6. Reagents

6.1 Distilled, deionized (DDI) water

6.2 Hydrochloric acid (HCl), concentrated, 12 *N*

6.3 Citric acid solution, 10%. Dissolve 100 g of anhydrous citric acid ($C_6H_8O_7$) in 1-L volumetric flask.

6.4 Citric acid solution, 1%. Dilute 100.0 ml of 10% citric acid solution to 1-L with DDI water.

6.5 Ammonium molybdate solution, 1.5%. Dissolve 15.0 g of ammonium molybdate [$(NH_4)_6MO_7O_{24}•4H_2O$] in 300 mL of distilled water. Transfer to a 1-L volumetric flask and carefully add 310 mL of concentrated HCl. Allow to cool. Make to 1-L volume with DDI water. Store in brown bottle in the dark. Solution is stable for ~3 months.

6.6 Stock stannous chloride solution (SSCS). Dissolve 10 g of stannous chloride ($SnCl_2•2H_2O$) in 100 mL of concentrated HCl.

6.7 Working stannous chloride solution (WSCS). Dilute 2 mL of SSCS with 100 mL of DDI water. Use immediately as solution is only stable for ~4 h.

6.8 Stock standard P_2O_5 solution (SSPS), 250 ppm P. Dissolve 1.099 g of potassium dihydrogen orthophosphate (KH_2PO_4) with DDI water in 1-L volumetric flask. Add 5 ml of 2 *N* HCL. Make to 1-L volume with DDI water.

6.9 Working stock standard P_2O_5 solution (WSSPS), 2.5 ppm P. Pipette 10.0 mL of SSPS and dilute to 1-L in a volumetric flask with DDI water.

6.10 Standard P_2O_5 calibration solutions (SPCS). Pipette 0, 1, 2, 3, 4, and 5 mL of WSSPS into 50-mL oakridge tubes. Add 1 ml of 1% citric acid solution. Continue color development as for samples. Distilled water may be used as a blank.

7. Procedure

7.1 Weigh 3.00 g of <2-mm, air-dry soil into a bottle with gas release tops. If the soil does not contain free carbonates, proceed to step 7.3.

7.2 If the soil contains free $CaCO_3$, refer to Table 1 to determine the amount of 10% citric acid solution required to neutralize the $CaCO_3$. Add required mLs of 10% citric acid into a graduated cylinder and bring to a volume of 30-ml with DDI water. Add this solution to the soil. Swirl the bottle over a period of 6 h at 100 oscillations min^{-1} to dissolve and neutralize the $CaCO_3$. Proceed to step 7.4.

Table 1.—Volume of 10% Citric Acid (mL) Required to Decompose $CaCO_3$ (%) and to Bring to Solution Concentration to 1% in a Final Volume of 30 mL for 3-g Sample.

%CC[1]	mL CA[2]	% CC	mL CA	% CC	mL CA	%CC	mL CA
0	3.0	16	9.7	32	16.4	48	23.2
1	3.4	17	10.2	33		49	23.6
2	3.8	18	10.6	34		50	24.0
3	4.3	19	11.0	35	17.7	51	24.4

%CC[1]	mL CA[2]	% CC	mL CA	% CC	mL CA	%CC	mL CA
4	4.7	20	11.4	36	18.1	52	24.8
5	5.1	21	11.8	37	18.6	53	25.3
6	5.5	22	12.2	38	19.0	54	25.7
7	6.0	23	12.7	39	19.4	55	26.1
8	6.4	24	13.1	40	19.8	56	26.5
9	6.8	25	13.5	41	20.2	57	27.0
10	7.2	26	14.0	42	20.6	58	27.4
11	7.6	27	14.4	43	21.0	59	27.8
12	8.0	28	14.8	44	21.5	60	28.2
13	8.5	29	15.2	45	21.9	61	28.6
14	8.9	30	15.6	46	22.4	62	29.0
15	9.3	31	16.0	47	22.8	63	29.5

[1] %CC = percent calcium carbonate in a sample

[2] CA = ml of 10% citric acid needed to be diluted to 30-mL volume with RODI water and added to sample

7.3 If the soil contains no free $CaCO_3$, add 30 mL of 1% citric acid solution to the sample.

7.4 Cap the bottles, place in a shaker, and shake for 16 h at 100 oscillations min^{-1}.

7.5 Remove the sample from shaker and filter.

7.6 Pipette 1 mL of sample extract into a 50-mL oakridge tube. Add 4 mL of ammonium molybdate solution to all samples and standards. Bring up to 25 mL mark with DDI water. Add 2 mL stannous chloride. Shake to mix and allow to stand 20 min for color development.

7.7 Set the spectrophotometer to read at 660 nm. Set the zero against distilled water (blank). A blank has all reagents contained in the sample extract except the soil.

7.8 Record the percent transmittance to the nearest 0.01 unit for the sample extract and each SPCS.

8. Calculations

8.1 Transmittance of a solution is the fraction of incident radiation transmitted by the solution, i.e., $T = P/P_o$, and is often expressed as a percentage, i.e., $\%T = P/P_o \times 100$. The absorbance of a solution is directly proportional to concentration and is defined by the equation, $A = -\log_{10} T$. These relationships are derived from Beer's law.

Calibration Calculations

8.2 Use transmission of each SPCS to either construct a calibrated curve to plot P_2O_5 or use a least squares analysis to calculate P_2O_5. The P_2O_5 is reported in ppm.

8.3 *Calibration Curve*: Plot the transmittances against the ppm P_2O_5 of each SPCS on semilog graph paper or convert to absorbances and plot on linear graph paper. Construct the calibration curve by finding the "best" line that fits the plotted SPCS.

8.4 *Linear Squares Analysis*: Use a least squares criterion, i.e. best moving average. Refer to a statistical analysis book for additional information on least squares analysis. To facilitate data manipulation in a least squares analysis, the following SPCS curve is developed using the concentration of SPCS as a f[ln(%T)]. Final calculated analyte concentration with either $\log_{10}$ or ln base would be the same. Refer to method 6S3 for an example of least squares analysis.

Analyte Calculation

8.5 *Calibration Curve*: Read the P_2O_5 (ppm) directly from the calibration curve.

8.6 *Least Squares Analysis*: Refer to method 6S3 for an example of least squares analysis.

8.7 Convert the extract P_2O_5 (ppm) to soil P_2O_5 (ppm or lbs/A) as follows:

Soil P_2O_5 = Extract P_2O_5 x DR x 100 x AD/OD / Sample Weight (g)

where:

Soil P_2O = P_2O_5 in soil (ppm)

Extract P_2O_5 = P_2O_5 in extract (ppm)

DR = Dilution ratio, if necessary, otherwise 1

100 = Conversion factor

AD/OD = Air-dry/oven-dry ratio (method 4B5)

9. Report

Report the 1% citrate acid extractable P_2O_5 in mg kg^{-1} (ppm) to nearest whole number.

10. Precision

Precision data are not available for this procedure.

11. References

Dyer, B. 1894. On the analytical determination of probably available "mineral" plant food in soils. Trans. Chem. Soc. 65:115–167.

Metson, A.J. 1956. Methods of chemical analysis for soil survey samples. Soil Bureau Bulletin no. 12. NZ Dept. Sci. and Industrial Res.

Snell, F.D., and C.T. Snell. 1949. Colorimetric methods of analysis. Phosphorus. Vol. 2. 3rd ed. p. 630–681. D. Van Nostrand Co., Inc.

Soil Survey Staff. 1975. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys. USDA–SCS Agric. Handb. 436. Appendix III: Tests of organic materials. p. 483. U.S. Govt. Print. Office. Washington, DC.

Soil Survey Staff. 1994. Keys to soil taxonomy. 6th ed. USDA–SCS. Govt. Print. Office, Washington DC.

MINERALOGY (7)

Instrumental Analyses (7A)
X-Ray Diffraction (7A2)
Phillips XRG-300 X-Ray Diffractometer
Thin Film on Glass, Resin Pretreatment II (7A2i)
(Mg Room Temp, Mg Glycerol Solvated, K 300°C, K 500°C)

1. Application

Clay fractions of soils are commonly composed of mixtures of one or more phyllosilicate minerals together with primary minerals inherited directly from the parent material (Whittig and Allardice, 1986). Positive identification of mineral species and quantitative estimation of their proportions in these polycomponent systems usually require the application of several complementary qualitative and quantitative analyses (Whittig and Allardice, 1986). One of the most useful methods to identify and to make semiquantitative estimates of the crystalline mineral components of soil is x-ray diffraction analysis.

The operational strategy at the SSL and the preceding Lincoln Soil Survey Laboratory has been to adjust instrumental parameters to keep peak intensity of a soil reference constant from 1964 to present through the evolution of instrumentation. The intent is to keep the same quantitative interpretations consistent from sample to sample.

2. Summary of Method

Soils are dispersed and separated into fractions of interest. Sands and silts are mounted on glass slides as slurries or on double sticky tape for analysis. Clay suspensions are placed on glass slides to dry and to preferentially orient the clay minerals. The soil clay minerals of greatest interest are phyllosilicates, e.g., kaolinite, mica (illite), smectite, vermiculite, hydroxy-interlayered vermiculite, and chlorite.

Generally, no two minerals have exactly the same interatomic distances in three dimensions and the angle at which diffraction occurs is distinctive for a particular mineral (Whittig and Allardice, 1986). These interatomic distances within a mineral crystal result in a unique array of diffraction maxima, which help to identify that mineral. When several minerals are present in a sample, species identification is usually accomplished most easily and positively by determining the interatomic spacings that give rise to the various maxima and by comparing these with known spacings of minerals (Whittig and Allardice, 1986).

X-ray diffraction produces peaks on a chart that correspond to 2θ angles on a goniometer. The angle of incidence of the goniometer is relative to the surface plane of the sample. Standard tables to convert θ or 2θ 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). At the SSL, conversions are made by the analysis program on the Philips diffractometer, d-spacings are recorded on an IBM-compatible 486 DOS-based computer system, and hard copies are printed for interpretation and filing. The crystal "d" spacings of minerals, i.e., the interval between repeating planes of atoms, can be calculated by Bragg's Law as follows:

$$n\lambda = 2d \sin \theta$$

where:

n = order of diffraction (integer)

λ = x-radiation wavelength (Angstroms, Å)

d = crystal "d" spacing (Å)

θ = angle of incidence

When n = 1, diffraction is of the first order. The wavelength of radiation from an x-ray tube is constant and characteristic for the target metal in the tube. Copper radiation (CuKα) with a wavelength of 1.54 Å (0.154 nm) is used at the SSL. Because of similar structures of layer silicates commonly present in soil clays, several treatments which characteristically affect the "d" spacings are necessary to identify components. At the SSL, four treatments are used, i.e., Mg^{2+} (room temperature); Mg^{2+}-glycerol (room temperature); K^{+} (300 °C); and K^{+} (500 °C).

3. Interferences

Intimate mixtures of similar phyllosilicate minerals on a fine scale cause problems in identification. The mixtures, differences in crystal size and purity, and background or matrix interferences affect quantification. No pretreatments other than dispersion with sodium hexametaphosphate are used for separation and isolation of the crystalline clay fraction. Impurities such as organic matter and iron oxides may act as matrix interferences causing peak attenuation during x-ray analysis or may interfere with clay dispersion and separation. The separation procedure 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. Dried clay may peel from the XRD slide. One remedy is to rewet the peeled clay on the slide with 1 drop of glue-water mixture (1:7). Other remedies are as follows:

a. Place double sticky tape on the slide prior to adding the dried clay.
b. Dilute the suspension by half, if thick.
c. Crush with ethanol and dry, and then add water to make a slurry slide.
d. Roughen the slide surface with a fine grit sand paper.

Sufficient glycerol on the slides is required to solvate the clay, i.e., to expand smectites to 18 Å. X-ray analysis should be performed 1 to 2 days after glycerol addition. If excess glycerol is applied to the slide and free glycerol remains on

the surface, XRD peaks are attenuated. Some suggestions to dry the slides and achieve optimum glycerol solvation are as follows:

a. Use a desiccator to dry slide, usually when the clay is thin.
b. If the center of slide is whitish and dry, usually with thick clay, brush slide with glycerol or add an additional drop of glycerol.

4. Safety

Operate the centrifuge with caution. Keep the centrifuge lid closed when in operation. Ensure that all hangers and tubes are seated firmly in proper location. Use tongs and appropriate thermal protection when operating the muffle furnace. The diffraction unit presents an electrical and radiation hazard. Analysts must receive radiation safety training before operating the equipment. Employees must wear a radiation film badge while in the room when the diffraction unit is in operation.

5. Equipment

5.1 Teaspoon (5 g)

5.2 Dispenser, 5 mL, for sodium hexametaphosphate solution

5.3 Centrifuge, International No. 2, with No. 240 head and carriers for centrifuge tubes, International Equip. Co., Boston, MA

5.4 Centrifuge tubes, plastic, 100 mL, on which 10-cm solution depth is marked

5.5 Rubber stoppers, No. 6, for centrifuge tubes

5.6 Mechanical shaker, reciprocal, 120 oscillations min^{-1}

5.7 Plastic cups, 60 mL (2 fl. oz.) with lids

5.8 Label machine

5.9 Hypodermic syringes, plastic, 12 mL, with tip caps

5.10 Screen, 80 mesh, copper

5.11 Dropper bottle, plastic, 30 mL (1 fl. oz.), for a 1:7 glycerol:water mixture

5.12 Muffle furnace

5.13 X-ray diffractometer, Philips XRG-300, with PW-1170 automated sample changer

5.14 PC-APD, Philips, software for Automatic Powder Diffraction (PW-1877), Version 3.5

5.15 Computer, IBM-compatible 486, Gateway 2000 4D X2-66V

5.16 Printer, Hewlett Packard LaserJet IV

5.17 Plotter, Hewlett Packard 7550 Plus

5.18 XRD slides, glass, 14 x 19 mm

5.19 XRD sample preparation board, wood, with 32 places for glass XRD slides

5.20 Slide holder. Accepts 14 x 19 mm XRD glass slides. Modified so slide surfaces rest flush with surface of holder.

5.21 Magazine for slide holder, 35 positions

5.22 Reference slides: quartz and clay from reference soil

6. Reagents

6.1 Distilled deionized (DDI) water

6.2 Sodium hexametaphosphate solution. Dissolve 35.7 g of sodium hexametaphosphate $(NaPO_3)_6$ and 7.94 g of sodium carbonate (Na_2CO_3) in 1 L DDI water.

6.3 Potassium chloride (KCl), 1.0 *N*. Dissolve 74.60 g KCl in 1 L DDI water or 671.40 g KCl in 9 L DDI water.

6.4 Magnesium chloride ($MgCl_2$), 1.0 *N*. Dissolve 47.61 g $MgCl_2$ in 1 L DDI water or 428.49 g $MgCl_2$ in 9 L DDI water.

6.5 Glycerol:water mixture (1:7). Add 4 mL of glycerol to 28 mL DDI water plus 2 drops of toluene.

6.6 Exchange resin, Rexyn 101 (H), analytical grade. Pretreatment of resin as follows:

6.6.1 Divide equally Rexyn 101 (H), approximately 250-g portions, into two 600-mL beakers labeled K and Mg and add appropriate salt solution (1.0 *N* KCl or 1.0 *N* $MgCl_2$). Cover resin with salt solution.

6.6.2 Stir, let settle for 10 min, decant clear solution, and add salt solution. Repeat 3 times. Leave resin covered in salt solution for 8 to 12 h.

6.6.3 Repeat step 6.6.2 second day. Resin is ready for syringes. Saturated resin not used initially for syringes can be saved for future use.

6.7 White glue, diluted 1:7 with DDI water

7. Procedure

Preparation (Recharge) of Resin-Loaded Syringes

7.1 Place a small circle of 80-mesh screen in a 12-mL syringe and add 4 cm^3 of exchange resin from which salt solution has been drained. Our procedure requires each sample to have 2 Mg and 2 K slides prepared, so we produce our syringes in sets of two.

7.2 Saturate the resin in each of the four syringes with 4 mL of the appropriate 1.0 *N* salt solution ($MgCl_2$ or KCl) and expel. Repeat saturation of resin.

7.3 Fill syringe completely with the salt solution and allow to equilibrate for 4 to 20 h.

7.4 Rinse syringe twice with 4 mL of DDI water and rinse tip cap.

7.5 Completely fill syringe with DDI water and allow to equilibrate for 4 to 20 h.

7.6 Rinse syringe twice with DDI water.

7.7 Expel water, cap syringe, and store.

Preparation of Clay Suspension

7.8 Place ≈5 g (1 tsp) of air-dry <2-mm soil in a 100-mL plastic centrifuge tube. If the sample appears to be primarily sand, use 10 g (2 tsp) of <2-mm soil to obtain sufficient clay.

7.9 Add 5 mL of sodium hexametaphosphate solution. If the soil contains gypsum or is primarily calcium carbonate, use 10 mL of sodium hexametaphosphate dispersing agent.

7.10 Fill tube to 9.5-cm height with DDI water.

7.11 Place rubber stopper in tube and shake overnight in mechanical shaker.

7.12 Remove stopper from tube and rinse stopper and sides of tube with enough water to bring the volume to the 10-cm mark.

7.13 Balance the pairs of tubes and place in centrifuge. Centrifuge at 750 rpm for 3.0 min.

7.14 If the clay is dispersed, carefully decant 30 mL of suspension into a labeled, 60-mL, plastic cup. Place cap on cup.

7.15 If the clay did not disperse after being shaken overnight, remove the rubber stopper and carefully decant the clear supernatant liquid.

7.16 Add an additional 10 mL of sodium hexametaphosphate dispersing agent to sample and then add DDI water to 9.5-cm depth.

7.17 Stopper and shake overnight to disperse the clay. Rinse stopper and fill tube to 10-cm mark.

7.18 Centrifuge, decant, and store clay suspension.

7.19 Use the clay suspension for x-ray diffraction analysis and HF plus aqua regia dissolution analysis. Dry clay suspension for use in thermal analysis.

Thin Film on Glass, Resin Pretreatment

7.20 The SSL uses a sample board which holds 32 slides, i.e., 8 samples x 4 treatments. Prepare the sample board with glass XRD slides to receive the following 4 treatments per clay suspension sample.

Mg^{2+} — room temperature

Mg^{2+} — glycerol (room temperature)

K^{+} — 300 °C (heated for 2 h)

K^{+} — 500 °C (heated for 2 h)

7.21 Place one small drop of the glycerol:water mixture (1:7) on each Mg^{2+}-glycerol slide.

7.22 Draw 1 mL of <2-µm clay suspension into the resin-loaded syringe and invert back and forth to facilitate cation exchange.

7.23 Dispense 3 drops to clear the tip.

7.24 Dispense ≈0.1 mL (6 to 10 drops) to cover the appropriate XRD slide. Draw DDI water into the syringe and expel 3 times to remove all of the clay suspension. Recharge the syringe after 10 times of use.

7.25 When the clay suspension has dried, transfer the slides with the K^{+}-saturated clays to transite plates and heat for a minimum of 2 h in a muffle furnace.

7.26 Heat the following sample slides on the XRD sample board.

K^{+}-300 °C —slides 3, 7, 11, 15, 19, 23, 27, and 31

K^{+}-500 °C —slides 4, 8, 12, 16, 20, 24, 28, and 32

7.27 After heating, remove the transite plate from the furnace, cool to air temperature, and return slides to XRD sample board.

X-Ray Diffraction Operation

7.28 The x-ray analysis of the glycerol slide must be done within 1 to 2 days after the slide dries. If this is not possible, skip Step 7.21 when slide is prepared. Add one small drop of glycerol:water mixture (1:7) to dry slide 24 h prior to x-ray analysis.

7.29 Transfer the slides (1 to 32) from XRD sample board to slide holders (1 to 32) and place in slots (1 to 32) in a magazine for the automated sample changer.

7.30 Analyze one reference soil sample in each run. Place this sample in slot 33.

7.31 Analyze one quartz standard for 2θ and intensity calibrations in each run. Place this sample in slot 34. Intensity is measured at peak maximum at or near 26.66° 2θ for 10 s.

7.32 The 32 samples from one XRD board constitute one run on the diffraction unit. Prepare a run sheet for samples on each XRD sample board. Refer to example run instruction (7.33). Refer to the manufacturer's manual for operation of the x-ray diffractometer.

7.33 Place the magazine in the automated sample changer. Confirm that the XRD shutter is off when changing magazines. Set the XRD unit parameters as follows:

CuKα radiation, λ: 1.54 Å (0.154 nm)

Scan range: 2° to 34° 2θ

Generator settings: 40 kv, 20 ma

Divergence slit: 1°

Receiving slit: 0.2 mm

Monochrometer: Yes

Step size and scan speed vary depending on intensity of x-rays generated from tube. Adjust settings to maintain same long-term peak intensities on standard reference clay and quartz standard regardless of tube intensities.

7.34 Enter run instruction from the keyboard. Create a batch file for the automated run. File names specified are of the sample number. An example run instruction is as follows:

Batch File Name: Project number (e.g., CP95LA022)

Raw Data File Name: Run number

First Sample: 1

Last Sample: 33

(reference soil clay)

7.35 Activate program. The run stores raw data on the hard disk under the subdirectory designated by project type and year, e.g., CP95. Refer to example run instruction (7.34).

7.36 Print a hard copy of the “Detected Peaks File” for each sample and perform level 1 smoothing on diffraction patterns.

7.37 Prepare and print a 4-color graphics chart. The 4 colors are blue (Mg^{2+}); green (Mg^{2+}-glycerol); pink (K^{+} 300 °C); and red (K^{+} 500 °C). Stamp chart with label; enter run parameter information, and complete soil information, e.g., soil name, horizon designation, and depth. File hard copies of detected peaks and graphics chart in pasteboard binders by State, county, and chronology.

7.38 Record “d” spacing and intensity of quartz standard in the logbook. Record the peak intensities for designated peaks for the reference soil clay.

7.39 File the detected peaks printout and graph for the reference soil in the reference soil-clay folder.

Interpretation of X-Ray Diffraction Data

7.40 The angle in degrees two theta (2θ) measured in x-ray diffraction analyses is converted to angstroms (Å) using tables complied according to Bragg's Law. Refer to summary of method. Angstroms convert to nanometers (nm) by a factor of 0.1, e.g., 14 Å = 1.4 nm.

7.41 Use the following x-ray diffraction criteria to identify some common crystalline minerals. The reported "d" values are for 00*l* basal spacings. The Miller index (*hkl*) specifies a crystal face which has some orientation to the three crystallographic axes of a, b, and c. The Miller index (00*l*) indicates a crystal face that is parallel to the a and b axes, e.g., phyllosilicate minerals. The following x-ray diffraction criteria also have some questions (Q) that may aid the analyst in interpreting the diffraction patterns. These questions are a suggested procedural approach to help the analyst identify the relative locations of a few peaks and to confirm key criteria.

X-Ray Diffraction Criteria

1. Kaolinite and Halloysite

a. Crystal structure missing at 500 °C.

b. 7 Å (7.2 to 7.5 Å) with all other treatments.

Q. Is there a 7 Å peak? Is it destroyed at 500 °C? Kaolinite or Halloysite.

Q. Is the peak sharp and at ~7.1 Å? Kaolinite.

Q. Is the peak broad and at 7.2 to 7.5 Å? Halloysite.

2. Mica (Illite)

a. 10 Å with all treatments.

b. 10 Å with Mg^{2+}-saturation.

Q. Is there a 10 Å peak with Mg^{2+}-saturation? Mica (Illite).

3. Chlorite

a. Crystal structure of Fe-chlorites destroyed at 650 to 700 °C.

b. 14 Å with all other treatments.

c. 14 Å at 500 °C.

d. Generally also has strong 7 A peak.

Q. Is there a 14 Å peak when heated to 500 °C? Chlorite.

4. Vermiculite

a. 14 Å with Mg^{2+}-saturation.

b. 14 Å with Mg^{2+}-glycerol solvation.

c. Nearly 10 Å with K^{+} saturation.

d. 10 Å when K^{+}-saturated and heated to 300 °C.

Q. Is there an enhanced 10 Å peak with K^{+}-saturation in comparison to Mg^{2+}-saturation that cannot be attributed to smectite? Vermiculite.

5. Smectite

a. 14 Å with Mg^{2+}-saturation

b. 12 to 12.5 Å with K^{+}- or Na^{+}-saturation.

c. 17 to 18 Å with Mg^{2+}-glycerol solvation.

d. 10 Å with K^{+}-saturation and heating to 300 °C.

Q. Is there a 17 to 18 Å peak upon solvation? Smectite.

6. Gibbsite

a. Peak at 4.83 Å with Mg^{2+} and Mg^{2+}-glycerol but destroyed when heated to 300 °C.

7. Goethite

a. Peak at 4.18 Å with Mg^{2+} and Mg^{2+}-glycerol but destroyed when heated to 300 °C.

8. Hydroxy-interlayed Vermiculite or Smectite

a. Incomplete collapse to 10 Å of smectite or vermiculite when K^{+}-saturated and heated to 300 °C.

9. Quartz

a. Peaks at 4.27 Å and 3.34 Å with all treatments (only 3.34 if small amounts).

10. Lepidocrocite

a. Peak at 6.2 to 6.4 Å with Mg^{2+} and Mg^{2+}-glycerol but destroyed when heated to 300 °C.

11. Potassium Feldspar

a. Peak at 3.24 Å with all treatments.

12. Plagioclase Feldspar

a. Twin peaks between 3.16 and 3.21 with all treatments.

13. Calcite

a. Peak at 3.035 Å with all treatments.

14. Dolomite

a. Peak at 2.88 to 2.89 Å with all treatments.

15. Gypsum

a. Peak at 4.27 Å with Mg^{2+} and Mg^{2+}-glycerol, but destroyed when heated to 300 °C.

16. Mixed Layer Vermiculite-Mica

a. Peak at 11 to 13 Å with Mg^{2+} that does not expand with Mg^{2+}-glycerol.

b. Peak collapses to 10 Å with K^{+}-saturation and heating to 300 °C.

17. Mixed Layer Smectite-Mica

a. Peak at 11 to 13 Å with Mg^{2+} that expands to 14–16 Å with Mg-glycerol.

b. Peak collapses to 10 Å with K^{+}-saturation and heating to 300 °C.

18. Mixed Layer Chlorite-Mica

a. Peak at 14 Å with Mg^{2+} and Mg^{2+}-glycerol.

b. Peak collapses toward 10 Å with K^{+}-saturation and heating to 300 °C, and more completely with heating to 500 °C, but never to 10 Å.

19. Mixed Layer Chlorite-Smectite

a. Peak at 11 to 13 Å with Mg^{2+}-saturation that expands to about 16 Å with Mg^{2+}-glycerol.

b. Collapses to about 12 Å with K^{+}-saturation and heating to 300 °C and 500 °C.

7.42 Use the x-ray diffraction criteria, i.e., diagnostic basal 00*l* spacings (Å), in Table 1 for identification and ready reference of some common crystalline minerals as affected by differentiating sample treatments.

7.43 Preferential orientation of clay mineral samples enhances diffraction from the basal (00*l*) 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:

Smectite (Mg^{2+}-glycerol):

a. 17 to 18 Å.

b. 8.5 to 9 Å (weak).

Chlorite, vermiculite, and smectite:

a. 14, 7, 4.7, and 3.5 Å.

b. 7, 4.7, and 3.5 Å weak for smectite.

Mica:

a. 10, 5 (weak in biotites and moderate in muscovites), and 3.3 Å.

Kaolinite:

a. 7 and 3.5 Å.

7.44 The differentiation of kaolinite and halloysite in a sample can be aided by the use of formamide (Churchman et al., 1984). The intercalation and expansion of halloysite to a d-spacing of ≈10.4 Å is relatively rapid (20 to 30 min), whereas kaolinite expansion requires ≈4 h upon treatment. The procedure is as follows:

a. Lightly spray formamide as an aerosol on the dried Mg^{2+}-saturated slide.

b. Wait 15 min but not more than 1 h and x-ray approximately 7.6 to 13.5° 2θ (d = 11.6 to 6.55 Å).

c. Halloysite will expand to ≈10.4 Å, whereas kaolinite will remain unchanged.

d. Heating the sample to 110 °C for 15 min will collapse the halloysite to ≈7 Å.

e. The total amount of kaolinite and halloysite can be determined by thermal analysis. The intensity ratio of the 10.4 to 7.2 Å peaks of the formamide-treated sample can be used to determine the relative percentage of halloysite and kaolinite.

8. Calculations

X-ray diffraction produces peaks on a chart that corresponds to 2θ angle on a goniometer. Standard tables to convert θ or 2θ 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 crystal "d" spacings of minerals, i.e., the interval between repeating planes of atoms, can be calculated by Bragg's Law. Refer to summary of method.

Table 1.—X-ray diffraction parameters of common soil clay minerals.

Mineral	Treatment						
	Na^+	Mg^{2+}	Mg^{2+} Gly	K^+	K^+ 300 °C	K^+ 500 °C	K^+ 700 °C
	00l 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

Mineral	Treatment						
	Na^+	Mg^{2+}	Mg^{2+} Gly	K^+	K^+ 300 °C	K^+ 500 °C	K^+ 700 °C
	00l diffraction spacing in angstroms						
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
Interlayer	10-14	10-14	10-18	10-14	10-14	10-14	10-14
Quartz	3.14 and 4.27 for all treatments						
Calcite	3.035 for all treatments						
Dolomite	2.88 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. Report

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 s^{-1}, to assign each layer silicate mineral to one of the 5 semiquantitative classes.

Class	Peak height above background (counts sec^{-1})
5 (Very Large)	$>1.88 \times 10^3$
4 (Large)	1.12 to 1.88×10^3
3 (Medium)	0.36 to 1.12×10^3
2 (Small)	0.11 to 0.36×10^3
1 (Very Small)	$<0.11 \times 10^3$

Adjust class placement to reflect area under the curve if peak is broad relative to peak height or if thermal, elemental, clay activity data, or other evidence warrants class adjustment. If there are no peaks or no evidence of crystalline components, place the sample in NX class (noncrystalline).

10. Precision

Precision data are not available for this procedure. Method 7A2i (X-ray diffraction) is semiquantitative.

11. References

Brown, G. 1980. Appendix I (Tables for the determination of d in Å from 2θ for the KA and KB radiations of copper, cobalt, and iron). *In* G.W. Brindley and G. Brown (eds.) Crystal structures of clay minerals and their x-ray identification. Mineralogical Soc. Monograph No. 5. Mineralogical Soc. Great Britain. p 439–475.

Churchman, G.J., J.S. Whitton, G.G.C. Claridge, and B.K.G. Theng. 1984. Intercalation method using formamide for differentiating halloysite from kaolinite. Clays and Clay Minerals 32:241–248.

Switzer, G., J.M. Axelrod, M.L. Lindberg, and E.S. Larsen. 1948. Tables of d spacings for angle 2Ɵ. U.S. Dept. Interior. Geological Survey. Circular 29. Washington, DC.

Whittig, L.D., and W.R. Allardice. 1986. X-ray diffraction techniques. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:331–362.

Total Analysis (7C)

HF Plus Aqua Regia (HF + HNO_3 + HCl) Dissolution (7C4a)

1. Application

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 to determine mineral structural formulas and to identify and quantify specific mineral species through elemental allocation to minerals. Many clay mineral groups are subdivided based on composition.

Analysis of the entire fine-earth (<2-mm) fraction or specific particle-size separates 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 in elemental concentrations, elemental ratios such as Si/Al, Si/Al+Fe, or Ti/Zr, or from differences in total elemental concentrations compared 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, especially when compared to other P measurements, such as water-soluble or Bray-extractable P.

Hydrofluoric acid (HF) is efficient in the digestion and dissolution of silicate minerals for elemental dissolution (Bernas, 1968; Sawhney and Stilwell, 1994). Aqua regia (HNO_3 and HCl) aids in digestion of soil components, especially the organic fraction. Method 7C4a is a digestion of 100 mg of dried clay suspension, the fine-earth (<2-mm) fraction, or other particle-size separate with HF and aqua regia. Closed digestion vessels (Parr Bombs) are heated in the oven at 110 °C for at least 6 hours. Elemental concentration of the digestate is determined by inductively coupled plasma-atomic emission spectrometry (ICP–AES).

2. Summary of Method

A clay suspension (method 7A2i) containing approximately 100 mg of clay material is pipeted into a Teflon digestion container and dried at 110 °C. An equal amount of suspension is pipeted into a tared aluminum-weighing dish and dried at 110 °C to obtain a dried sample weight. An oven-dry 100-mg soil sample (<80 mesh) or a specific particle-size separate may be substituted for the clay suspension. The P and Na content of the clay fraction is not measurable when the soil is dispersed in sodium hexametaphosphate (method 7A2i). Total P and Na are measurable on the fine-earth fraction or other particle-size separates not dispersed in Na- or P-containing reagents, and the analyses are included as a part of this procedure.

Following evaporation of the aqueous portion of the suspension, 0.75 mL HNO_3, 0.25 mL HCl, and 5 mL HF are added. The vessel is inserted into a stainless steel retainer vessel, heated, cooled, and 15 mL of 2.5 percent boric acid solution is added to neutralize the excess HF acid. The digestate is quantitatively transferred with boric acid solution, diluted to 100 mL, shaken, and allowed to stand overnight. Approximately 60 mL are saved for analysis. The concentration of Fe, Mn, Al, Ca, Mg, Na, K, P, Si, Zr, Cu, Zn, As, Ti, Se, Cd, and Pb are determined by ICP analysis in methods 6C7b, 6D6a, 6G11b, 6N5b, 6O5b, 6P3b, 6Q3b, 6S6a, 6V1b, 8K1a, 8L1a, 8M1a, 8N1a, 8O1a, 8P1a, 8Q1a, and 8R1a, respectively. Data are reported in method 7C4a.

3. Interferences

Insoluble fluorides of various metals may form. Formation of SiF_4 results in gaseous losses of Si, but additions of boric acid retards formation of this molecule as well as dissolves other metal fluorides.

4. Safety

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Restrict the use of concentrated acids to the fume hood. Keep HF acid refrigerated and avoid skin contact with all acids. Wash hands thoroughly after handling reagents. Filling the Teflon cup of the acid digestion bomb to greater than 25 percent of the free volume or adding organic reagents or oxidizing agents to the cup may result in explosion of the digestion bomb.

5. Equipment

5.1 Pipette(s) capable of delivering 5, 0.75, and 0.25 mL

5.2 Volumetric flasks, Nalgene, 100 mL

5.3 Polypropylene bottles, 60 mL, with cap

5.4 Electronic balance, ±0.1 mg sensitivity

5.5 Acid digestion bombs: 25-mL Teflon containers with stainless steel retainer vessels

5.6 Oven, 110 °C

5.7 Desiccator with P_2O_5 drying agent

5.8 Disposable aluminum-weighing dishes

6. Reagents

6.1 Deionized distilled (DDI) water

6.2 Hydrofluoric acid (HF), 48%, low trace metal content

6.3 Concentrated hydrochloric acid (HCl), 12 *N*. Use instrumental grade reagents which contain low levels of impurities.

6.4 Concentrated nitric acid (HNO_3), 16 *N*. Use instrumental grade reagents which contain low levels of impurities.

6.5 Boric acid solution, 2.5 percent. Dissolve 25.0 g low trace metal, granular boric acid (H_3BO_3) in 1000 mL DDI water.

7. Procedure

HF plus Aqua Regia Dissolution

7.1 Prepare Na-saturated clay as in method 7A2i, Preparation of Clay Suspension, Steps 7.8 to 7.19. Clay dispersion by this method eliminates quantitative analysis of Na and P in the clay due to dispersion by sodium hexametaphosphate. Digestion of the entire fine-earth (<2-mm) fraction or any fraction not derived by dispersion with sodium hexametaphosphate (or other Na- and P-containing dispersing agents) can be quantitatively analyzed for Na and P. Dispersion of clays and cleaning of test tubes and dishware should be with DDI water.

7.2 Pipette a known aliquot of clay suspension containing approximately 100 mg clay into a 25-mL Teflon container. The milliliters of suspension required depends on the clay concentration of the suspension but is generally from 2 to 6 mL. More dilute suspensions should be partially evaporated under a fume hood to concentrate the clay prior to transfer to the Teflon container. Fine-earth (<2-mm) or a specific particle-size separate ground to <80-mesh

may be used instead of clay. Samples with greater than 3 percent organic C should be ashed in a muffle furnace at 400 °C for 2 h prior to analysis to destroy the organic matter. Oven-dry the sample (110 °C), cool over P_2O_5, and weigh to 100 ±0.1 mg. If a clay suspension is used, Steps 7.3 to 7.4 are performed. Proceed to Step 7.5 if using fine-earth or other oven-dried material.

7.3 Pipette a duplicate aliquot of suspension (as used in Step 7.2) into a tared Al weighing dish, dry at 110 °C, cool in a desiccator with P_2O_5, and weigh to the nearest 0.1 mg. Use this value as the sample weight in the calculations.

7.4 Dry the Teflon container and clay suspension in an oven for 4 h or until the aqueous portion of the suspension is completely evaporated. Remove from oven and cool on the bench top or in a fume hood. Cooling in a desiccator is not required.

7.5 Pipette 0.75 mL HNO_3 and 0.25 mL HCl into the sample and allow to completely wet and then pipette 5 mL HF into sample.

7.6 Place covered Teflon container in stainless steel retainer vessel. Place sample in oven at 110 °C for a minimum of 6 h. Samples can be left in the oven overnight at 110 °C.

7.7 Remove samples from oven and cool for at least 4 h.

7.8 Under a hood, remove Teflon container from steel retainer vessel, open the Teflon container, and add 15 mL 2.5 percent boric acid solution.

7.9 Quantitatively transfer contents of Teflon container to a 100 mL Nalgene volumetric flask and adjust to volume with 2.5 percent H_3BO_3.

7.10 Cap flask and mix well by inverting at least three times. Allow to stand overnight to dissolve any metal fluorides.

7.11 Invert the volumetric flask to mix and decant approximately 60 mL into a labeled polypropylene container.

7.12 Prepare working standards of a blank, a clay suspension from a SSL reference soil sample, and a National Institute of Standards and Technology (NIST) standard reference material by the same digestion method. Run one of these standards with each set of 20 samples.

7.13 Solutions and standards are analyzed by ICP spectrometry. Refer to methods 6C7b, 6D6a, 6G11b, 6N5b, 6O5b, 6P3b, 6Q3b, 6S6a, 6V1b, 8K1a, 8L1a, 8M1a, 8N1a, 8O1a, 8P1a, 8Q1a, and 8R1a for analysis of Fe, Mn, Al, Ca, Mg, Na, K, P, Si, Zr, Cu, Zn, As, Ti, Se, Cd, and Pb, respectively.

8. Calculations

8.1 Data are transferred as an ASCII file from the ICP computer onto a 3.5-in floppy disk via “Report Writer” in the TJA software ThermoSpec, Version 5.06.

8.2 On a MS–DOS based PC computer, import the ASCII file of ICP data into the DOS editor and strip off unnecessary headers and data from standards. Save the file after editing, renaming using a format that can be imported into LOTUS, e.g., rename to .wk3 file for LOTUS 123, Version 3.1.

8.3 Import the file into an established total analysis spreadsheet in LOTUS 123. The spreadsheet has columns for sample number, soil fraction digested, soil weight, concentration of each element in ppm, and the calculated elemental percent. Each line of elemental data for a sample is imported as a single data string.

8.4 Parse the components of each data string into separate columns. Rearrange the data set in order to have all elemental values on a single line for a particular sample. Move the data into the correct columns of the spreadsheet.

8.5 Insert values for elements requiring dilution into the original line of sample data and replace all negative values with zero.

8.6 Input sample weights, or if possible, import sample weights (dried soil weights) from the ASCII file generated by computer attached to balance via RS-232.

8.7 Calculate the percent of an element in the soil from ppm in solution as shown in the Si example as follows:

Si (ppm) in solution = 75.2 ppm (75.2 µg/mL)

Volume extract = 100 mL

Sample weight (110 °C) = 100.0 mg

Calculate as follows:

$$\% \text{ Si} = 75.2 \text{ µg mL}^{-1} \times 100 \text{ mL} \times (1 \text{ g} / 10^6 \text{ µg}) \times (1 / 0.1 \text{ g soil}) \times 100 = 7.52 \%$$

8.8 The fraction digested needs to be identified with each sample. Use proper SSL database abbreviations.

8.9 Delete the Na and P data for clay samples dispersed in sodium hexametaphosphate.

8.10 Prepare the file to send to CMS. Save the file as an unformatted ASCII file using LOTUS.

8.11 Enter data for Si, Al, Fe, Mg, Mn, K, Ti, Ca, Zr, P, and Na into the SSL CMS database on a 110 °C weight basis as percent of the element in the fraction digested. Data are converted to the oxide form on the data sheet.

8.12 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

Calculate percent Si in SiO_2 as follows:

Si (%) = (28.09/60.09) x 100 = 46.7 %

There is 46.7 percent Si in SiO_2. To convert from percent Si to percent Si oxide (SiO_2) in the soil, divide the percent Si by 0.467 or multiply by the inverse of this value. The following table lists the element, the oxide form, and the elemental percent in the oxide form.

Element Form	Oxide	Elemental %
Si	SiO_2	46.7
Al	Al_2O_3	52.9
Fe	Fe_2O_3	69.9
Mg	MgO	60.3
Mn	MnO	77.4
K	K_2O	83.0
Ti	TiO_2	59.9
Ca	CaO	71.5
Zr	ZrO_2	74.0
P	P_2O_5	43.6
Na	Na_2O	74.2

9. Report

Data are reported as percent to the nearest tenth for Fe, Al, Mg, Na, K, and Si; to the nearest hundredth for Mn, Ca, P, and Ti; and to the nearest thousandth for Zr. The remaining trace elements (Cu, Zn, As, Se, Cd, and Pb) are reported in mg kg^{-1} (ppm).

10. Precision

The mean, standard deviation, and C.V. are calculated for each element for both the NIST standard and the SSL reference standard.

11. References

Bain, D.C., and B.F.L. Smith. 1994. Chemical analysis. *In* M.J. Wilson (ed.) Clay mineralogy: Spectroscopic and chemical determinative methods. pp. 300–332. Chapman and Hall, Inc. London, England.

Bernas, B. 1968. A new method for decomposition and comprehensive analysis of silicates by atomic absorption spectrometry. Anal. Chem. 40:1682–1686.

Sawhney, B.L., and D.E. Stilwell. 1994. Dissolution and elemental analysis of minerals, soils, and environmental samples. *In* J.E. Amonette and L.W. Zelazny (eds.) Quantitative methods in soil mineralogy. pp. 49–82. Soil Sci. Soc. Am. Miscellaneous Publ. Madison, WI.

Washington, H.S. 1930. The chemical analysis of rocks. 4th ed. John Wiley and Sons, Inc., New York, NY.

Surface Area (7D)
Ethylene Glycol Monoethyl Ether (EGME) Retention (7D2)

1. Application

Surface area determines many physical and chemical properties of materials. Water retention and movement, cation exchange capacity, pesticide adsorption, and many biological processes are closely related to specific surface (Carter et al., 1986). Soils vary widely in their reactive surface area because of differences in mineralogical and organic composition and in their particle-size distribution (Carter et al., 1965). Specific surface, defined as surface area per unit mass of soil, is usually expressed in units of $m^2\ g^{-1}$ or $cm^2\ g^{-1}$ soil. Specific surface has been measured for several clays, e.g., 810 $m^2\ g^{-1}$ for smectite and 20 to 40 $m^2\ g^{-1}$ for kaolinite and mica.

2. Summary of Method

Ethylene glycol monoethyl ether (EGME) retention is a surface-area determination. A soil sample is dried over phosphorus pentoxide (P_2O_5). The sample is saturated with EGME. A monomolecular layer of EGME is established by desorbing the EGME by vacuum over EGME-saturated $CaCl_2$. The solvate of $CaCl_2$ and EGME helps to maintain an EGME vapor pressure in the desiccator which results in the formation of a monomolecular layer of EGME on sample surfaces.

The weight of a monomolecular layer of EGME on the sample is determined by weighing the dried sample. EGME is determined by weighing the sample and sample plus EGME (Carter et al., 1965). The SSL determines EGME retention by method 7D2. The SSL reports EGME retention as mg EGME per g of soil to the nearest mg on a <2-mm base.

3. Interferences

The loss or contamination of sample and the variation in sample weight may cause erroneous results. Handle the weighing vessels with finger cots or tongs

to prevent vessel contamination and the resulting weighing errors. High relative humidity in the laboratory may result in high moisture absorption by sample.

4. Safety

Wear protective clothing (e.g., coats, aprons, and gloves) and eye protection (e.g., face shields, goggles, or safety glasses) when handling reagents and working with vacuum desiccators. Follow standard laboratory safety procedures in handling reagents and vacuum devices. The P_2O_5 is corrosive and reacts violently with water. Use caution in cleaning P_2O_5 spills. The EGME is combustible and harmful if swallowed, inhaled, or absorbed through the skin. Keep samples and desiccators with EGME under fume hood at all times.

5. Equipment

5.1 Electronic balance, ±0.1-mg sensitivity, Mettler AE 160

5.2 Vacuum desiccator, 250 mm, Nalgene No. 5310, with desiccator plate, 230 mm

5.3 Laboratory vacuum or vacuum pump, 0.65 to 0.75 bars

5.4 EGME trap, anhydrous $CaCl_2$ in a large tube between desiccator and vacuum source

5.5 Syringe, polypropylene, 3 mL

5.6 Weighing bottle, cylindrical, low form, 50 x 30 mm

6. Reagents

6.1 Ethylene glycol monoethyl ether (EGME), reagent

6.2 Phosphorus pentoxide (P_2O_5), anhydrous

6.3 Calcium chloride ($CaCl_2$), pellets, 40 mesh, reagent grade

7. Procedure

7.1 Dry 3 to 5 g of <2-mm, air-dry soil in a weighing bottle in a vacuum desiccator over P_2O_5 for 2 days.

7.2 Prepare solvated $CaCl_2$ by weighing 100 g oven-dried $CaCl_2$, without cooling, into a large beaker. Add 20 g EGME and mix by stirring. Transfer to a desiccator in which EGME-saturated samples equilibrate.

7.3 Weigh the P_2O_5-dried soil sample to the nearest 0.1 mg. When working outside the desiccator, cover the sample to avoid moisture adsorption from the atmosphere.

7.4 Use a 3-mL syringe to saturate the soil with EGME. Add 5 drops in excess of saturation.

7.5 Place the uncovered, EGME-soil mixture in a vacuum desiccator over solvated $CaCl_2$. Use a laboratory vacuum of 0.65 to 0.75 bar pressure.

7.6 Loosely cover the tops of weighing bottles with a piece of aluminum foil that is smaller than the inside diameter of desiccator.

7.7 Apply suction for 16 to 24 h.

7.8 Carefully release the suction. Remove weighing bottles and weigh the EGME-soil mixture.

7.9 If a 3-g sample is used, the difference between the EGME-soil mixture and P_2O_5-dry soil is ≈10 mg EGME/g P_2O_5-dry soil. When this difference is <10 mg, reduce the vacuum time to 1 h day^{-1} and weigh twice daily.

7.10 Repeat the vacuum and weighing procedure until a constant weight is attained. Constant weight is defined as three successive daily weighings within 1 mg of EGME per gram P_2O_5-dry soil. When a constant weight is attained, make calculations.

8. Calculations

8.1 The EGME retention is calculated as follows:

$$\text{Retention of EGME (mg g}^{-1}) = (Wt_1 - Wt_2) \times (1000 / Wt_3)$$

where:

Wt_1 = Soil weight with monomolecular layer of EGME + Tare weight of bottle

Wt_2 = Soil weight after drying with P_2O_5 + Tare weight of bottle

Wt_3 = Soil weight after drying with P_2O_5 − Tare weight of bottle

1000 = Conversion factor (mg g^{-1})

The surface area in units of mg EGME per g of soil is converted to m^2 g^{-1}, the convention commonly used in clay mineralogy. The conversion is as follows:

$$\text{Surface area (m}^2\ \text{g}^{-1}) = (\text{EGME retention (mg g}^{-1})) / 0.286$$

where:

0.286 = Conversion factor (mg EGME m^{-2})

The constant, 0.286, is the amount of EGME (mg) that is required to cover a m^2 of clay surface with a monomolecular layer (Carter et al., 1986). This value is calculated from the measured value of 231.7 mg EGME per g of pure montmorillonite assumed to have 810 m^2 g^{-1} on the basis of other measurements.

9. Report

Report EGME as mg EGME per g of soil to the nearest mg.

10. Precision

Precision data are not available for this procedure. Two quality control checks, a high and a low standard, are routinely analyzed in EGME. The mean (mg EGME per g soil), standard deviation, and C.V. for the quality control check sample are as follows:

	Mean	n	Std. Dev.	C.V.
High Std	109.0	10	7.4	7.3
Low Std.	37.5	10	0.64	4.8

11. References

Carter. D.L., M.D. Heilman, and C.L. Gonzalez. 1965. Ethylene glycol monoethyl ether for determining surface area of silicate minerals. Soil Sci. 100:356–360.

Carter, D.L., M.M. Mortland, and W.D. Kemper. 1986. Sampling. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:413–423.

MISCELLANEOUS (8)

Ratios and Estimates (8D)
To Noncarbonate Clay (8D2)

Divide the CEC-7 (method 5A8c), extractable Fe (method 6C2), or 15-bar water retention (method 4B2a or 4B2b) by the noncarbonate clay percentage. Noncarbonate clay is determined by subtracting the carbonate clay (method 3A1d or 3A2d) from total clay (method 3A1 or 3A2).

Ratios and Estimates (8D)
Ca to Mg (Extractable) (8D3)

Divide extractable Ca^{2+} (method 6N2) by extractable Mg^{2+} (method 6O2).

Ratios and Estimates (8D)
Estimated Clay Percentage (8D4)

For most soils, clay percentage can be approximated as 2.5 x 15-bar water percentage (method 4B2a or 4B2b). Use caution in applying this factor to any particular situation, especially if organic matter or other amorphous material is present in significant quantities.

Ratios and Estimates (8D)
Estimated Total Salt (8D5)

Use the charts and graphs available in U.S. Salinity Laboratory Staff (1954) to estimate total salt content from the electrical conductivity (EC_s) of the saturation extract (method 8A3a). The essential relations are summarized in the equations as follows:

$$\text{Log total salt in soil (ppm)} = 0.81 + 1.08 \times \text{Log ECs (mmhos cm}^{-1}\text{)} + \text{Log SP}$$

where:

ECs = Electrical conductivity of saturation extract

SP = Saturation percentage of saturation extract

$$\text{Total salt in soil (\%)} = \text{Total salt (ppm)} \times 10^{-4}$$

These equations are applicable to saturation extracts with an EC_s <20 mmhos cm^{-1}. Deviations occur at higher salt concentrations.

Ratios and Estimates (8D)
Iron Plus Aluminum, Pyrophosphate Extractable to Dithionite-Citrate Extractable (8D6)

Divide the sum of the pyrophosphate-extractable Fe plus Al (methods 6C8a and 6G10a, respectively) by the sum of dithionite-citrate-extractable Fe plus Al (methods 6C2 and 6G7, respectively). Pyrophosphate and dithionite-citrate extractable Fe and Al are former criteria for spodic placement (Soil Survey Staff, 1975).

Ratios and Estimates (8D)
Index of Accumulation (8D7)

Subtract ½ the clay percentage (method 3A1 or 3A2) of a subhorizon from the CEC at pH 8.2 (method 5A3a) and multiply the remainder by the thickness of subhorizon (cm). The combined index of accumulation of amorphous material is a former criterion for spodic placement (Soil Survey Staff, 1975).

References

Soil Survey Staff. 1975. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys. USDA–SCS Agric. Handb. 436. U.S. Govt. Print. Office, Washington, DC.

U.S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. L.A. Richards (ed.) U.S. Dept. of Agric. Handb. 60. U.S. Govt. Print. Office, Washington, DC.

Use Table 1 with the SSL preparation methods 1B1, 1B2, 1B5, 1B6, and 1B7. Gravel codes are also defined in Table 1. In the “Code” column, “Char” refers to characterization sample. Laboratory preparation and >2-mm porosity are defined in footnotes on laboratory data sheet.

Table 1.—Laboratory Preparation Codes and Procedural Summaries.

Code		Laboratory Preparation
Char	>2 mm	
S	Blank	Weigh sample at field-moisture content and record weight. Air-dry, weigh, and record weight. Sieve >2-mm fractions, weigh, record weights, and discard. Report all analytical results on <2-mm basis. Refer to method 1B1, Standard Air-dry.

Code		Laboratory Preparation
Char	**>2 mm**	
S	P	Lab preparation is same as S-blank. However, report clod parameters and Cm (correction factor for >2-mm content moist soil) on an whole-soil basis. Refer to method 1B1, Standard Air-dry.
N	Blank	Lab preparation is same as S-blank except do not record the weight of the >2-mm fraction. All analytical results are reported on a <2-mm basis. Refer to method 1B1, Standard Air-dry.
M	Blank	Lab preparation is same as S-blank except sieve <2-mm moist subsample for 15-bar moist analysis. Use <2-mm air-dry soil for all other analyses. Report all analytical results on <2-mm basis. Refer to method 1B2, Field-moist.
S	K	Lab preparation is same as S-blank except grind the 2- to 20-mm fraction to <2 mm and keep for CO_3 analyses, etc. Report the analytical results for the ground 2- to 20-mm fraction on a 2- to 20-mm basis and all other analytical results on a <2-mm basis. Refer to method 1B5, Coarse Fragments.
S	R	Lab preparation is same as S-blank except recombine the 2- to 20-mm fraction with the <2-mm fraction and grind the entire sample to <2 mm. Report all analytical results for ground sample on a <2-mm basis. Refer to method 1B5, Coarse Fragments.
G	P	Weigh sample at field-moisture content and record weight. Air-dry, weigh, and record weight. Grind entire sample to <2 mm. Report all analytical results for ground sample on a whole-soil basis. Refer to method 1B6, Whole-soil.
W	P	Weigh sample at field-moisture content and record weight. Air-dry, weigh, and record weight. Sieve >2-mm fractions, weigh, and record weights. Recombine the >2-mm fractions with the <2-mm fraction and grind entire sample to <2 mm. Report all analytical results on a whole-soil basis. This procedure is no longer performed at the SSL.

Code		Laboratory Preparation
Char	**>2 mm**	
H	Blank	Obtain a moist whole-soil subsample for Histosol analysis. Obtain a <2-mm moist subsample for 15-bar moist analysis. Weigh remaining sample at field-moisture content and record weight. Air-dry, weigh, and record weight. Sieve >2-mm fractions, weigh, record weights, and discard. Pulverize subsample of <2-mm air-dry soil to a <80-mesh size and use for lab analyses. Use <80-mesh air-dry for all analyses except AD/OD, 15-, $^{1}/_{10}$-, and 2-bar analyses. For the AD/OD, 15-, $^{1}/_{10}$-, and 2-bar analyses, use <2-mm air-dry soil. Use <2-mm moist subsample for 15-bar moist. Report all analytical results except fabric on a <2-mm basis. Refer to method 1B7, Organic Material.
A (L)	Blank	Lab preparation is same as N-blank except pulverize subsample of <2-mm air-dry soil to a <80-mesh size and use for lab analyses. Use <80-mesh air-dry for all analyses except AD/OD and 15-bar analyses. For the AD/OD and 15-bar analyses, use <2-mm air-dry soil. All analytical results are reported on a <2-mm basis. Refer to method 1B1, Standard Air-dry.

Gravel codes

P = Porous >2-mm material that is considered soil is used for clod or core measurements.

V = Volume estimate is used to calculate the weight percentage of a >2-mm fraction. If that fraction is porous (P), code the samples with “P” rather than with “V”.

OBSOLETE METHODS SECTION IV: SSIR NO. 42, SOIL SURVEY LABORATORY METHODS MANUAL, VERSIONS 1.0 and 2.0 (1989 and 1992)

ION EXCHANGE ANALYSES (5)

Cation Exchange Capacity (5A)
NH_4Oac, pH 7.0 (5A8)
Automatic Extractor (CEC-7)
Steam Distillation (5A8b)

1. Application

The CEC determined with 1 *N* NH_4OAc buffered at pH 7.0 is a commonly used method and has become a standard reference to which other methods are compared (Peech et al., 1947). The advantages of using this method are that the extractant is highly buffered so that the extraction is performed at a constant, known pH (7.0) and that the $NH4^+$ on the exchange complex is easily determined.

2. Summary of Method

Displacement after washing is the basis for this procedure. The CEC is determined by saturating the exchange sites with an index cation ($NH4^+$); washing the soil free of excess saturated salt; displacing the index cation ($NH4^+$) adsorbed by the soil; and measuring the amount of the index cation ($NH4^+$). A sample is leached using 1 *N* NH_4OAc and a mechanical vacuum extractor (Holmgren et al., 1977). 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. Steam distillation and titration are used to determine the NH_4^+ adsorbed on the soil exchange complex. The CEC by NH_4OAc, pH 7 is reported in meq/100 g oven-dry soil in method 5A8b (Soil Conservation Service, 1984).

3. 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 and/or can contribute to erroneously high cation levels in the extract.

4. Safety

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses) when preparing reagents, especially concentrated acids and bases. Dispense concentrated acids and bases in a fume hood. Thoroughly wash hands after handling reagents. Use the safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids.

Ethanol is flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the vacuum extractor and the Kjeltec Auto 1030 Analyzer.

5. Equipment

5.1 Mechanical vacuum extractor, 24 place, Centurion International, Inc., Lincoln, NE

5.2 Syringes, polypropylene, disposable, 60 mL, for sample tube, extractant reservoir, and tared extraction syringe

5.3 Rubber tubing, 3.2 ID x 6.4 OD x 25.4 mm (⅛ ID x ¼ OD x 1 in) for connecting syringe barrels

5.4 Polycons, Richards Mfg. Co.

5.5 Kjeltec Auto 1030 Analyzer, Tecator, Fisher Scientific Inc.

5.6 Digestion tubes, straight neck, 250 mL

5.7 Analytical filter pulp, Schleicher and Schuell, no. 289

5.8 Plunger, modified. Remove rubber and cut plastic protrusion from plunger end.

5.9 Electronic balance, ±1-mg sensitivity

6. Reagents

6.1 Distilled deionized (DDI) water

6.2 Ammonium acetate solution (NH_4OAc), 1 *N*, pH 7.0. Add 1026 mL of glacial acetic acid (CH_3COOH) to 15 L DDI water. Add 1224 mL of conc. ammonium hydroxide (NH_4OH). Mix and cool. Dilute with DDI water to 18 L and adjust to pH 7.0 with CH_3COOH or NH_4OH.

6.3 Ethanol (CH_3CH_2OH), 95%, U.S.P.

6.4 Nessler's reagent. Add 4.56 g of potassium iodide (KI) to 30 mL DDI water. Add 5.68 g of mercuric iodide (HgI_2). Stir until dissolved. Dissolve 10 g of sodium hydroxide (NaOH) in 200 mL of DDI water. Transfer NaOH solution to a 250-mL volumetric flask and slowly add K-Hg-I solution. Dilute to volume with DDI water and thoroughly mix. Solution should not contain a precipitate. Solution can be used immediately.

6.5 Sodium chloride (NaCl), reagent, crystal

6.6 Antifoam agent, slipicone release spray, Dow Chemical Corp. Alternatively, mix equal parts of mineral oil and n-octyl alcohol.

6.7 Boric acid, 4% (w:v), with bromcresol green-methyl red indicator (0.075% bromcresol green and 0.05% methyl red), Ricca Chemical Co.

6.8 Hydrochloric acid (HCl), 0.1 *N*, standardized. Dilute 148 mL of conc. HCl in 16 L of DDI water.

6.9 NaOH, 1 *M*. Add 500 mL of 50% NaOH solution to 8 L of DDI water. Dilute to 9 L with DDI water.

7. Procedure

Extraction of Bases

7.1 Prepare sample tube by tightly compressing a 1-g ball of filter pulp into the bottom of a syringe barrel with a modified plunger.

7.2 Weigh 2.50 g of <2-mm, air-dry soil and place in sample tube. Prepare one quality control check sample per 48 samples.

7.3 Place sample tube on upper disk of the extractor and connect a tared extraction syringe. Use 25.4-mm (1 in) length rubber tubing and insert the plunger in the slot of the stationary disk of the extractor.

7.4 Use a squeeze bottle to fill sample tube to the 20-mL mark with NH_4OAc solution (≈10 mL). Thoroughly wet the sample. Let stand for at least 20 min.

7.5 Put reservoir tube on top of the sample tube. Rapidly extract the NH_4OAc solution to a 0.5- to 1.0-cm height above sample. Turn off extractor. Add ≈45 mL of NH_4OAc solution to the reservoir tube. Set extractor for an overnight (12 to 16 h) extraction.

7.6 Next morning turn off the extractor. Pull the plunger of the syringe down. Do not pull plunger from the barrel of the syringe. Carefully remove the syringe containing the extract. Leave the rubber tubing on the sample tube. Weigh each syringe containing the NH_4OAc extract to the nearest 0.01 g.

7.7 Mix the extract in each syringe by manually shaking. Fill a polycon with extract solution and discard the excess. The solution in the polycon is reserved for analyses of extracted cations (methods 6N2e, 6O2d, 6P2b, and 6Q2b).

Removal of Excess Ammonium Acetate

7.8 Return the extractor to starting position. Attach syringe to the sample tube and rinse the sides of the sample tube with ethanol from a wash bottle. Fill

the sample tube to the 20-mL mark with ethanol and let stand for 15 to 20 min.

7.9 Place reservoir tube on the sample tube. Rapidly extract the ethanol level to a 0.5- to 1.0-cm height above the sample. Turn off the extractor and add 55 to 60 mL of ethanol to the reservoir. Extract at a 45-min rate.

7.10 After the extractor has stopped, turn off the switch. Pull the plunger of the syringe down. Do not pull the plunger from the syringe barrel. Remove the syringe and discard the ethanol.

7.11 Repeat the ethanol wash.

7.12 After the second wash, collect a few drops of ethanol extract from the sample tube on a spot plate. Test for NH_4^+ by using Nessler's reagent. A yellow, red to reddish brown precipitate is a positive test. If the test is positive, repeat the ethanol wash and retest with Nessler's reagent. Repeat until a negative test is obtained.

Steam Distillation: Samples and Reagent Blanks

7.13 Remove the sample tube and transfer the sample with filter pulp to a 250-mL digestion tube. Add 6 to 7 g of NaCl to the digestion tube. Use a gentle flow of compressed air to blow the filter pulp and sample out of the syringe. Wash the tube with DDI water and use a rubber policeman to complete transfer. The amount of distilled water that is added depends on the amount that is required to complete the transfer of tube contents.

7.14 Perform the same transfer and addition of reagents for blanks as for samples.

7.15 Spray silicone antifoam agent (or 2 drops of octyl alcohol) into the digestion tubes for each of the samples and reagent blanks.

7.16 When using new reagents, e.g., boric acid, reagent blanks are distilled in 2 sets of 6, one set per Kjeltec machine. Each set of 6 is averaged and recorded on bench worksheet and manually set on each machine. During the steam distillation, the mean reagent blank titer is automatically subtracted from the sample titer.

7.17 On bench worksheet, record the normality of standardized acid, i.e., ≈0.1 *N* HCl.

7.18 Connect the tube to the distillation unit. Close the safety door. Distillation and titration are performed automatically. Record the titer in mL of titrant.

8. Calculations

$$\text{CEC (meq/100 g)} = (\text{Titer} \times N \times 100 \times \text{AD/OD}) / (\text{Weight})$$

where:

Titer = Titer of sample (mL)

N = Normality of HCl titrant

Weight = Sample weight (g)

100 = Conversion factor to 100 g basis

AD/OD = Air-dry/oven-dry ratio (method 4B5)

9. Report

Report CEC-7 in units of meq/100 g of oven-dry soil to the nearest 0.1 meq/100 g.

10. Precision

Precision data are not available for this procedure. A quality control check sample is run with every batch of 48 samples. With 113 observations of the quality control check sample, the mean, standard deviation, and C.V. for the CEC are 27.1, 0.57, and 2.1%, respectively.

11. References

Holmgren, G.G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Amer. 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. U.S. Dept. Agr. Circ. 757, 25 pp.

Soil Conservation Service. 1984. Procedures for collecting soil samples and methods of analysis for soil survey. USDA–SCS Soil Surv. Invest. Rep. No. 1. U.S. Govt. Print. Office, Washington, DC.

NH_4Cl, pH 7.0 (5A9)

Steam Distillation (5A9b)

1. Application

The CEC determined with a neutral unbuffered 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 value should be < CEC measured with a buffered solution at pH 7.0. The NH_4Cl CEC is ≈ equal to the NH_4OAc extractable bases plus the KCl extractable Al for noncalcareous soils.

2. Summary of Method

Displacement after washing is the basis for this procedure. The CEC is determined by saturating the exchange sites with an index cation ($NH4^+$); washing the soil free of excess saturated salt; displacing the index cation ($NH4^+$) adsorbed

by the soil; and measuring the amount of the index cation ($NH4^+$). A sample is leached using 1 *N* NH_4Cl and a mechanical vacuum extractor (Holmgren et al., 1977). 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. Steam distillation and titration are used to determine the NH_4^+ adsorbed on the soil exchange complex. The CEC by NH_4Cl is reported in meq/100 g oven-dry soil in method 5A9b (Soil Conservation Service, 1984).

3. 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 and/or can contribute to erroneously high cation levels in the extract.

4. Safety

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses) when preparing reagents, especially concentrated acids and bases. Dispense concentrated acids and bases in a fume hood. Thoroughly wash hands after handling reagents. Use the safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids.

Ethanol is flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the vacuum extractor and the Kjeltec Auto 1030 Analyzer.

5. Equipment

5.1 Mechanical vacuum extractor, 24 place, Centurion International, Inc., Lincoln, NE

5.2 Syringes, polypropylene, disposable, 60 mL, for sample tube, extractant reservoir, and tared extraction syringe

5.3 Rubber tubing, 3.2 ID x 6.4 OD x 25.4 mm (⅛ ID x ¼ OD x 1 in), for connecting syringe barrels

5.4 Polycons, Richards Mfg. Co.

5.5 Kjeltec Auto 1030 Analyzer, Tecator, Fisher Scientific Inc.

5.6 Digestion tubes, straight neck, 250 mL

5.7 Analytical filter pulp, Schleicher and Schuell, no. 289

5.8 Plunger, modified. Remove rubber and cut plastic protrusion from plunger end.

5.9 Electronic balance, ±1-mg sensitivity

6. Reagents

6.1 Distilled deionized (DDI) water

6.2 Ammonium chloride solution (NH_4Cl), 1 *N*. Dissolve 535 g of NH_4Cl reagent in DDI water and dilute to 10 L.

6.3 Ethanol (CH_3CH_2OH), 95%, U.S.P.

6.4 Nessler's reagent. Add 4.56 g of potassium iodide (KI) to 30 mL DDI water. Add 5.68 g of mercuric iodide (HgI_2). Stir until dissolved. Dissolve 10 g of sodium hydroxide (NaOH) in 200 mL DDI water. Transfer NaOH solution to a 250-mL volumetric flask and slowly add K-Hg-I solution. Dilute to volume with DDI water and thoroughly mix. Solution should not contain a precipitate. Solution can be used immediately.

6.5 Sodium chloride (NaCl), reagent, crystal

6.6 Antifoam agent, slipicone release spray, Dow Chemical Corp. Alternatively, mix equal parts of mineral oil and n-octyl alcohol.

6.7 Boric acid, 4% (w:v), with bromcresol green-methyl red indicator (0.075% bromcresol green and 0.05% methyl red), Ricca Chemical Co.

6.8 Hydrochloric acid (HCl), 0.1 *N*, standardized. Dilute 148 mL of conc. HCl in 16 L of DDI water.

6.9 NaOH, 1 *M*. Add 500 mL of 50% NaOH solution to 8 L of DDI water. Dilute to 9 L with DDI water.

7. Procedure

Extraction of Bases

7.1 Prepare sample tube by tightly compressing a 1-g ball of filter pulp into the bottom of a syringe barrel with a modified plunger.

7.2 Weigh 2.50 g of <2-mm, air-dry soil and place in sample tube. Prepare one quality control check sample per 48 samples.

7.3 Place sample tube on upper disk of the extractor and connect a tared extraction syringe. Use 25.4-mm (1 in) length rubber tubing and insert the plunger in the slot of the stationary disk of the extractor.

7.4 Use a squeeze bottle to fill sample tube to the 20-mL mark with NH_4Cl solution (~10 mL). Thoroughly wet the sample. Let stand for at least 20 min.

7.5 Put reservoir tube on top of the sample tube. Rapidly extract the NH_4Cl solution to a 0.5- to 1.0-cm height above sample. Turn off extractor. Add ≈45 mL of NH_4Cl solution to the reservoir tube. Set extractor for an overnight (12 to 16 h) extraction.

7.6 Next morning turn off the extractor. Pull the plunger of the syringe down. Do not pull plunger from the barrel of the syringe. Carefully remove the syringe containing the extract. Leave the rubber tubing on the sample tube. Weigh each syringe containing the NH_4Cl extract to the nearest 0.01 g.

7.7 Mix the extract in each syringe by manually shaking. Fill a polycon with extract solution and discard the excess. The solution in the polycon is reserved for analyses of extracted cations (methods 6N2e, 6O2d, 6P2b, and 6Q2b).

Removal of Excess Ammonium Chloride

7.8 Return the extractor to starting position. Attach syringe to the sample tube and rinse the sides of the sample tube with ethanol from a wash bottle. Fill the sample tube to the 20-mL mark with ethanol and let stand for 15 to 20 min.

7.9 Place reservoir tube on the sample tube. Rapidly extract the ethanol level to a 0.5- to 1.0-cm height above the sample. Turn off the extractor and add 55 to 60 mL of ethanol to the reservoir. Extract at a 45-min rate.

7.10 After the extractor has stopped, turn off the switch. Pull the plunger of the syringe down. Do not pull the plunger from the syringe barrel. Remove the syringe and discard the ethanol.

7.11 Repeat the ethanol wash.

7.12 After the second wash, collect a few drops of ethanol extract from the sample tube on a spot plate. Test for NH_4^+ by using Nessler's reagent. A yellow, red to reddish brown precipitate is a positive test. If the test is positive, repeat the ethanol wash and retest with Nessler's reagent. Repeat until a negative test is obtained.

Steam Distillation: Samples and Reagent Blanks

7.13 Remove the sample tube and transfer the sample with filter pulp to a 250-mL digestion tube. Add 6 to 7 g of NaCl to the sample. Use a gentle flow of compressed air to blow the filter pulp and sample out of the syringe. Wash the tube with DDI water and use a rubber policeman to complete transfer. The amount of distilled water that is added depends on the amount that is required to complete the transfer of tube contents.

7.14 Perform the same transfer and addition of reagents for blanks as for samples.

7.15 Spray silicone antifoam agent (or 2 drops of octyl alcohol) into the digestion tubes for each of the samples and reagent blanks.

7.16 When using new reagents, e.g., boric acid, reagent blanks are distilled in 2 sets of 6, one set per Kjeltec machine. Each set of 6 is averaged and recorded on bench worksheet and manually set on each machine. During the steam distillation, the mean reagent blank titer is automatically subtracted from the sample titer.

7.17 On bench worksheet, record the normality of standardized acid, i.e., ≈0.1 *N* HCl.

7.18 Connect the tube to the distillation unit. Close the safety door. Distillation and titration are performed automatically. Record the titer in mL of titrant.

8. Calculations

CEC (meq/100 g) = (Titer x *N* x 100 x AD/OD) / (Weight)

where:

Titer = Titer of sample (mL)

N = Normality of HCl titrant

Weight = Sample weight (g)

100 = Conversion factor to 100 g basis

AD/OD = Air-dry/oven-dry ratio (method 4B5)

9. Report

Report neutral salts CEC in units of meq/100 g of oven-dry soil to the nearest 0.1 meq/100 g.

10. Precision

Precision data are not available for this procedure. A quality control check sample is run with every batch of 48 samples. With 19 observations of the quality control check sample, the mean, standard deviation, and C.V. for the CEC are 26.0, 0.37, and 1.4%, respectively.

11. References

Holmgren, G.G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Amer. 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. U.S. Dept. Agr. Circ. 757, 25 pp.

Soil Conservation Service. 1984. Procedures for collecting soil samples and methods of analysis for soil survey. USDA–SCS Soil Surv. Invest. Rep. No. 1. U.S. Govt. Print. Office, Washington, DC.

CHEMICAL ANALYSES (6)

Total Carbon (6A)
Dry Combustion (6A2)
LECO CR-12 Carbon Analyzer (6A2d)

1. Application

Total C in soils 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 found with carbonate minerals. The organic C in mineral soils generally ranges from 0 to 12%.

Total C is quantified by two basic methods, i.e., wet or dry combustion. The SSL uses dry combustion. 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. Organic C also can be determined directly (method 6A1c). The inorganic C should be equivalent to carbonate values measured by CO_2 evolution with strong acid (Nelson and Sommers, 1982).

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, 1975).

2. Summary of Method

An 80-mesh soil sample is oxidized at high temperatures. The released gases are scrubbed, and the CO_2 in the combustion gases is measured by using an infrared detector. Percent total C is reported on an oven-dry soil basis.

3. Interferences

This procedure simultaneously measures inorganic and organic C.

4. Safety

Wear protective clothing and safety glasses. Magnesium perchlorate may form explosive mixtures. Magnesium perchlorate may contain traces of perchloric acid, which remain from manufacturer's operations. This acid is anhydrous because of the strong desiccating capability of the salt. Avoid prolonged contact with oxidizable material or material capable of forming unstable perchlorate esters or salts. Remove magnesium perchlorate by using an excess of water to thoroughly dilute the material.

The use of high temperatures in the oxidation of samples requires that extreme caution be used to prevent burns and fires. Follow standard laboratory procedures when handling compressed gases. Oxygen is highly flammable.

Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the carbon analyzer.

5. Equipment

5.1 Carbon analyzer, Leco Model CR-12 781-600 Carbon System, Leco Corp., St. Joseph, MI

5.2 Data transmit card, part no. 772-573, Leco Corp., St. Joseph, MI

5.3 Combustion boats, part no. 529-203, Leco Corp., St. Joseph, MI

5.4 Single-stage regulator, oxygen service, part no. E11-W-N115Box, Air Products and Chemicals, Inc., Box 538, Allentown, PA 18105

5.5 Electronic balance, ±1-mg sensitivity

6. Reagents

6.1 Anhydrone, anhydrous magnesium perchlorate, granular

6.2 Glass wool

6.3 Compressed oxygen, >99.5% @ 30 psi

6.4 Calcium carbonate, $CaCO_3$, reagent grade

7. Procedure

7.1 Use a fine-ground 80-mesh, air-dry soil.

7.2 Weigh sample in a tared combustion boat. The sample size is dependent upon the C content. The product of sample weight (g) multiplied by C percentage should not be >10%. In most cases, the sample size is 1.00 g, unless the C content is >10%.

7.3 Refer to the manufacturer's manual for operation of carbon analyzer.

7.4 Combust sample in an O_2 atmosphere in which the C is oxidized to CO_2. Moisture and dust are removed by the instrument, and the CO_2 gas is then measured by a solid state infrared detector. The microprocessor formulates the analytical results (C_i) by combining the outputs of the infrared detector and the system ambient sensors with pre-programmed calibration, linearization and weight compensation factors. Analytical results are displayed and printed on the control console.

8. Calculations

$C\ (\%) = C_i \times AD/OD$

where:

C (%) = C (%), oven-dry basis

C_i = C (%) instrument

AD/OD = air-dry/oven-dry ratio (method 4B5)

9. Report

Report total C percentage on an oven-dry basis to the nearest 0.1%.

10. Precision

Precision data are not available for this procedure. A quality control check sample is included in every batch of 10 samples. For 41 observations of the quality control check sample, the mean, standard deviation, and C.V. for total carbon are 11.38, 0.062, and 5.5%, respectively.

11. References

Nelson, D.W., and L.E. Sommers. 1982. Total carbon, organic carbon, and organic matter. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:539–579.

Soil Survey Staff. 1975. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys. USDA–SCS Agric. Handb. 436. U.S. Govt. Print. Office, Washington, DC.

Nitrogen (6B)

Kjeldahl Digestion II (6B3)

Ammonia Steam Distillation, Automatic Titrator (6B3a)

1. Application

The total N content of the soil may range from <0.02% in subsoils, 2.5% in peats, and 0.06 to 0.5% in surface layers of many cultivated soils (Bremmer and Mulvaney, 1982). The total N data may 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 between 10 to 12. Variations in the C:N ratio may serve as an indicator of the amount of soil inorganic N. Uncultivated soils usually have higher C:N ratios than do cultivated soils.

Soils with 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). Since the organic C of many soils diminishes with depth while 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.

2. Summary of Method

A soil sample is digested using the Kjeldahl technique. The digest is made alkaline, the steam is distilled to release NH_4^+-N, and the NH_4^+-N is complexed with boric acid. The complexed NH_4^+-N is titrated with HCl, and the total N is calculated against a reagent blank (Soil Conservation Service, 1984).

3. Interferences

The total N that is measured by the Kjeldahl method does not distinguish among the types of N that are present in the soil. Practically all of the N is measured, but some forms of N are not recovered. Generally, soils have small amounts of N in the nonrecoverable forms, i.e., NO_3^- and NO_2^-. Soils with significant amounts of NO_3^- or NO_2^- are usually saline. The anion analysis of the saturated paste extracts measures NO_3^- and NO_2^- (methods 6M1c and 6W1a, respectively).

The most significant error in the Kjeldahl method is the heating of the digestion mixture over 400 °C. Loss of N occurs when the temperature of the digestion is >400 °C (Bremmer and Mulvaney, 1982).

4. Safety

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses) when handling acids and bases. Use heat resistant gloves when handling hot digestion tubes during digestion and steam distillation. Use the provided safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids. Digestion blocks are used at high temperatures, i.e., 250 and 400 °C. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Use the fume hood and fume aspiration devices to control and dispose of the acid fumes when digesting samples.

Boric acid is toxic and must not be ingested. Hengar granules contain Se which is toxic. Concentrated H_2SO_4 reacts violently with water and must be handled with caution. The 50% NaOH solution is very corrosive. Follow prudent laboratory safety precautions when handling these chemicals. Follow the manufacturer's safety precautions when using the Kjeltec Auto 1030 Analyzer.

5. Equipment

5.1 Electronic balance, ±0.001-g sensitivity

5.2 Digestion tubes, 250 mL, with constricted neck, Ace Glass Co., Inc.

5.3 Digestion blocks, 250 and 400 °C

5.4 Dispenser, Zippette, 30 mL or equivalent, for conc. sulfuric acid (H_2SO_4), Brinkmann Instruments Inc.

5.5 Kjeltec Auto 1030 Analyzer, Tecator, Fisher Scientific Inc.

6. Reagents

6.1 Distilled water

6.2 Distilled deionized (DDI) water

6.3 Hydrochloric acid (HCl), conc., 12 *N*

6.4 Sodium hydroxide (NaOH), 50% (w:v), reagent

6.5 Hengar granules (selenized)

6.6 Digestion salt mixture. Mix 1000 g of potassium sulfate powder, 55 g of ferrous sulfate powder (anhydrous), and 32 g of copper II sulfate powder (anhydrous) in a tumbling mill for at least 30 min.

6.7 Antifoam, silicone spray bottle, Slipicone release spray, Dow Chemical Corp.

6.8 Boric acid, 4% (w:v), with bromcresol green-methyl red (0.075% bromcresol green and 0.05% methyl red) indicator, Ricca Chemical Co.

6.9 HCl, 0.1 *N*, standardized. Dilute 148 mL of conc. HCl in 16 L of DDI water.

6.10 Sucrose

7. Procedure

Kjeldahl Digestion of Sample

7.1 Weigh 3.000 g of <2-mm, air-dry soil into a 250-mL digestion tube. Refer to Table 1 for sample size.

7.2 Prepare 3 to 5 reagent blanks in every batch of 20 analyses. Reagent blanks contain 0.5 g of sucrose plus all reagents used in sample analysis, i.e., 12 mL of H_2SO_4, 4.5 g of digestion salt mixture, and 1 or 2 Hengar granules. Samples do not receive the 0.5 g of sucrose. Reagent blanks are run as samples and are not automatically subtracted during distillation procedure.

7.3 Use a dispenser to add 5 mL of distilled water to sample tube. Shake the tube to wet the sample.

7.4 Use a dispenser to add 12 mL of conc. H_2SO_4 to sample.

7.5 Allow sample to stand overnight.

7.6 Use a calibrated scoop to add 4.5 g of digestion salt mixture to sample.

7.7 Add 1 or 2 Hengar granules to sample.

7.8 Preheat one digestion heating block to 250 °C and the other to 400 °C.

7.9 Place the tube in the 250 °C block, attach a fume aspirator, and digest for at least 30 min.

7.10 Remove the tube, place in the 400 °C block, and digest sample for 1 h.

7.11 Remove the tube, place on a cooling board, and allow sample to cool for at least 15 min.

7.12 Remove the aspirator. Add 50 mL of distilled water.

Table 1.—Sample Size for Total N Based on Volume of Titrant ($FeSO_4$) Used in Organic C Analysis (method 6A1c).

Fe_2SO_4	Sample Size
(mL)	*(g)*
>6.00	3.0
4.00 to 5.00	2.0
3.00 to 4.00	1.5
<2.00	1.0

If >10.00 mL of $K_2Cr_2O_7$ (method 6A1c) is used and/or sample size is <1.00 g, then divide the volume of $FeSO_4$ by 2 and then use Table 1. To obtain a representative sample, do not use a sample size <0.5 g for total N analysis.

Ammonia Steam Distillation, Automatic Titrator

7.13 Spray silicone antifoam solution (or 2 drops of octyl alcohol) into the digestion tube and connect to the distillation unit.

7.14 Close the safety door.

7.15 Distillation and titration are performed automatically.

7.16 On bench worksheet, record the mL that are titrated for samples and reagent blanks. On bench worksheet, also record the normality of standardized HCl.

8. Calculations

$$N\ (\%) = [(Titer_{sample} - Titer_{blank}) \times N \times 1.4 \times AD/OD] / (Sample\ Weight)$$

where:

$Titer_{sample}$ = Titer of sample (mL)

$Titer_{blank}$ = Average titer of reagent blank (mL)

N = Normality of HCl titrant solution

1.4 = Conversion factor

AD/OD = Air-dry/oven-dry ratio (method 4B5)

9. Report

Report total N as a dimensionless value to the nearest 0.001 unit on an oven-dry basis.

10. Precision

Precision data are not available for this procedure. For 105 observations of the quality control check sample, the mean, standard deviation, and C.V. for total N are 0.143, 0.004, and 2.7%, respectively.

11. References

Bremmer, J.M., and C.S. Mulvaney. 1982. Nitrogen—Total. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:595–624.

Nommik, H., and K. Vahtras. 1982. Retention and fixation of ammonium and ammonia in soils. *In* F.J. Stevenson (ed.) Nitrogen in agricultural soils. Agronomy 22:123–171.

Soil Conservation Service. 1984. Procedures for collecting soil samples and methods of analysis for soil survey. USDA–SCS Soil Surv. Invest. Rep. No. 1. U.S. Govt. Print. Office, Washington, DC.

Young, J.L., and R.W. Aldag. 1982. Inorganic forms of nitrogen in soil. *In* F.J. Stevenson (ed.) Nitrogen in agricultural soils. Agronomy 22:43–66.

Iron, Aluminum, and Potassium (6C, 6G, and 6Q)

HF Dissolution (6C7, 6G11, and 6Q3)

Atomic Absorption (6C7a, 6G11a, and 6Q3a)

1. Application

Historically, elemental analysis was developed for the analysis of rocks and minerals (Washington, 1930). The elemental analysis of soils, sediments, and rocks necessitates their decomposition into soluble forms. Hydrofluoric acid (HF) is efficient in the digestion and dissolution of silicate minerals for elemental decomposition. Elemental concentrations of Fe, Al, and K are determined by atomic absorption using 100 mg of clay suspension contained in a closed vessel with boric acid (H_3BO_3) to neutralize excess acid (Berdanier, Lynn, and Threlkeld, 1978; Soil Conservation Service, 1984).

2. Summary of Method

To 100 mg of clay suspension (method 7A2i), 5 mL of HF acid are added. The solution is heated, cooled, and 2 to 3 g of H_3BO_3 are added to neutralize excess acid. The solution is diluted to 100 mL, allowed to stand overnight, and 20 mL are decanted (method 7C3). The concentrations of Fe, Al, and K are determined by

atomic absorption (AA) in methods 6C7a, 6G11a, and 6Q3a, respectively. Data are reported in method 7C3.

3. Interferences

There are four types of interferences (matrix, spectral, chemical, and ionization) in AA analyses of these cations. These interferences vary in importance, depending upon the particular analyte selected.

The stable matrix system (HBF_4-H_3BO_3-ionic constituents of silicates) provides a suitable salt-free single matrix that greatly diminishes the chemical ionization, matrix, and instrumental interferences for AA determinations. One of the principal advantages of this technique is that all elements may be determined from a single sample solution (Lim and Jackson, 1982).

4. Safety

There are no significant hazards to analyst by this procedure. Wear protective clothing, e.g., coats and aprons. Follow standard laboratory practices when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene gas is highly flammable. Follow the manufacturer's safety precautions when using the AA.

5. Equipment

5.1 Atomic Absorption spectrophotometer (AA), Perkin-Elmer Corp., Norwalk, CT

5.2 Autosampler, AS-50, Perkin-Elmer Corp., Norwalk, CT

5.3 Microcomputer, 7500 Professional Computer, Perkin-Elmer Corp., Norwalk, CT

5.4 Dot matrix printer, P-132, Interdigital Data Systems, Inc.

5.5 Digital diluter/dispenser, product no. 100004, with hand probe and actuator, product no. 230700, Hamilton Co., P.O. box 10030, Reno, NV, 89510

5.6 Syringes, 10,000 and 1000 µL, 1001 DX and 10110-TEL LL gastight, Hamilton Co., P.O. Box 10030, Reno, NV, 89510

5.7 Centrifuge tubes, polystyrene, 15 mL, conical bottom, graduated, part no. 2087, for sample dilution and sample changer, Becton Dickinson Labware, Becton Dickinson and Co., 2 Bridgewater Lane, Lincoln, Park, NJ 07035

5.8 Containers, polypropylene or teflon

6. Reagents

6.1 Distilled Deionized (DDI) water

6.2 Sodium chloride (NaCl) solution, 1143 ppm Na. Dissolve 5.81 g of NaCl in 2 L of DDI water.

6.3 Boric acid, H_2BO_3

6.4 Hydrofluoric acid (HF) solution, 2.47 *N*. Fill a polyethylene volumetric flask ⅓ full with DDI water. In hood, slowly and carefully add 49.36 g of HF. Slowly and carefully add 20 g of H_2BO_3. Hot reaction. May not completely dissolve. Make to 1-L volume with DDI water. Store HF solution in refrigerator. Use HF solution as reagent blank.

6.5 Fe stock solution, 1000 ppm. Commercial. Weigh 1.0000 g of Fe wire, dissolve in HCl, and make to 1-L volume with DDI water. Store in polypropylene container.

6.6 Al stock solution, 1000 ppm. Commercial. Weigh 1.0000 g of Al wire, dissolve in HCl, and make to 1-L volume with DDI water. Store in polypropylene container.

6.7 K stock solution, 50 meq L^{-1}. Dissolve 3.7279 g of KCl in 1 L of DDI. Store in polypropylene container.

6.8 Fe standard, 200 ppm. To 50 ml of Fe stock solution, add 12.34 ml of HF solution and 5 g of H_2BO_3. Make to 250-ml volume with DDI water. Store in polypropylene container.

6.9 Al standard, 200 ppm. To 50 ml of Al stock solution add 12.34 ml of HF solution and 5 g of H_2BO_3. Store in polypropylene container.

6.10 K standard, 1 meq L^{-1}. Add 12.34 ml of HF solution and 5 g of H_2BO_3 to 10 ml of K stock solution. Store in polypropylene container.

6.11 NaCl solution (1143 ppm Na). Dissolve 2.54 g of NaCl in DDI and make to 1-L volume.

7. Procedure

Dilution of Sample Extracts and Standards

7.1 Set the digital settings at 60 for the diluent (NaCl solution) and 99 for the HF sample, calibration reagent blanks, and calibration standards.

7.2 Dilute 1 part HF sample with 7 parts of NaCl solution (1:7 dilution).

7.3 Dilute 1 part calibration reagent blank (HF solution) with 7 parts NaCl solution (1:7 dilution).

7.4 Dilute 1 part of each calibration standard (200 ppm Fe, 200 ppm Al, and 1 meq^{-1} K) with 7 parts of NaCl solution (1:7 dilution).

7.5 Dispense the diluted solutions into 15-mL conical polystyrene centrifuge tubes. Place tubes in carousels of the sample changer.

AA Calibration

7.6 Use calibration reagent blank (HF solution) and calibration standards to

calibrate the AA. The AA program requires a blank and a standard, in that order, to establish a single point calibration curve for element determination. During AA determinations, perform one calibration, i.e., blank plus standard, for every 8 samples.

AA Operation

7.7 The following parameters are only very general guidelines for instrument conditions for the analyte.

Element	Wavelength	Angle	Fuel/Oxidant
Fe	302.1	Parallel	C_2H_2/Air 20/25
Al	308.2	Parallel	C_2H_2/N_2O 30/17
K	766.5	30°	C_2H_2/Air 20/25

7.8 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

7.9 If a sample exceeds the calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record the dilution. Remember to keep the matrix the same after dilution.

8. Calculations

Calculations are reported in method 7C3.

9. Report

Report concentrations of Fe, Al, and K by atomic absorption. Elemental concentrations are converted to percent oxides. Data are reported in method 7C3.

10. Precision

Precision data are not available for this procedure.

11. References

Berdanier, C.R., W.C. Lynn, and G.W. Threlkeld. 1978. Illitic mineralogy in Soil Taxonomy: X-ray vs. total potassium. Agron. Absts. 1978 Annual Mtgs.

Lim, C.H., and M.L. Jackson. 1982. Dissolution for total elemental analysis. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:1–12.

Soil Conservation Service. 1984. Procedures for collecting soil samples and methods of analysis for soil survey. USDA–SCS Soil Surv. Invest. Rep. No. 1. U.S. Govt. Print. Office, Washington, DC.

Washington, H.S. 1930. The chemical analysis of rocks. 4th ed. John Wiley and Sons, Inc., New York, NY.

Iron, Aluminum, and Silicon (6C, 6G, and 6V)
Ammonium Oxalate Extraction (6C6, 6G12, and 6V2)
Inductively Coupled Plasma Spectrometry (6C9a, 6G12a, and 6V2a)

Optical Density (8J) (of Ammonium Oxalate Extract)

1. Application

Oxalic acid-ammonium oxalate (acid oxalate) is used as a selective dissolution extractant for organically complexed Fe and Al, noncrystalline hydrous oxides of Fe and Al, allophane, and amorphous aluminosilicates (Wada, 1989). Acid oxalate is a poor extractant of imogolite and layer silicates and does not extract crystalline hydrous oxides of Fe and Al, opal, or crystalline silicate (Wada, 1989). A more reliable and accurate estimation of soil properties and a better understanding of the soil exchange complex is provided when acid oxalate extraction is used in conjunction with other selective dissolution procedures, thermal techniques, and chemical tests. In “Soil Taxonomy,” acid oxalate extractable Fe and Al are criteria for andic soil properties (Soil Survey Staff, 1990).

2. Summary of Method

A soil sample is extracted with a mechanical vacuum extractor (Holmgren et al., 1977) in a 0.2 *M* acid oxalate solution buffered at pH 3.0 under darkness. The acid oxalate extract is weighed. The acid oxalate extract is diluted with 0.1 *N* HCl. The diluted extract is vaporized and atomized by a inductively coupled plasma emission spectrophotometer (ICP). The atoms or ions of the analyte are energized in high temperatures, resulting in the movement of valence electrons to higher orbits from the nucleus. As the electrons fall back to a lower orbit, electromagnetic energy at a specific wavelength for a given atom is emitted in measurable amounts (Soltanpour et al., 1982). Data are automatically recorded by a microcomputer and printer. The percent acid oxalate extractable Fe, Al, and Si are reported in methods 6C9a, 6G12a, and 6V2a, respectively (Soil Conservation Service, 1984). On a less routine basis, Mn is also measured. To date, however, a National Soil Survey Laboratory (NSSL) method code has not been assigned to the Mn determination by acid oxalate extraction. In method 8J, the optical density of the extract is measured with a UV spectrophotometer at 430 nm.

3. Interferences

There are four types of interferences (matrix, spectral, chemical, and ionization) in the ICP analyses of these elements. These interferences vary in importance, depending upon the particular analyte chosen.

The acid oxalate buffer extraction is sensitive to light, especially UV light. The exclusion of light reduces the dissolution effect of crystalline oxides and clay minerals. If the sample contains large amounts of amorphous material (>2% Al), an alternate method should be used, i.e., shaking with 0.275 *M* acid oxalate, pH 3.25, 1:100 soil:extractant.

4. Safety

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Restrict the use of concentrated HCl to a fume hood. Follow standard laboratory practices when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Follow the manufacturer's safety precautions when using the UV spectrophotometer and ICP.

5. Equipment

5.1 Electronic balance, ±1-mg sensitivity

5.2 Mechanical vacuum extractor, 24 place, Centurion International, Inc., Lincoln, NE

5.3 Syringes, polypropylene, disposable, 60 mL, for sample tube, extractant reservoir, and tared extraction syringe

5.4 Rubber tubing, 3.2 ID x 6.4 OD x 25.4 mm (⅛ ID x ¼ OD x 1 in) for connecting syringe barrels

5.5 Polycons, Richards Mfg. Co.

5.6 Plunger, modified. Remove rubber and cut plastic protrusion from plunger end.

5.7 UV-visible spectrophotometer, DU-7, Beckmann Instruments, Inc.

5.8 Cuvettes, disposable, polystyrene, 1-cm light path

5.9 Inductively coupled plasma spectrophotometer (ICP), Perkin-Elmer model 6000

5.10 Autosampler, AS-50, Perkin-Elmer Corp., Norwalk, CT

5.11 Microcomputer, 7500 Professional Computer, Perkin-Elmer Corp., Norwalk, CT

5.12 Dot matrix printer, P-132, Interdigital Data Systems, Inc.

5.13 Single-stage regulator, high-purity, high-flow, argon, product no. E11-X-N145DHF, Air Products and Chemicals, Inc., Box 538, Allentown, PA 18105

5.14 Digital diluter/dispenser, product no. 100004, with hand probe and actuator, product no. 230700, Hamilton Co., P.O. Box 10030, Reno, NV, 89510

5.15 Syringes, 10,000 and 1000 µL, 1001 DX and 1010-TEL LL gastight, Hamilton Co., P.O. Box 10030, Reno, NV, 89510

5.16 Centrifuge tubes, polystyrene, 15 mL, conical, graduated, part no. 2087, for sample dilution and sample changer, Becton Dickinson Labware, Becton Dickinson and Co., 2 Bridgewater Lane, Lincoln Park, NJ 07035

5.17 Containers, polypropylene

6. Reagents

6.1 Distilled deionized (DDI) water

6.2 Hydrochloric acid (HCl), conc., 12 *N*

6.3 HCl, 1:1 HCl:DDI, 6 *N*. Carefully mix 1 part of conc. HCl to 1 part DDI water.

6.4 HCl, 1% wt. Carefully dilute 25 mL of conc. HCl to 1 L with DDI water.

6.5 HCl, 0.1 *N*. Add 8.33 mL of conc. HCl to DDI water and make to 1-L volume.

6.6 Acid oxalate buffer solution, 0.2 *M*, pH 3.0. *Solution A* (base): Dissolve 284 g of $(NH_4)_2C_2O_4 \cdot H_2O$ in 10 L of DDI water. *Solution B* (acid): Dissolve 252 g of $H_2C_2O_4 \cdot H_2O$ in 10 L of DDI water. Mix 4 parts solution A with 3 parts solution B. Adjust acid oxalate solution pH by adding either acid or base solution. Store in a polypropylene bottle.

6.7 pH buffers, pH 4.00 and 7.00, for electrode calibration

6.8 Primary Fe standard, 1000 ppm. Dissolve 1.000 g of Fe wire in a minimum volume of 1:1 HCl:DDI. Dilute to 1-L volume in a volumetric flask using 1% HCl. Store in a polypropylene bottle.

6.9 Primary Al standard, 1000 ppm. Dissolve 1.000 g of Al wire in a minimum volume of 1:1 HCl:DDI. Dilute to 1-L volume in a volumetric flask using 1% HCl water. Store in a polypropylene bottle.

6.10 Primary Si standard, 1000 ppm. Fuse 0.2139 g of SiO_2 with 2 g of Na_2CO_3 in a platinum crucible. Dissolve the melt with DDI water and transfer to a 100-mL volumetric flask. Dilute to 1-L volume with DDI water. Store in a polypropylene bottle.

6.11 Primary Mn standard, 1000 ppm. Dissolve 1.000 g of Mn wire in a minimum volume of 1:1 HCl:DDI. Dilute to 1-L volume in a volumetric flask using 1:1 HCl:DDI. Store in a polypropylene bottle.

6.12 High calibration standard. Mix 30 mL of each primary standard (Al, Fe, and Si) with 5 mL of primary Mn standard. Add 50 mL of 0.4 *M* acid oxalate solution, 20 mL of conc. HCl, and make to 1-L volume with DDI water. Resulting solution contains 5 ppm Mn and 30 ppm each of Al, Fe, and Si. Store in a polypropylene bottle.

6.13 Low calibration standard. Mix 10 mL of each primary standard (Al, Fe, and Si) with 2 mL of primary Mn standard. Add 30 mL of 0.4 *M* acid oxalate

solution, 20 mL of conc. HCl, and make to 1-L volume with DDI water. Resulting solution contains 2 ppm Mn and 10 ppm each of Al, Fe, and Si. Store in a polypropylene bottle.

6.14 Calibration reagent blank solution. Add 30 mL of 0.4 *M* acid oxalate solution, 20 mL of conc. HCl, and make to 1-L volume with DDI water.

6.15 Argon gas, purity 99.9

7. Procedure

Extraction of Fe, Al, Si, and Mn

7.1 Prepare sample tube by tightly compressing a 1-g ball of filter pulp into the bottom of a syringe barrel with a modified plunger.

7.2 Weigh 0.500 g of <2-mm, air-dry soil and place in sample tube. Prepare two reagent blanks (no sample in tube) per set of 48 samples.

7.3 Place the sample tube on the upper disk of the extractor and connect a tared extraction syringe. Use 25.4-mm (1-in) length rubber tubing to insert the handle of the plunger in the slot of the stationary extractor disk.

7.4 Use a dispenser to add 15.00 mL of acid oxalate buffer to the sample tube. Make sure that the sample is thoroughly wetted. During the addition, wash sides of the tube and wet the sample. Shaking, swirling, or stirring may be required to wet organic samples. Allow sample to stand for at least 30 min.

7.5 Set extractor for 30-min extraction rate and extract until the acid oxalate buffer solution is at a 0.5 to 1.0-cm height above sample. Turn off extractor.

7.6 Put reservoir tube on top of the sample tube.

7.7 Add 35 mL of acid oxalate buffer to the reservoir tube.

7.8 Cover the extractor with a black plastic bag to exclude light. Adjust the extraction rate for a 12-h extraction.

7.9 After the extraction, shut off the extractor and pull plunger of syringe down. Do not remove the plunger from syringe barrel. Carefully remove the syringe with extract leaving the rubber tubing on the sample tube.

7.10 Weigh each syringe containing acid oxalate extract to the nearest 0.01 g.

7.11 Mix extract in each syringe by manually shaking. Fill a polycon with extract solution. This solution is reserved for determinations of Fe, Mn, Al, and Si. If optical density is to be measured, fill a disposable cuvette with extract solution. Discard excess solution.

Determination of Optical Density of Extract

7.12 Place 4 mL of acid oxalate extract in disposable cuvette.

7.13 Place 4 mL of acid oxalate reagent blank in disposable cuvette.

7.14 On DU-7 spectrophotometer, select a 430-nm wavelength. Select normal slit width and height.

7.15 Use the acid oxalate extract reagent blank to set spectrophotometer.

7.16 Record optical density of acid oxalate extract to nearest 0.000.

Dilution of Sample Extracts and Standards

7.17 For better nebulization, add one drop of DDBSA solution to each tube (sample extracts, calibration standards, and reagent blanks) to reduce surface tensions. Add DDBSA to tube before the addition of diluted solution.

7.18 Set the digital settings of the Hamilton diluter at 63 for the diluent (0.1 *N* HCl) and 70 for the acid oxalate extracts for a 1:10 dilution. Calibration reagent blanks and calibration standards are not diluted.

7.19 Dilute 1 part acid oxalate sample extract with 10 parts of 0.1 *N* HCl (1:10 dilution).

7.20 Dispense the diluted solutions into 15-mL conical polystyrene centrifuge tubes which have been placed in carousels of the sample changer.

ICP Calibration

7.21 Use high calibration standard and calibration reagent blank to calibrate ICP. The ICP requires a standard and a blank, in that order, for calibration. During ICP determinations, perform one calibration, i.e., standard plus blank, for every 6 samples.

7.22 Use the low calibration standard as a check sample.

ICP Set-up and Operation

7.23 The following parameters are only very general guidelines for instrument conditions for the various analytes.

Parameter	Value
ICP power	1250 W
Plasma gas flow	Ar 12 L min^{-1}
Nebulizer gas flow	Ar 0.5 L min^{-1}
Auxiliary gas flow	Ar 0.05 to 1 L min^{-1}

Use a high solids nebulizer instead of the cross flow nebulizer.

7.24 Analyte data for some elements are reported at 2 wavelengths which serve as data checks.

Analyte	Wave-length	Low Standards	High Standards
	(nm)	*(ppm)*	*(ppm)*
Fe	238.204 / 239.562	30.00	10.00
Al	394.400 / 396.150	30.00	10.00
Si	212.412 / 251.611	30.00	10.00
Mn	257.610	5.00	2.00

7.25 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings. The instrument readings are usually programmed in ppm.

7.26 If sample exceeds calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record dilution. Remember to keep the matrix the same after dilution by diluting with 0.1 *N* HCl at the 1:1 ratio.

8. Calculations

$$\text{Analyte (\%)} = [\text{ICP} \times (\text{Syr}_{fin} - \text{Syr}_{init}) \times \text{DR} \times \text{AD/OD}] / [\text{Sample} \times 10{,}000 \times \text{Density}]$$

where:

ICP = ICP analyte concentration (ppm)

Syr_{fin} = Weight of syringe + extract (g)

Syr_{init} = Tare weight of syringe (g)

DR = Dilution ratio of samples over calibration range

Sample = Weight of sample (g)

Density = Density of acid oxalate solution (1.007)

AD/OD = Air-dry/oven-dry ratio (method 4B5)

9. Report

Report the percent acid oxalate extractable Fe, Al, and Si to the nearest 0.01%. Percent acid oxalate extractable is also reported. To date, however, no method code has been assigned to Mn determination by acid oxalate extraction. Report the optical density of the acid oxalate extract to the nearest 0.001 unit.

10. Precision

Precision data are not available for this procedure. The mean, standard deviation, and CV for Fe, Al, Si, and optical density for both the low and high standards are as follows:

High Standard	n	Mean	Std. Dev.	C.V.
Optical density	18	0.18	0.03	14.2
Fe	17	0.94	0.17	18.2
Al	17	2.6	0.19	7.6
Si	17	1.2	0.09	7.3

Low Standard	N	Mean	Std. Dev.	C.V.
Optical density	25	0.06	0.00	7.5
Fe	24	0.26	0.03	9.7
Al	25	0.17	0.01	8.4
Si	26	0.02	0.01	53.2

11. References

Holmgren, G.G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Amer. J. 41:1207–1208.

Soil Conservation Service. 1984. Procedures for collecting soil samples and methods of analysis for soil survey. USDA–SCS Soil Surv. Invest. Rep. No. 1. U.S. Govt. Print. Office, Washington, DC.

Soil Survey Staff. 1990. Keys to soil taxonomy. 4th ed. SMSS technical monograph no. 6. Blacksburg, VA.

Soltanpour, P.N., J.B. Jones Jr., and S.M. Workman. 1982. *In* A. Klute (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:29–65.

Wada, K. 1989. Allophane and imogolite. *In* J.B. Dixon and S.B. Weed (eds.) Minerals in soil environments. 2nd ed. Soil Sci. Soc. Amer. No. 1. p. 1051–1087.

Manganese and Aluminum (6D and 6G)

1 *N* KCl Extractable, Automatic Extractor (6D3 and 6G9)

Inductively Coupled Plasma Spectrometry (6D3 and 6G9b)

1. Application

The Al extracted by 1 *N* KCl approximates exchangeable Al and is a measure of the “active” acidity present in soils with a 1:1 water pH <5.5. Above pH 5.5, precipitation of Al occurs during analysis. This method does not measure the acidity component of hydronium ions (H_3O^+). If Al is present in measurable amounts, the hydronium is a minor component of the active acidity. Because the 1 *N* KCl extractant is an unbuffered salt and usually affects the soil pH one unit or less, the extraction is determined at or near the soil pH. The KCl extractable

Al is related to the immediate lime requirement and existing CEC of the soil. The "potential" acidity is better measured by the $BaCl_2$-TEA method (method 6H5a) (Thomas, 1982).

2. Summary of Method

A soil sample is leached with 1 *N* KCl using the mechanical vacuum extractor (Holmgren et al., 1977). The leachate is weighed. The KCl extracted solution is diluted with 0.5 *N* HCl. The diluted extract is vaporized and atomized by a inductively coupled plasma emission spectrophotometer (ICP). The atoms or ions of the analyte are energized in high temperatures, resulting in the movement of valence electrons to higher orbits from the nucleus. As the electrons fall back to a lower orbit, electromagnetic energy at a specific wavelength for a given atom is emitted in measurable amounts (Soltanpour et al., 1982). Data are automatically recorded by a microcomputer and printer. The Mn and Al are reported in meq/100 g oven-dry soil in methods 6D3 and 6G9b (Soil Conservation Service, 1984).

3. Interferences

There are four types of interferences (matrix, spectral, chemical, and ionization) in the ICP analyses of these cations. These interferences vary in importance, depending upon the particular analyte selected.

The soil:extractant ratio must remain constant. A soil:extractant ratio of 1:10 (w:v) for batch procedures is most commonly used. Using a leaching technique, a 1:20 (w:v) ratio gives comparable results. If the sample size is changed, the amount of extractable Al is changed. No other significant interferences have been identified for this procedure.

4. Safety

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Restrict the use of concentrated HCl to a fume hood. Follow standard laboratory practices when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Follow the manufacturer's safety precautions when using the ICP.

5. Equipment

5.1 Electronic balance, ±1-mg sensitivity

5.2 Analytical filter pulp, Schleicher and Schuell, no. 289

5.3 Mechanical vacuum extractor, 24 place, Centurion International, Inc., Lincoln, NE

5.4 Syringes, polypropylene, disposable, 60 mL, for sample tube, extractant reservoir, and tared extraction syringe

5.5 Rubber tubing, 3.2 ID x 6.4 OD x 25.4 mm (⅛ ID x ¼ OD x 1 in), for connecting syringe barrels

5.6 Plunger, modified. Remove rubber and cut plastic protrusion from plunger end.

5.7 Wash bottle, 20 mL, to dispense KCl

5.8 Polycons, Richards Mfg. Co.

5.9 Inductively coupled plasma (ICP) atomic emission spectrophotometer, Perkin-Elmer model 6000

5.10 Autosampler, AS-50, Perkin-Elmer Corp., Norwalk, CT

5.11 Microcomputer, 7500 Professional Computer, Perkin-Elmer Corp., Norwalk, CT

5.12 Dot matrix printer, P-132, Interdigital Data Systems, Inc.

5.13 High-purity, high-flow, single-stage regulator, argon, product no. E11-X-N145DHF, Air Products and Chemicals, Inc., Box 538, Allentown, PA 18105

5.14 Digital diluter/dispenser, product no. 100004, with hand probe and actuator, product no. 230700, Hamilton Co., P.O. Box 10030, Reno, NV, 89510

5.15 Syringes, 10,000 and 1000 µL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV, 89510

6. Reagents

6.1 Distilled deionized (DDI) water

6.2 Hydrochloric acid (HCl), conc., 12 *N*

6.3 HCl, 1:1 HCl:DDI, 6 *N*. Carefully mix 1 part of conc. HCl to 1 part DDI water.

6.4 HCl, 1% wt. Carefully dilute 25 mL of conc. HCl to 1 L with DDI water.

6.5 HCl, 0.5 *N*. Add 1 part of conc. HCl to 24 parts DDI water (1:25 dilution).

6.6 Potassium chloride solution (KCl), 1.0 *N*. Dissolve 1342 g of KCl reagent in 16 L DD water. Allow solution to equilibrate to room temperature. Dilute to 18 L with DDI water. Use 1.0 *N* KCl for Al and Mn extraction.

6.7 Potassium chloride solution (KCl), 2.0 *N*. Dissolve 298.24 g of KCl reagent in 1.5 L DDI water. Allow solution to equilibrate to room temperature. Dilute to 2 L with DDI water. Use 2.0 *N* KCl for standards.

6.8 Primary Al standard, 2248.5 ppm (250 meq L^{-1}). Dissolve 2.2485 g of Al wire in a minimum volume of 1:1 HCl:DDI. This is a very slow reaction. Dilute to 1 L in a volumetric flask using 1% HCl solution. Store in polypropylene container.

6.9 Primary Mn standard, 1000 ppm (36 meq L^{-1}). Commercial. Dissolve 1.000 g of Mn metal in a minimum volume of 1:1 HCl:DDI. When dissolved, dilute to 1 L in a volumetric flask using 1% HCl solution. Store in a polypropylene container.

6.10 Mn standard, 250 ppm (9 meq L^{-1}). Mix 25 mL of primary Mn standard (1000 ppm) with 10 mL of 1:1 HCl:DDI and dilute to 100-mL volume with DDI water. Store in polypropylene bottle.

6.11 Calibration Al and Mn standard, 10 meq L^{-1} Al and 5 ppm Mn. Mix 10 mL of primary Al standard (250 meq L^{-1}) with 125 mL 2.0 *N* KCl solution. Add 5 mL of Mn standard (250 ppm). Make to 250-mL volume with DDI water. Store in polypropylene container.

6.12 Calibration Al and Mn check standard, 5 meq L^{-1} Al and 2 ppm Mn. Mix 5 mL of primary Al standard (250 meq L^{-1}) with 125 mL 2.0 *N* KCl solution. Add 2 mL of Mn standard (250 ppm). Store in polypropylene container.

6.13 Calibration reagent blank solution, 1.0 *N* KCl. Add 125 mL of 2.0 *N* KCl to a volumetric flask and make to 250-mL volume with DDI water. Store in polypropylene container.

6.14 Dodecylbenzenesulfonic acid (DDBSA), tech 97%. Working stock is 0.1 *M*. Dilute 25 mL of 0.1 *M* DDBSA to 1-L volume with DDI water.

6.15 Argon gas, purity 99.9%

7. Procedure

Extraction of Al and Mn

7.1 Prepare sample tube by tightly compressing a 1-g ball of filter pulp into the bottom of a syringe barrel with a modified plunger.

7.2 Weigh exactly 2.50 g of <2-mm, air-dry soil and place in sample tube. Prepare one quality control check sample per 48 samples.

7.3 Place the sample tube on the upper disk of the extractor and connect a tared extraction syringe. Use 25.4-mm (1-in) length rubber tubing to insert the handle of the plunger in the slot of the stationary extractor disk.

7.4 Use a squeeze bottle and fill sample tube to the 20-mL mark with 1.0 *N* KCl solution (≈10 mL). Make sure that the sample is thoroughly wetted. During the addition, wash sides of the tube and wet the sample. Shaking, swirling, or stirring may be required to wet organic samples. Allow sample to stand for at least 30 min.

7.5 Put reservoir tube on top of the sample tube. Set extractor for fast extraction rate and extract until the KCl solution is at a 0.5- to 1.0-cm height above sample. Turn off extractor.

7.6 Add 45 mL KCl solution to reservoir tube. Set extractor for 45-min extraction.

7.7 After the extraction, shut off extractor and pull plunger of syringe down. Do not remove the plunger from syringe barrel. Carefully remove the syringe with extract leaving the rubber tubing on the sample tube.

7.8 Weigh each syringe containing KCl extract to the nearest 0.01 g.

7.9 Mix extract in each syringe by manually shaking. Fill a polycon with extract solution and discard the excess. This solution is reserved for extractable Al and Mn analyses.

Dilution of Extracts and Standards

7.10 For better nebulization, add one drop of DDBSA solution to KCl sample extracts, calibration reagent blanks, and calibration standards to reduce surface tensions. Add DDBSA to tube before adding diluted solution.

7.11 Set the digital settings at 40 for the diluent (0.5 *N* HCl) and 99 for the KCl sample extracts, calibration reagent blanks, calibration standards, and calibration check standards for a 1:5 dilution as follows:

7.12 Dilute 1 part KCl sample extract with 4 parts of 0.5 *N* HCl (1:5 dilution).

7.13 Dilute 1 part calibration reagent blank with 4 parts of 0.5 *N* HCl (1:5 dilution).

7.14 Dilute 1 part calibration standard (10 meq L^{-1} Al and 5 ppm Mn) with 4 parts of 0.5 *N* HCl (1:5 dilution).

7.15 Dilute 1 part calibration check standard (5 meq L^{-1} Al and 2 ppm Mn) with 4 parts of 0.5 *N* HCl (1:5 dilution).

7.16 Dispense the diluted solutions into 15-mL conical polystyrene centrifuge tubes which have been placed in carousels of the sample changer.

ICP Calibration

7.17 Use calibration standard (10.00 meq L^{-1} Al and 5.00 ppm Mn) and calibration reagent blank (1.0 *N* KCl) to calibrate ICP. The ICP requires a standard and a blank, in that order, for calibration. During ICP determinations, perform one calibration, i.e., standard plus blank, for every 6 samples.

7.18 Use the calibration check standard (5.00 meq L^{-1} Al and 2.00 ppm Mn) as a check sample.

7.19 The following parameters are only very general guidelines for instrument conditions for the analytes.

ICP Set-up and Operation

Parameter	Al	Fe
Plasma flow (ml Ar min^{-1})	12.0	12.0
Nebulizer flow (mL Ar min^{-1})	0.5	0.5
Auxiliary flow (mL Ar min^{-1})	0.5	0.5
Viewing height (nm)	15.0	15.0
	Wavelength 1	
Wavelength (nm)	394.400	259.373
Scan speed (s)	2.0	1.0
Bkg. correction (nm)	−0.069, +0.055	0.0
	Wavelength 2	
Wavelength (nm)	396.152	294.920
Scan speed (s)	2.0	2.0
Bkg. correction (nm)	−0.069, +0.055	−0.046, +0.049

High solids nebulizer has a 20 s read delay.

7.20 Load sample tubes in the carousel so that the calibration standard, reagent blank, calibration check standard, and 6 unknown samples are determined in order. Determine a set of 24 unknown samples with each carousel.

7.21 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

7.22 If a sample exceeds the calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record dilution. Remember to keep the matrix the same after dilution by diluting with the 0.5 *N* HCl solution (1:5 dilution).

7.23 Analyze one quality control check sample for every 48 samples.

8. Calculations

8.1 The instrument readings are the analyte concentration (meq L^{-1} Al and ppm Mn) in undiluted extract. Use these values to calculate the analyte concentration on an oven-dry soil basis (meq/100 g).

$$\text{Analyte (meq/100 g)} = [\text{ICP} \times (Wt_{syr+ext} - Wt_{syr}) \times \text{DR} \times 100 \times \text{AD/OD}] / [\text{Smp. Wt.} \times 1.0412 \times 1000]$$

where:

ICP = ICP analyte reading

$Wt_{syr+ext}$ = Weight of extraction syringe & extract (g)
Wt_{syr} = Weight of tared extraction syringe (g)
DR = Dilution ratio of samples over calibration range
Smp. Wt. = Sample weight (g)
1.0412 = Density of 1 *N* KCl @ 20 °C
1000 = g L^{-1}
100 = Conversion factor (100-g basis)
AD/OD = Air-dry/oven-dry ratio (method 4B5)

9. Report

Report KCl extractable Al and Mn in units of meq/100 g of oven-dry soil to the nearest 0.01 meq/100 g.

10. Precision

Precision data are not available for this procedure.

11. References

Holmgren, G.G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Amer. J. 41:1207–1208.

Soil Conservation Service. 1984. Procedures for collecting soil samples and methods of analysis for soil survey. USDA–SCS Soil Surv. Invest. Rep. No. 1. U.S. Govt. Print. Office, Washington, DC.

Soltanpour, P.N., J.B. Jones Jr., and S.M. Workman. 1982. *In* A. Klute (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:29–65.

Thomas, G.W. 1982. Exchangeable cations. *In* A. Klute (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:159–165.

Aluminum (6G)

KCl, Automatic Extractor (6G9)

Atomic Absorption (6G9a)

1. Application

The Al extracted by 1 *N* KCl approximates exchangeable Al and is a measure of the “active” acidity present in soils with a 1:1 water pH <5.5. Above pH 5.5, precipitation of Al occurs during analysis. This method does not measure the acidity component of hydronium ions (H_3O^+). If Al is present in measurable amounts, the hydronium is a minor component of the active acidity. Because the

1 *N* KCl extractant is an unbuffered salt and usually affects the soil pH one unit or less, the extraction is determined at or near the soil pH. The KCl extractable Al is related to the immediate lime requirement and existing CEC of the soil. The "potential" acidity is better measured by the $BaCl_2$-TEA method (method 6H5a) (Thomas, 1982).

2. Summary of Method

A soil sample is leached with 1 *N* KCl using the mechanical vacuum extractor (Holmgren et al., 1977). The leachate is weighed. The KCl extract is diluted with distilled deionized (DDI) water. The diluted extract is aspirated into an atomic absorption spectrophotometer (AA). The analyte is measured by absorption of the light from a hollow cathode lamp. An automatic sample changer is used to aspirate a series of samples. The AA converts absorption to analyte concentration. The data are automatically recorded by a microcomputer and printer. The Al is reported in meq/100 g oven-dry soil in method 6G9a.

3. Interferences

There are four types of interferences (matrix, spectral, chemical, and ionization) in the AA analyses of these cations. These interferences vary in importance, depending upon the particular analyte selected.

The soil:extractant ratio must remain constant. A soil:extractant ratio of 1:10 (w:v) for batch procedures is most commonly used. Using a leaching technique, a 1:20 (w:v) ratio gives comparable results. If the sample is changed, the amount of extractable Al is changed. No other significant interferences have been identified for this procedure.

4. Safety

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Restrict the use of concentrated HCl to a fume hood. Many metal salts are extremely toxic and may be fatal if ingested. Follow standard laboratory practices when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene gas is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the AA.

5. Equipment

5.1 Electronic balance, ±1-mg sensitivity

5.2 Mechanical vacuum extractor, 24 place, Centurion International, Inc., Lincoln, NE

5.3 Syringes, polypropylene, disposable, 60 mL, for sample tube, extractant reservoir, and tared extraction syringe

5.4 Rubber tubing, 3.2 ID x 6.4 OD x 25.4 mm (⅛ ID x ¼ OD x 1 in) for connecting syringe barrels

5.5 Wash bottle, 20 mL, to dispense KCl

5.6 Plunger, modified. Remove rubber and cut plastic protrusion from plunger end.

5.7 Polycons, Richards Mfg. Co.

5.8 Atomic absorption spectrophotometer (AA), Perkin-Elmer model 5000

5.9 Autosampler, AS-50, Perkin-Elmer Corp., Norwalk, CT

5.10 Microcomputer, 7500 Professional Computer, Perkin-Elmer Corp., Norwalk, CT

5.11 Dot matrix printer, P-132, Interdigital Data Systems, Inc.

5.12 Single-stage regulator, acetylene service, part number E11-0-N511A, Air Products and Chemicals, Inc., Box 538, Allentown, PA 18105

5.13 Heated regulator, single-stage, nitrous oxide, stock number 808 8039, Airco Welding Products, P.O. Box 486, Union, NJ 07083

5.14 Digital diluter/dispenser, product no. 100004, with hand probe and actuator, product no. 230700, Hamilton Co., P.O. Box 10030, Reno, NV, 89510

5.15 Syringes, 10,000 and 1000 µL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV, 89510

5.16 Centrifuge tubes, polystyrene, 15 mL, conical bottom, graduated, part no. 2087, for sample dilution and sample changer, Becton Dickinson Labware, Becton Dickinson and Co., 2 Bridgewater Lane, Lincoln Park, NJ 07035

5.17 Containers, polypropylene or teflon

6. Reagents

6.1 Distilled deionized (DDI) water

6.2 Hydrochloric acid (HCl), conc., 12 *N*

6.3 HCl, 1:1 HCl:DDI, 6 *N*. Carefully mix 1 part of conc. HCl to 1 part DDI water.

6.4 HCl, 1% wt. Carefully dilute 25 mL of conc. HCl to 1 L with DDI water.

6.5 Potassium chloride solution (KCl), 1.0 *N*. Dissolve 1342 g of KCl reagent in 16 L DDI water. Allow solution to equilibrate to room temperature. Dilute to 18 L with DDI water. Use 1.0 *N* KCl solution for Al extraction.

6.6 Potassium chloride solution (KCl), 2.0 *N*. Dissolve 298.24 g of KCl reagent in 1.5 L DDI water. Allow solution to equilibrate to room temperature. Dilute to 2 L with DDI water. Use 2.0 *N* KCl solution for standards.

6.7 Primary Al standard, 2248.5 ppm (250 meq L^{-1}). Dissolve 2.2485 g of Al wire in a minimum volume of 1:1 HCl:DDI. This is a very slow reaction. Dilute to 1 L in a volumetric flask using 1% HCl solution. Store in polypropylene bottle.

6.8 Calibration Al standard, 10 meq L^{-1}. Mix 10 mL of primary Al standard (250 meq L^{-1}) with 125 mL of 2.0 *N* KCl solution. Make to 250-mL volume with DDI water. Store in polypropylene bottle.

6.9 Calibration Al check standard, 5 meq L^{-1}. Mix 5 mL of primary Al standard (250 meq L^{-1}) with 125 mL of 2.0 *N* KCl solution. Make to 250-mL volume with DDI water. Store in polypropylene bottle.

6.10 Calibration reagent blank solution, 1.0 *N* KCl. Add 125 mL of 2.0 *N* KCl to a volumetric flask and make to 50-mL volume with DDI water. Store in polypropylene bottle.

6.11 Nitrous oxide gas, compressed

6.12 Acetylene gas, compressed, purity 99.6%

6.13 Compressed air with water and oil traps

7. Procedure

Extraction of Al

7.1 Prepare sample tube by tightly compressing a 1-g ball of filter pulp into the bottom of a syringe barrel with a modified plunger.

7.2 Weigh exactly 2.50 g of <2-mm, air-dry soil and place in sample tube. Prepare one quality control check sample per 48 samples.

7.3 Place the sample tube on the upper disk of the extractor and connect a tared extraction syringe. Use 25.4-mm (1-in) length rubber tubing to insert the handle of the plunger in the slot of the stationary extractor disk.

7.4 Use a squeeze bottle and fill sample tube to the 20-mL mark with 1.0 *N* KCl solution (~10 mL). Make sure that the sample is thoroughly wetted. During the addition, wash sides of the tube and wet the sample. Shaking, swirling, or stirring may be required to wet organic samples. Allow sample to stand for at least 30 min.

7.5 Put reservoir tube on top of the sample tube. Set extractor for fast extraction rate and extract until the KCl solution is at a 0.5- to 1.0-cm height above sample. Turn off extractor.

7.6 Add 45 mL KCl solution to reservoir tube. Set extractor for 45-min extraction.

7.7 After the extraction, shut off extractor and pull plunger of syringe down. Do not remove the plunger from syringe barrel. Carefully remove the syringe with extract leaving the rubber tubing on the sample tube.

7.8 Weigh each syringe containing KCl extract to the nearest 0.01 g.

7.9 Mix extract in each syringe by manually shaking. Fill a polycon with extract solution and discard the excess. This solution is reserved for extractable Al analysis.

Dilution of Sample Extracts and Standards

7.10 No ionization suppressant is required as the K in the extractant is present in sufficient quantity. Set the digital settings at 40 for the diluent (DDI water) and 99 for the KCl sample extracts, calibration reagent blanks, calibration standards, and calibration check standards for a 1:5 dilution as follows:

7.11 Dilute 1 part KCl sample extract with 4 parts of DDI water (1:5 dilution).

7.12 Dilute 1 part calibration reagent blank with 4 parts of DDI water (1:5 dilution).

7.13 Dilute 1 part calibration standard (10 meq L^{-1} Al) with 4 parts of DDI water (1:5 dilution).

7.14 Dilute 1 part calibration check standard (5 meq L^{-1} Al) with 4 parts of DDI water (1:5 dilution).

7.15 Dispense the diluted solutions into 15-mL conical polystyrene centrifuge tubes which are placed in carousels of the sample changer.

AA Calibration

7.16 Use calibration reagent blank (1.0 *N* KCl) and calibration standard (10 meq L^{-1} Al) to calibrate the AA. The AA program requires a blank and a standard, in that order, to establish a single point calibration curve for element determination. During AA determinations, perform one calibration, i.e., blank plus standard, for every 12 samples.

7.17 Use the calibration check standard (5 meq L^{-1} Al) as a check sample.

AA Set-up and Operation

7.18 The following parameters are only very general guidelines for instrument conditions for the analyte.

Element Head = Al

Wavelength (nm) = 309.3

Burner head & angle = 5 cm Parallel

Fuel/Oxidant (C_2H_2/N_2O) = 30/17

Typical read delay is 6 s, and integration by peak area is 8 s.

7.19 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

7.20 If a sample exceeds the calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record dilution. Remember to keep the matrix the same after dilution by diluting with DDI water (1:5 dilution).

7.21 Analyze one quality control check sample for every 48 samples.

8. Calculations

8.1 The instrument readings are the analyte concentration (meq L^{-1} Al) in undiluted extract. Use these values to calculate the analyte concentration on an oven-dry soil basis (meq/100 g).

$$\text{Al (meq/100 g)} = [AA_{Al} \times (Wt_{syr+ext} - Wt_{syr}) \times DR \times 100 \times AD/OD] / [\text{Smp. Wt.} \times 1.0412 \times 1000]$$

where:

AA_{Al} = AA Al reading (meq L^{-1})

$Wt_{syr+ext}$ = Weight of extraction syringe and extract (g)

Wt_{syr} = Weight of tared extraction syringe (g)

DR = Dilution ratio for samples over calibration range

Smp.Wt. = Sample weight (g)

1.0412 = Density of 1 *N* KCl @ 20 °C

1000 = g L^{-1}

100 = Conversion factor (100-g basis)

AD/OD = Air-dry/oven-dry ratio (method 4B5)

9. Report

Report KCl extractable Al in units of meq/100 g of oven-dry soil to the nearest 0.1 meq/100 g.

10. Precision

Precision data are not available for this procedure. A quality control check sample is run with every batch of 48 samples. For 21 observations of the quality control sample, the mean, standard deviation, and C.V. for extractable Al are 3.1, 0.18, and 5.7 %, respectively.

11. References

Holmgren, G.G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Amer. J. 41:1207–1208.

Thomas, G.W. 1982. Exchangeable cations. *In* A. Klute (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:159–165.

Chloride, Sulfate, Nitrate, Fluoride, and Nitrite (6K, 6L, 6M, 6U, and 6W)

Saturation Extract (6K1, 6L1, 6M1, 6U1, and 6W1)

Chromatograph (6K1c, 6L1c, 6M1c, 6U1a, and 6W1a)

1. Application

The soluble anions that are commonly determined in saline and alkali soils are carbonate, bicarbonate, sulfate, chloride, nitrate, nitrite, fluoride, phosphate, silicate, and borate (Khym, 1974; U.S. Salinity Laboratory Staff, 1954). Carbonate and bicarbonate are determined by titration in methods 6I1b and 6J1b, respectively (Soil Conservation Service, 1984). Phosphate, silicate, and borate usually are not determined because they are found only occasionally in measurable amounts in soils. Chloride, sulfate, nitrate, fluoride, and nitrite are measured in solution in methods 6K1c, 6L1c, 6M1c, 6U1a, and 6W1a, respectively (Soil Conservation Service, 1984). In saline and alkali soils, carbonate, bicarbonate, sulfate, and chloride are the anions that are found in the greatest abundance. In general, soluble sulfate is usually more abundant than soluble chloride.

2. Summary of Method

The saturation extract 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 determine the anion. A chart recording is made of the chromatograph. Standard anions are used to calibrate the system. A calibration curve is determined, and the anion concentrations are calculated. The saturated extract anions, Cl^-, SO_4^{2}, NO_3^-, F^-, and NO_2^-, are reported in meq L^{-1} in methods 6k1c, 6L1c, 6M1c, 6U1a, and 6W1a, respectively (Soil Conservation Service, 1984).

3. Interferences

Some saturation extracts contain suspended solids. Filtering after dilution removes the particles. Saturation extracts of acid soils that contain Fe and/or Al may precipitate and clog the separator column. Saturation extracts of very high pH may contain organic material which may clog or poison the column. Low molecular weight organic anions will co-elute with inorganic anions from the column.

4. Safety

Wear protective clothing and safety glasses. When preparing reagents, exercise special care. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts. Follow the manufacturer's safety precautions when using the chromatograph.

5. Equipment

5.1 Ion chromatograph, Series 2110i, with conductivity detector, Dionex Corp., 1228 Titan Way, Sunnyvale, CA 94086

5.2 HPIC AS3 analytical column, P/N 030985, Dionex Corp., 1228 Titan Way, Sunnyvale, CA 94086

5.3 HPIC AG3 analytical guard column, P/N 030986, Dionex Corp., 1228 Titan Way, Sunnyvale, CA 94086

5.4 Anion micro membrane suppressor, P/N 037072, Dionex Corp., 1228 Titan Way, Sunnyvale, CA 94086

5.5 Automated sampler, Dionex Corp., 1228 Titan Way, Sunnyvale, CA 94086

5.6 Poly-vials, 5 mL, P/N 038008, Dionex Corp., 1228 Titan Way, Sunnyvale, CA 94086

5.7 Poly-vials, filter caps, 5 mL, P/N 038009, Dionex Corp., 1228 Titan Way, Sunnyvale, CA 94086

5.8 Chart recorder, Honeywell Corp., chart speed 0.5 cm min^{-1}, span 1000 mV F.S.

5.9 Digital diluter/dispenser, product number 100004, with hand probe and actuator, product number 230700, Hamilton Co., P.O. Box 10030, Reno, NV 89510

5.10 Syringes, gas tight, Hamilton 1001 DX and 1010-TEF LL, Hamilton Co., P.O. Box 10030, Reno, NV 89510

5.11 Syringes, disposable, polypropylene, 12 mL

5.12 Disposable 0.2-µm pore size, 25-mm filter assembly, Gelman Sciences, Inc., 674 South Wagner Road, Ann Arbor, MI 48106. Use for saturation extracts and standards.

5.13 Disposable 0.2-µm pore size, Ultipor N_{66} DFA3001NAEY, Pall Trinity Micro Corp., Cortland, NY 13045. Use for filtering distilled deionized (DDI) water.

6. Reagents

6.1 Distilled deionized (DDI) filtered water

6.2 Sulfuric acid (H_2SO_4), conc., reagent

6.3 Toluene

6.4 Isopropanol to de-gas column

6.5 Regenerant solution for membrane suppressor columns, 0.025 *N* H_2SO_4. Carefully mix 22.92 g of conc. H_2SO_4 with filtered DDI water and dilute to

18-L volume. Store in a clean glass carboy with a solid stopper. Cover the carboy top with aluminum foil to protect the contents from dust.

6.6 Stock $NaHCO_3$ solution, 0.480 *M*. Mix 40.34 g of dried $NaHCO_3$ with filtered DDI water and dilute to 1-L volume.

6.7 Stock Na_2CO_3 solution, 0.3838 *M*. Mix 40.68 g of dried Na_2CO_3 with filtered DDI water and dilute to 1-L volume.

6.8 Working eluent solution. Mix 112.5 mL of 0.480 *M* $NaHCO_3$ and 112.5 mL of 0.3838 *M* Na_2CO_3 with filtered DDI water and dilute to 18-L volume. Add 3 drops of toluene to retard microbial growth.

6.9 Primary SO_4^{2-} standard, 0.5 *M* (1.0 *N*). Mix 17.7560 g of Na_2SO_4 with filtered DDI water and dilute to 250-mL volume.

6.10 Primary Cl^- standard, 1.0 *M* (1.0 *N*). Add 18.6392 g of KCl with filtered DDI water and dilute to 250-mL volume.

6.11 Primary F^- standard, 0.125 *M* (0.125 *N*). Add 1.3122 g of NaF with filtered DDI water and dilute to 250-mL volume.

6.12 Primary NO_3^- standard, 1.0 *M* (1.0 *N*). Add 25.2770 g of KNO_3 with filtered DDI water and dilute to 250-mL volume.

6.13 Primary mixed standard. Prepare 1 primary mixed standard by taking aliquots of each of the proceeding primary standards and diluting the combined aliquots to a 1-L volume with working eluent as follows:

Primary Stds.	Aliquot	Final	Conc. Vol. w/ Eluent
	(mL)	*(mL)*	*(Meq/L)*
Na_2SO_4	50	1000	50
KCl	10	1000	10
NaF	100	1000	12.5
KNO_3	30	1000	30

Add eight drops of toluene to primary mixed standard to retard microbial growth and store in a glass container.

6.14 Mixed calibration standards. Prepare 4 mixed calibration standards (0.5, 1.0, 3.0, and 7.0 readings) by taking aliquots of primary mixed standard and diluting each aliquot to 100-mL volume with working eluent as follows:

Primary Mixed Stds.	Final Vol. w/ Eluent	SO_4^{2-}	Cl^-	F^-	NO_3^-
(mL)	*(mL)*	*(meq L^{-1})*	*(meq L^{-1})*	*(meq L^{-1})*	*(meq L^{-1})*
0.5	100	0.25	0.05	0.0625	0.15
1.0	100	0.50	0.10	0.125	0.30
3.0	100	1.5	0.30	0.375	0.90
7.0	100	3.5	0.70	0.875	2.1

6.15 $NaNO_2$, Baker reagent grade, 99.5% purity

6.16 Primary NO_2^- standard, 1 *N* (1000 meq L^{-1}). Mix 69.3568 g of reagent grade $NaNO_2$ with filtered DDI water and dilute to 1-L volume. Take 5 mL aliquot of primary NO_2^- standard and dilute with 500 mL of filtered DDI water (10 meq L^{-1}). Add eight drops of toluene to primary NO_2^- standard to retard microbial growth and store in a glass container.

6.17 NO_2^- calibration standards. Prepare 4 NO_2^- calibration standards (0.5, 1.0, 3.0, and 7.0 readings) by taking aliquots of primary NO_2^- standard (10 meq L^{-1}) and diluting each aliquot to 100-mL volume with working eluent as follows:

Primary Mixed Stds.	Final Vol. w/ Eluent	NO_2^-
(mL)	*(mL)*	*(meq L^{-1})*
0.5	100	0.5
1.0	100	1.0
3.0	100	3.0
7.0	100	7.0

7. Procedure

Dilution of Extracts

7.1 To estimate the total soluble anion concentration (meq L^{-1}), multiply the EC_s (method 8A3a) by 10. Subtract the CO_3^{2-} and HCO_3^- concentrations (methods 6I1b and 6J1b) from the total anion concentration. The remainder is the ≈ concentration (meq L^{-1}) of anions to be separated by ion chromatography.

$$\text{Anion concentration (meq } L^{-1}) = EC_s \times 10 - (HCO_3^- + CO_3^{2-})$$

7.2 Dilute the saturation extract with the working eluent. Some typical dilutions are as follows:

EC_s	Dilution Factor
(mmhos cm^{-1})	
0.0 to 0.4	1:3
0.4 to 0.7	1:5
0.8 to 1.2	1:9
1.2 to 1.8	1:17
1.8 to 2.9	1:39
3.0 to 5.5	1:80
5.5 to 7.5	1:150
7.5 to 9.7	1:200
9.7 to 13.5	1:290
13.5 to 15.5	1:350
15.5 to 25.0	1:660
25.0 to 40.0	1:1100
40.0 to 55.0	1:2100
55.0 to 75.0	1:4800
+75.0	1:15,500

7.3 Place the diluted samples in 12-mL syringes. Cap syringes to prevent evaporation or contamination.

7.4 Place the mixed calibration standards in 12-mL syringes.

Set-up and Operation of Ion Chromatograph (IC)

7.5 Because any number of factors may cause a change in IC operating conditions, only a general set-up of the Dionex 2110i ion chromatograph is presented. Individual analysts may modify some or all of the operating conditions to achieve satisfactory results. The µS cm^{-1} units are equivalent to mmhos cm^{-1}. Typical operation parameters are as follows:

Parameter	Range
Conductivity cell range	3 µS cm^{-1} full scale to 100 µS cm^{-1}
Auto offset	"On"
Analytical pump flow rate	2.0 to 2.5 mL min^{-1}
Low pressure limit	200
High pressure limit	1000
Regenerant flow	3 to 4 mL min^{-1}
Injector loom	0.50 mL
Air pressure	3 to 6 psi
Chart recorder speed	0.5 cm min^{-1}
Chart recorder span	1000 mV full scale

7.6 Initial IC operation should be long enough to establish a stable baseline.

7.7 Inject the most concentrated standard. The IC adjustment may be necessary to obtain adequate stability, resolution, and reproducibility.

7.8 Inject standards in random order to detect if memory effects are evident.

7.9 Analyze blanks at frequent intervals.

7.10 The injection loop requires complete flushing, i.e., 3 to 5x the loop volume.

7.11 Inject samples, standards, and blanks in the IC after achievement of stability. The analyst may change the detector range to suit the sample.

7.12 The analyst records the detector range and peak height for each detected anion. The anion identity may be determined by comparison to standards. Peak height is determined from the baseline to the peak.

8. Calculations

Calibration Calculations

8.1 Use the peak height of each anion standard to either construct a calibrated curve to plot anion concentration or use a least squares analysis to calculate anion concentration. The analytes are reported in meq L^{-1}.

8.2 *Calibration Curve*: Plot the peak height against the meq L^{-1} of each anion standard on graph paper. Construct the calibration curve by finding the "best" line that fits the plotted standards.

8.3 *Linear Squares Analysis*: Use a least squares criterion, i.e. best moving average. Refer to a statistical analysis book for additional information on least squares analysis. An example for the anion Cl^- is as follows:

Cl^- (meq L^{-1}) = Y = 0.1 1.5 4.0

Peak height = X = 8.43 170.0 441.5

Number of standards = n = 3

$\sum Y_i = 5.6$ $\sum X_i = 619.93$

$\sum Y_i/n = Y = 1.866$ $\sum X_i/n = X = 206.6433$
$\sum X_i Y_i = 2021.843$ $\sum X_i^2 = 223893.31$
$\sum X_i \sum Y_i = 3471.608$

$$b = \frac{\sum X_i Y_i - \sum X_i \sum Y_i/n}{\sum X_i^2 - (\sum X_i)^2/n} = \frac{2021.843 - 1157.2027}{223893.31 - 128104.4} = 0.0090265$$

b = slope of the line, i.e., the amount that Y changes when X changes by 1 unit

The equation is as follows:

$$Y = \bar{Y} + b (X - \bar{X})$$

$$Y = 1.866 + 0.0090265 (X) - 1.8653$$

Analyte Calculation

8.4 *Calibration Curve*: Read the analyte concentration (meq L^{-1}) directly from the calibration curve.

8.5 *Linear Regression*: Put the peak height in the preceding equation and solve for analyte concentration (meq L^{-1}). Thus, if sample extract has 204 peak height, the preceding equation is as follows:

$$Y = 1.866 + 0.0090265 (204) - 1.8653 = 1.84 \text{ meq } L^{-1}$$

8.6 Repeat the calibration set and analyte calculation for each anion.

9. Report

Report the saturation extract anions in units of meq L^{-1} to the nearest 0.1 meq L^{-1}.

10. Precision

Precision data are not available for this procedure.

11. References

Khym, J.X. 1974. Analytical ion-exchange procedures in chemistry and biology: Theory, equipment, techniques. Prentice-Hall, Inc., Englewood Cliffs, NJ.

Soil Conservation Service. 1984. Procedures for collecting soil samples and methods of analysis for soil survey. USDA–SCS Soil Surv. Invest. Rep. No. 1. U.S. Govt. Print. Office, Washington, DC.

U.S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. L.A. Richards (ed.) U.S. Dept. of Agric. Handb. 60. U.S. Govt. Print. Office, Washington, DC.

Total Sulfur (6R)

SO_2 Evolution, Infrared (6R3)

LECO SC-132 Sulfur Analyzer (6R3b)

1. Application

Organic and inorganic S forms are found in soils, with the organic S fraction accounting for >95% of the total S in most soils from humid and semi-humid regions (Tabatabai, 1982). 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%.

In well-drained, well-aerated soils, most of the inorganic S normally occurs as sulfate. In marine tidal flats, other anaerobic marine sediments, and mine spoils, there are usually large amounts of reduced S compounds which 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.

The typical use of total S is as an index of the total reserves of this element, which may be converted to plant available S. The SSL uses the combustion technique (LECO sulfur analyzer) for analysis of total S (method 6R3b). 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 and other carbonates, ammonium chloride and other chlorides, potassium phosphate and 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, 1982). Extraction reagents for organic S include hydrogen peroxide, sodium bicarbonate, sodium hydroxide, sodium oxalate, sodium peroxide, and sodium pyrophosphate. There are other methods available for determination of soil S, especially for total S and SO_4^{2}-S. The investigator may refer to the review by Beaton et al. (1968).

2. Summary of Method

A fine-ground (<80-mesh) soil sample is oxidized at high temperature. The gases released are scrubbed, and the SO_2 in the combustion gases are measured using an infrared detector. Percent S is reported on an oven-dry soil basis.

3. Interferences

No significant interferences are known to affect the oxidizable S measurement.

4. Safety

Wear protective clothing and safety glasses. Magnesium perchlorate may form explosive mixtures. Magnesium perchlorate may contain traces of perchloric acid, which remain from manufacturer's operations. This acid is anhydrous because of the strong desiccating capability of the salt. Avoid prolonged contact with oxidizable material or material capable of forming unstable perchlorate esters or salts. Remove magnesium perchlorate by using an excess of water to thoroughly dilute the material.

The use of high temperatures in the oxidation of samples requires that extreme caution be used to prevent burns and fires. Follow standard laboratory procedures when handling compressed gases. Oxygen is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the sulfur analyzer.

5. Equipment

5.1 Sulfur analyzer, Leco Model SC-132 781-400 Sulfur System, Leco Corp., St. Joseph, MI

5.2 Data transmit card, part no. 772-573, Leco Corp., St. Joseph, MI

5.3 Combustion boats, part no. 529-203, Leco Corp., St. Joseph, MI

5.4 Single-stage regulator, Oxygen Service, Part No. E11-W-N115BOX, Air Products and Chemicals, Inc., Box 538, Allentown, PA 18105

5.5 Electronic balance, ±1-mg sensitivity

6. Reagents

6.1 Anhydrone, anhydrous magnesium perchlorate, granular

6.2 Glass wool

6.3 Compressed oxygen, >99.5% @ 30 psi

7. Procedure

7.1 Weigh an air-dry, fine-ground (<80-mesh) soil sample in a tared combustion boat. Sample size depends upon S content. The product of sample weight in g multiplied by the S percent must not be >2. In most cases, the sample size is 1.00 g, unless the S content is >2%.

7.2 Refer to the manufacturer's manual for operation of sulfur analyzer. An overview of the sulfur analyzer is as follows:

a. Samples are combusted in an O_2 atmosphere in which the S is oxidized to SO_2.

b. Moisture and dust are removed, and the SO_2 gas is then measured by a solid state infrared detector.

c. The microprocessor formulates the analysis results. The control console displays and prints results by combining the outputs of the infrared detector and system ambient sensors with pre-programmed calibration, linearization, and weight compensation factors.

8. Calculations

$$S\ (\%) = S_i \times AD/OD$$

where:

S (%) = S (%) on oven-dry basis

S_i = S (%) instrument

AD/OD = air-dry/oven-dry ratio (method 4B5)

9. Report

Report total S as a percentage of oven-dry weight to the nearest 0.1%.

10. Precision

Precision data are not available for this procedure. A quality control check sample is run in every batch of 12 samples. A blank (crucible only) and a rerun of one of the 12 samples (unknowns) also are run in every batch. For 27 observations of the quality control check sample, the mean, standard deviation, and C.V. for total S are 0.57, 0.02, and 4.3%, respectively.

11. References

Beaton, James D., G.R. Burns, and J. Platou. 1968. Determination of sulfur in soils and plant material. Tech. Bull. No. 14. The Sulfur Inst., 1725 K Street, N.W., Washington, D.C. 20006

Tabatabai, M.A. 1982. Sulfur. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:501–538.

Phosphorus (6S)

New Zealand P Retention (6S4)

1. Application

In *Soil Taxonomy*, the P retention of soil material is a criterion for andic soil properties (Soil Survey Staff, 1990). Andisols and other soils that contain large amounts of allophane and other amorphous minerals have capacities for binding P (Gebhardt and Coleman, 1984). The factors that affect soil P retention are not well understood. However, allophane and imogolite have been considered as major materials that contribute to P retention in Andisols (Wada, 1985). Phosphate retention is also called P absorption, sorption, or fixation.

2. Summary of Method

A 5-g soil sample is shaken in a 1000-ppm P solution for 24 h. The mixture is centrifuged at 2000 rpm for 15 min. An aliquot of the supernatant is transferred to a colorimetric tube to which nitric vanadomolybdate acid reagent (NVAR) is added. The percent transmittance of the solution is read using a colorimeter. The New Zealand P retention is reported as percent P retained.

3. Interferences

No significant problems are known to affect the P retention measurement.

4. Safety

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses). When preparing reagents, exercise special care. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts. Restrict the use of concentrated HNO_3 to a fume hood. Use safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids.

5. Equipment

5.1 Electronic balance, ±0.01-g sensitivity

5.2 Shaker, Eberbach 6000 power unit, reciprocating speed of 60 to 260 epm, with 6040 utility box carrier and 6110 floor stand, Eberbach Corp., Ann Arbor, MI

5.3 Digital diluter/dispenser, product no. 100004, with hand probe and actuator, product no. 230700, Hamilton Co., P.O. Box 10030, Reno, NV, 89510

5.4 Syringes, 10,000 and 1000 µL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV, 89510

5.5 Diluter/dispenser, 25 mL

5.6 Calorimeter, Bausch and Lomb

5.7 Calorimeter tubes, glass, 10 mL, 1-cm light path, Bausch and Lomb

5.8 Centrifuge, International no. 2, Model V, with no. 250 A head, International Equip. Co., Boston, MA

5.9 Trunions, International no. 320, International Equip. Co., Boston, MA

5.10 Centrifuge tubes, 50 mL, Oak-Ridge, polyallomer, Nalgene 3119, Nalge Co., Box 20365, Rochester, NY 14602.

5.11 Plastic cups, 2 fl. oz.

5.12 Pipets, volumetric, class A, glass, various sizes of 1 to 20 mL

6. Reagents

6.1 Distilled deionized (DDI) water

6.2 Nitric acid (HNO_3), conc.

6.3 P retention solution, 1000 ppm P. Dissolve 8.80 g of KH_2PO_4 and 32.8 g of sodium acetate (CH_3COONa) in DDI water. Add 23 mL of glacial acetic acid. Dilute to 2 L with DDI water in a volumetric flask. The solution pH should range between 4.55 and 4.65.

6.4 Molybdate solution. Dissolve 16 g of ammonium molybdate (VI) $[(NH_4)_6MO_7O_{24}•4H_2O]$ in 50 °C DDI water. Allow the solution to cool to room temperature and dilute to 1 L with DDI water.

6.5 Nitric acid solution. Carefully and slowly dilute 100 mL of conc. HNO_3 to 1 L of DDI water. Add the acid to the water.

6.6 Nitric vanadomolybdate acid reagent (NVAR), vanadate solution. Dissolve 0.8 g of NH_4VO_3 in 500 mL of boiling DDI water. Allow the solution to cool to room temperature. Carefully and slowly add 6 mL of conc. HNO_3. Dilute to 1 L with DDI water. Mix the nitric acid solution with the vanadate solution and then add the molybdate solution. Mix well.

6.7 Stock P standard solution (SPSS), 4000 ppm P. Dissolve 17.6 g K_2HPO_4 in DDI water. Dilute to 1 L with DDI water.

6.8 Standard P calibration P solutions (SPCS), 100, 80, 60, 40, 20, and 0% P retained. Dilute the SPSS with a solution that contains 32.8 g of sodium acetate (CH_3COONa) and 23 mL of glacial acetic acid diluted to 2 L with DDI water as follows: 100% = DDI water (0 ppm); 80% = 1:20 (200 ppm); 60% = 1:10 (400 ppm); 40% = 3:20 (600 ppm); 20% = 1:5 (800 ppm); and 0% = 1:4 (1000 ppm). The percent amount refers to percent P retention.

7. Procedure

7.1 Weigh 5.00 g of air-dry soil into a 50-mL centrifuge tube.

7.2 Use the dispenser to add 25.0 mL of P-retention solution to centrifuge tube.

7.3 Cap centrifuge tube and place in shaker and shake for 24 h at room temperature (20 °C).

7.4 Add 2 to 3 drops of Superfloc, 0.02% w/v to each tube.

7.5 Centrifuge sample at 2000 rpm for 15 min.

7.6 Pour sample supernatant into plastic cup.

7.7 Use the digital diluter to add the nitric vanadomolybdate acid reagent (NVAR) to each sample supernatant and to each SPCS. To fill a 10-mL calorimeter tube, the diluter setting is 66 for diluent (NVAR) and 35 for sample (1:20 dilution).

7.8 The color reaction requires a minimum of 30 min before the analyst records readings.

7.9 Set the calorimeter (blue bulb) to read at 466 nm. Set the zero against DDI water (blank). A blank has all reagents contained in the sample extract except the soil.

7.10 Record the percent transmittance to the nearest 0.01 unit for the sample extract and each SPCS.

8. Calculations

8.1 Transmittance of a solution is the fraction of incident radiation transmitted by the solution, i.e., $T = P/P_o$, and is often expressed as a percentage,

i.e., $T = P/P_o \times 100$. The absorbance of a solution is directly proportional to concentration and is defined by the equation, $A = -\log_{10} T$. These relationships are derived from Beer's law.

Calibration Calculations

8.2 Use the transmittance of each SPCS to either construct a calibrated curve to plot P or use a least squares analysis to calculate P. The P is reported in percent retained.

8.3 *Calibration Curve*: Plot the transmittances against the ppm P of each SPCS on semilog graph paper or convert to absorbances and plot on linear graph paper. Construct the calibration curve by finding the "best" line that fits the plotted SPCS.

8.4 *Least Squares Analysis*: Use a least squares criterion, i.e. best moving average. Refer to a statistical analysis book for additional information on least squares analysis. To facilitate data manipulation in a least squares analysis, the following standard curve is developed using the concentration of SPCS as a f[ln(%T)]. Final calculated analyte concentration with either $\log_{10}$ or ln base would be the same. Refer to method 6S3b for an example of least squares analysis.

Analyte Calculation

8.5 *Calibration Curve*: Read the percent P directly from the calibration curve.

8.6 *Least Squares Analysis*: Refer to method 6S3 for an example of least squares analysis.

9. Report

Report the percent New Zealand P retention to the nearest whole number.

10. Precision

Precision data are not available for this procedure.

11. References

Gebhardt, H., and N.T. Coleman. 1984. Anion adsorption of allophanic tropical soils: III. Phosphate adsorption. p. 237–248. *In* K.H. Tan (ed.) Andosols. Benchmark papers in soil science series. Van Nostrand Reinhold, Co., Melbourne, Canada.

Soil Survey Staff. 1990. Keys to soil taxonomy. 4th ed. SMSS technical monograph no. 6. Blacksburg, VA.

Wada, K. 1985. The distinctive properties of Andosols. p. 173–229. *In* B.A. Stewart (ed.) Adv. Soil Sci. Springer-Verlag, NY.

MINERALOGY (7)

Instrumental Analyses (7A)

Thermal Gravimetric Analysis (7A4)

Perkin-Elmer 7 Series (7A4b)

1. 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). 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, e.g., gibbsite ($Al(OH)_3$), kaolinite ($Al_2Si_2O_5(OH)_4$), and 2:1 expandable minerals (smectite and vermiculite).

2. Summary of Method

A 5- to 10-mg sample of soil clay is weighed into a platinum sample pan and placed in the TGA balance. The instrument records the initial sample weight. The analyst zeros the balance. The sample is then heated from a temperature of 30 to 900 °C at a rate of 20 °C min^{-1} in a flowing N_2 atmosphere. The computer collects weight changes as a function of temperature and records a thermogravimetric curve. Gibbsite and kaolinite are quantified by noting the weight loss between 250 to 350 °C and 450 to 550 °C, respectively, and then relating these data to the theoretical weight loss of pure gibbsite or kaolinite (Soil Conservation Service, 1984). The weight loss is due to dehydroxylation, i.e., loss of crystal lattice water. Though not presently performed by the National Soil Survey Laboratory (NSSL), quantification of the 2:1 expandable minerals (smectite+vermiculite) is related to weight loss at <250 °C, i.e., loss of adsorbed water (Karathanasis and Hajek, 1982; Tan et al., 1986). At this low temperature, adsorbed water is proportional to the specific area of the sample (Jackson, 1956; Karathanasis and Hajek, 1982; Mackenzie, 1970; Tan and Hajek, 1977).

3. Interferences

Organic matter is objectionable because it has a weight loss by dehydrogenation and by oxidation to CO_2 between 300 to 900 °C (Tan, et al., 1986). Analysis in an inert N_2 atmosphere alleviates this problem. Mineral salts that contain water of crystallization also may be interferences. Samples should be washed free of any soluble salts.

A representative soil sample is important as sample size is small (<10 mg). Avoid large aggregates in sample, the presence of which may cause thermal

interferences, i.e., differential kinetics of gas diffusion through the sample and physical movement of sample in a reaction.

In general, the same reactions that interfere with DSC/DTA also interfere with TGA determinations of kaolinite, gibbsite, and 2:1 expandable minerals. However, TGA is more sensitive to small water losses at slow rates, whereas DSC/DTA is more sensitive to large water losses at rapid rates (Tan, et al., 1986). This sensitivity difference may help to explain why kaolinite and gibbsite quantifications in TGA vs. DSC/DTA often are not equivalent, i.e., TGA estimates tend to be greater than the corresponding DSC/DTA estimates. 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. This problem is particularly apparent with illitic samples, which characteristically contain more "structural" water than ideal structural formulae would indicate (Rouston, et al., 1972; Weaver and Pollard, 1973).

Even though it is well established that various minerals lose the major portion of their crystal lattice water at different temperature ranges (Tan et al., 1986), there are overlaps in these weight loss regions (WLR) of minerals which interfere in the identification and measurement of the minerals of interest. The goethite WLR (250 to 400 °C) overlaps the gibbsite WLR (250 to 350 °C) (Mackenzie and Berggen, 1970). The illite WLR (550 to 600 °C) overlaps the high end of the kaolinite WLR (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 the low end of the kaolinite WLR (450 to 550 °C), especially in the poorly crystalline kaolinites (Mackenzie and Caillere, 1975). Similarly, the dehydroxylation of nontronites, Fe-rich dioctahedral smectites (450 to 500 °C), may interfere with kaolinite identification and measurement (Mackenzie and Caillere, 1975).

4. Safety

Secure high pressure N_2 tanks and handle with care. When changing the tanks, protect valves with covers. Do not program the analyzer for >950 °C because it may present a safety hazard during sample analysis and cleaning cycles. Do not heat aluminum sample pans >600 °C. Aluminum melts at 660 °C, and the pans alloy with and destroy the sample holders. Always use high quality purge gases with the TGA. Minimum purity of 99.9% is recommended.

5. Equipment

5.1 Thermal analysis system, Perkin-Elmer 7 series, 7500 computer, TAC7 instrument controllers

5.2 Thermogravimetric analyzer module, TGA7, Hewlett-Packard digital plotter

5.3 Pressure tanks (2), N_2, purity 99.99%

5.4 Two-stage gas regulators (2), 50 psi outlet pressure

5.5 One-stage gas regulator for compressed air

5.6 Electronic balance, ±0.1-mg sensitivity, Mettler AE160

5.7 Forceps, flat-tipped

5.8 Weighing spatula

5.9 Desiccator, glass

5.10 Mortar and pestle

5.11 Sieves, 100 mesh or 80 mesh

5.12 Kaolinite, standard, poorly crystalline, Georgia Kaolinite, Clay Minerals Society, Source Clay Minerals Project, sample KGa-2

5.13 Gibbsite, standard, Surinam Gibbsite, National Soil Survey Laboratory (NSSL), 67L022

6. Reagents

6.1 Magnesium nitrate saturated solution [$Mg(NO_3)_2 \cdot 6H_2O$]

6.2 Ethanol

7. Procedure

Derived <2µm Clay Fractions

7.1 Prepare Na-saturated clay as in method 7A2i, preparation of clay suspension, 7.8 to 7.19.

7.2 Dry the clay suspension and transfer to mortar. Moisten sample with ethanol and grind with pestle to make a homogeneous slurry.

7.3 Air-dry sample using flowing air in hood. Lightly grind sample with pestle to make a homogeneous powder.

7.4 Sieve sample with 80-mesh screen. Equilibrate sample overnight over a saturated magnesium nitrate solution (55% rh) in a glass desiccator.

TGA Operation

7.5 Set-up the instrument and calibrate.

7.6 Turn on the N_2 purge gases and set to 6 and 3.5 psi for balance and sample purge, respectively. The balance purge pressure should always be greater than the sample purge pressure.

7.7 Turn on compressed air and set to 25 psi.

7.8 Place the platinum sample pan in the balance stirrup. Use the computer to raise the furnace tube and to zero the balance. Lower the furnace tube.

7.9 Remove the sample pan from the stirrup. Weigh ≈5 mg of sample, i.e., <100-mesh whole-soil or derived <2-µm clay fraction, into tared sample pan. Refer to section on derived <2-µm clay fractions, 7.1 to 7.4.

7.10 Use flat-tipped forceps to remove the sample pan from the analytical balance. Tap the sample pan against a hard surface several times to uniformly distribute the sample.

7.11 Carefully place sample pan in the stirrup of the TGA microbalance.

7.12 The standard sample run heating program has a heating rate of 20 °C min^{-1}, a starting temperature of 30 °C, and an ending temperature of 900 °C.

7.13 Raise the furnace tube and allow it to seat. Press "Read Weight" key (usually twice) until a relative weight percentage of 100.0% is displayed. The computer then reads the weight.

7.14 Immediately start the "Run" program.

7.15 At the end of the sample run (≈45 min), remove the sample pan from the microbalance stirrup. The furnace tube is lowered automatically at the end of run.

7.16 To store data, enter the appropriate file name on the computer for the completed run. If data are not stored by appropriate file name, data are stored under a default file name of "gsav". Only four of these files can be saved at any one time, after which files are overwritten. Once a file is named, it cannot be changed.

8. Calculations

8.1 The thermogravimetric curve is displayed on the computer monitor. The ordinate (Y) is expressed in a relative weight percentage, i.e., the initial sample weight is 100.0%. Use the computer to calculate the total change in sample weight (Δ Y), within the predetermined temperature range, as a 8 sample weight percent.

$$\% \text{ Kaolinite} = [(\Delta \text{ sample weight } \%_{450\text{-}550^\circ C})/14] \times 100$$

where:

Δ sample weight = total Δ in sample weight expressed as relative percent

14 = percent weight of hydroxyl water lost from pure kaolinite

$$\% \text{ Gibbsite} = [(\Delta \text{ sample weight } \%_{250\text{-}350^\circ C})/ 34.6] \times 100$$

where:

Δ sample weight = total Δ in sample weight expressed as relative percent

34.6 = percent weight of hydroxyl water lost from pure gibbsite

The percent weights of hydroxyl water lost from kaolinite and gibbsite are derived from the following assumed dehydroxylation reactions.

$Si_2Al_2O_5(OH)_4 \rightarrow 2SiO_2 + Al_2O_3 + 2H_2O$

(kaolinite)

$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$

(gibbsite)

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 $= (36/258) \times 100 = 34.6\%$

9. Report

Report percent gibbsite and/or kaolinite to nearest whole number.

10. Precision

Precision data are not available for this procedure.

11. References

Jackson, M.L. 1956. Soil chemical analysis. Advanced course. Private publication, Madison, WI.

Karathanasis, A.D., and B.F. Hajek. 1982. Revised methods for rapid quantitative determination of minerals in soil clays. Soil Sci. Soc. Am. J. 46:419–425.

Mackenzie, R.C. 1970. Simple phyllosilicates based on gibbsite- and brucite-like sheets. p. 498–537. *In* R. C. Mackenzie (ed.) Differential thermal analysis. Vol. 1. Acad. Press, London.

Mackenzie, R.C., and G. Berggren. 1970. Oxides and hydroxides of higher-valency elements. p. 272–302. *In* R.C. Mackenzie (ed.) Differential thermal analysis. Acad. Press, NY.

Mackenzie, R.C., and S. Caillere. 1975. The thermal characteristics of soil minerals and the use of these characteristics in the qualitative and quantitative determination of clay minerals in soils. p. 529–571. *In* J.E. Gieseking (ed.) Soil components. Vol. 2. Inorganic components. Springer-Verlag, NY.

Mackenzie, R.C., and B.D. Mitchell. 1972. Soils. p. 267–297. *In* R.C. Mackenzie (ed.) Differential thermal analysis. Vol. 2. Acad. Press. London.

Rouston, R.C., J.A. Kittrick, and E.H. Hope. 1972. Interlayer hydration and the broadening of the 10A x-ray peak in illite. Soil Sci. 113:167–174.

Soil Conservation Service. 1984. Procedures for collecting soil samples and methods of analysis for soil survey. USDA–SCS Soil Surv. Invest. Rep. No. 1. U.S. Govt. Print. Office, Washington, DC.

Tan, K.H., and B.F. Hajek. 1977. Thermal analysis of soils. p. 865–884. *In* J.B. Dixon and S.B. Weed (eds.) Minerals in soil environments. 2nd ed. SSSA Book Series 1. SSSA, Madison, WI.

Tan, K.H., B.F. Hajek, and I. Barshad. 1986. Thermal analysis techniques. p. 151–183. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical properties. 2nd ed. Agronomy 9:151–183.

Weaver, C.E., and L.D. Pollard. 1973. The chemistry of clay minerals. Elsevier Sci. Publ. Co., Amsterdam.

Instrumental Analyses (7A)
Differential Scanning Calorimetry (7A6)

1. Application

Calorimetry measures specific heat or thermal capacity of a substance. Differential scanning calorimetry (DSC) is a calorimetric technique in which the rate of heat flow between a sample and a reference material is measured as materials are held isothermal to one another. The DSC directly measures the magnitude of an energy change (H, enthalpy or heat content) in a material undergoing an exothermic or endothermic reaction. DSC is commonly used to quantify gibbsite ($Al(OH)_3$) and kaolinite ($Al_2Si_2O_5(OH)_4$) in soils and clays by measuring the magnitude of their dehydroxylation endotherms which are between 250 to 350 °C and 450 to 550 °C, respectively (Karathanasis and Hajek, 1982; Jackson, 1956; Mackenzie and Berggen, 1970; Mackenzie, 1970).

2. Summary of Method

An 8 mg sample of soil clay is weighed into an aluminum sample pan and placed in the DSC sample holder. The sample and reference are heated under flowing N_2 atmosphere from a temperature of 30 to 600 °C at a rate of 10 °C min^{-1}. Data are collected by the computer and a thermogram is plotted. Gibbsite and kaolinite are quantified by measuring the peak area of any endothermic reactions between 250 to 350 °C and 450 to 550 °C, respectively, and by calculating the H of the reaction. These values are related to the values for the respective known quantities of the two minerals (gibbsite and kaolinite).

3. Interferences

Organic matter is objectionable because it produces irregular exothermic peaks in air or O_2, commonly between 300 to 500 °C, which may obscure important reactions from the inorganic components of interest (Schnitzer and

Kodama, 1977). Analysis in an inert N_2 atmosphere alleviates this problem. Mineral salts that contain water of crystallization also may be interferences. Samples should be washed free of any soluble salts.

Use a representative soil sample as sample size is small (<10 mg). Avoid large aggregates in sample, the presence of which may cause thermal interferences because of differential kinetics of gas diffusion through the sample and physical movement of sample in a reaction.

The dehydroxylation of goethite is between 250 to 400 °C and may interfere with the identification and integration of the gibbsite endotherm (250 to 350 °C) (Mackenzie and Berggen, 1970). The dehydroxylation of illite is between 550 to 600 °C and partially overlaps the high end of the kaolinite endotherm (450 to 550 °C), resulting in possible peak integrations (Mackenzie and Caillere, 1975). The dehydroxylation of hydroxy-Al interlayers in hydroxy-Al interlayered vermiculite (HIV) is between 400 to 450 °C and may interfere with the low end of the kaolinite endotherm (450 to 550 °C), especially in the poorly crystalline kaolinites (Mackenzie and Caillere, 1975). Similarly, the dehydroxylation of nontronites, Fe-rich dioctahedral smectites, is between 450 to 500 °C and may interfere with kaolinite identification and measurement (Mackenzie and Caillere, 1975).

4. Safety

Secure high pressure N_2 tanks and handle with care. When changing the tanks, valves should be protected with covers. Do not program the analyzer for >950 °C because it may present a safety hazard during sample analysis and cleaning cycles. Do not heat aluminum sample pans >600 °C. Aluminum melts at 660 °C, and the sample pans alloy with and destroy the sample holders. Always use high quality purge gases with the DSC. Minimum purity of 99.9% is recommended.

5. Equipment

5.1 Thermal analysis system, Perkin-Elmer 7 series, 7500 computer, TAC7 instrument controllers

5.2 Differential scanning calorimeter module, DSC7, Hewlett-Packard digital plotter

5.3 Pressure tanks (2), N_2, purity 99.99%

5.4 Two-stage gas regulators (2), 50 psi outlet pressure

5.5 Electronic balance, ±0.1-mg sensitivity, Mettler AE160

5.6 Forceps, flat-tipped

5.7 Weighing spatula

5.8 Desiccator, glass

5.9 Mortar and pestle

5.10 Sieves, 100 mesh or 80 mesh

5.11 Kaolinite, standard, poorly crystalline, Georgia Kaolinite, Clay Minerals Society, Source Clay Minerals Project, sample KGa-2

5.12 Gibbsite, standard, Surinam Gibbsite, National Soil Survey Laboratory (NSSL), 67L022

6. Reagents

6.1 Magnesium nitrate saturated solution [$Mg(NO_3)_2 \cdot 6H_2O$]

6.2 Ethanol

7. Procedure

Derived <2µm Clay Fractions

7.1 Prepare Na-saturated clay as in method 7A2i, preparation of clay suspension, 7.8 to 7.19.

7.2 Dry the clay suspension and transfer to mortar. Moisten sample with ethanol and grind with pestle to make a homogeneous slurry.

7.3 Air-dry sample using flowing air in hood. Lightly grind sample with pestle to make a homogeneous powder. Transfer to original container for storage until use.

7.4 Prior to TGA analysis, sieve sample with 80-mesh screen. Equilibrate sample overnight over a saturated magnesium nitrate solution (55% rh) in a glass desiccator.

DSC Operation

7.5 Set up the instrument and calibrate.

7.6 Weigh ≈8 mg of sample, i.e., <100-mesh whole-soil or derived <2-µm clay fraction, into tared aluminum sample pan. Refer to section on derived <2-µm clay fractions, 7.1 to 7.4.

7.7 Use flat-tipped forceps to remove aluminum sample pan from balance. Drop sample from a 4- to 5-mm height to uniformly distribute sample in pan. Return the sample pan with sample to the balance and record weight to nearest ±0.1 mg. This weight is entered into computer in appropriate menu.

7.8 Carefully place aluminum sample pan in the center of DSC platinum sample side (left side) of sample holder. Place platinum two-hole lid on holder that covers the sample pan. Align lid holes with purge gas exit hole in DSC head.

7.9 Place empty aluminum sample pan in reference side (right side) of sample holder. Place remaining platinum two-hole lid on holder that covers the sample pan. Align lid holes as in previous step.

7.10 Close DSC head cover and lock.

7.11 The standard sample run heating program has a heating rate of 10 °C min^{-1}, 5.3 min data delay, 5.0 min N_2 purge.

7.12 Start the “Run” program.

7.13 Observe the milliwatts (mW) readout on the computer display terminal and when reading stabilizes (≈5 to 10 s), remove the sample pan and sample from the sample side of sample holder. Do not disturb the reference side.

7.14 To store data, enter the appropriate file name on the computer for the completed run. If data are not stored by appropriate file name, data are stored under a default file name of “gsav”. Only four of these files can be saved at any one time, after which files are overwritten. Once a file is named, it cannot be changed.

8. Calculations

The thermogram is displayed on the computer monitor. The area under the DSC curve is proportional to the enthalpy (H). Use the computer to calculate the H or enthalpy of reaction per g of kaolinite and/or gibbsite (joules g^{-1}) as appropriate.

8.1 % Kaolinite weight = H/12.62

where:

12.62 = factor obtained from standard curve of kaolinite mixtures using China clay of undetermined purity

8.2 % Gibbsite weight = H/15.03

where:

15.03 = factor obtained from standard curve of gibbsite values using deferrated Surinam gibbsite of undetermined purity

9. Report

Report percent kaolinite and/or gibbsite to the nearest whole number.

10. Precision

Precision data are not available for this procedure.

11. References

Jackson, M.L. 1956. Soil chemical analysis. Advanced course. Private publication, Madison, WI.

Karathanasis, A.D., and B.F. Hajek. 1982. Revised methods for rapid quantitative determination of minerals in soil clays. Soil Sci. Soc. Am. J. 46:419–425.

Mackenzie, R.C. 1970. Simple phyllosilicates based on gibbsite- and brucite-like sheets. p. 498–537. *In* R. C. Mackenzie (ed.) Differential thermal analysis. Vol. 1. Acad. Press, London.

Mackenzie, R.C., and G. Berggren. 1970. Oxides and hydroxides of higher-valency elements. p. 272–302. *In* R.C. Mackenzie (ed.) Differential thermal analysis. Acad. Press, NY.

Mackenzie, R.C., and S. Caillere. 1975. The thermal characteristics of soil minerals and the use of these characteristics in the qualitative and quantitative determination of clay minerals in soils. p. 529–571. *In* J.E. Gieseking (ed.) Soil components. Vol. 2. Inorganic components. Springer-Verlag, NY.

Mackenzie, R.C., and B.D. Mitchell. 1972. Soils. p. 267–297. *In* R.C. Mackenzie (ed.) Differential thermal analysis. Vol. 2. Acad. Press. London.

Rouston, R.C., J.A. Kittrick, and E.H. Hope. 1972. Interlayer hydration and the broadening of the 10A x-ray peak in illite. Soil Sci. 113:167–174.

Schnitzer, M., and H. Kodama. 1977. Reactions of minerals with soil humic substances. *In* J.B. Dixon and S.B. Weed (eds.) Minerals in soil environments. 2nd ed. SSSA Book Series 1. SSSA, Madison, WI.

Tan, K.H., and B.F. Hajek. 1977. Thermal analysis of soils. p. 865–884. *In* J.B. Dixon and S.B. Weed (eds.) Minerals in soil environments. 2nd ed. SSSA Book Series 1. SSSA, Madison, WI.

Tan, K.H., B.F. Hajek, and I. Barshad. 1986. Thermal analysis techniques. p. 151–183. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical properties. 2nd ed. Agronomy 9:151–183.

Total Analysis (7C)
HF Dissolution (7C3)

1. Application

Historically, elemental analysis was developed for the analysis of rocks and minerals (Washington, 1930). The elemental analysis of soils, sediments, and rocks necessitates their decomposition into soluble forms. Hydrofluoric acid (HF) is efficient in the digestion and dissolution of silicate minerals for elemental decomposition. Method 7C3 is an HF acid digestion. Elemental concentration is determined by atomic absorption using 100 mg of clay suspension contained in a closed vessel with boric acid (H_3BO_3) to neutralize excess acid (Berdanier, Lynn, and Threlkeld, 1978; Soil Conservation Service, 1984).

2. Summary of Method

To 100 mg of clay suspension (method 7A2i), 5 mL of HF acid are added. The solution is heated, cooled, and 2 to 3 g of H_3BO_3 are added to neutralize excess acid. The solution is diluted to 100 mL, allowed to stand overnight, and 20 mL are decanted. The concentrations of Fe, Al, and K are determined by atomic absorption in methods 6C7a, 6G11a, and 6Q3a, respectively. Data are reported in method 7C3.

3. Interferences

Organic material may remain as a residue with this method.

4. Safety

Perform procedure in hood. Keep HF acid refrigerated and avoid contact with skin.

5. Equipment

5.1 Pipette, 5 mL

5.2 Volumetric flask, Nalgene, 100 mL

5.3 Polyethylene container, 25 mL, with cover

5.4 Electronic balance, ±0.1-mg sensitivity

6. Reagents

6.1 Distilled water

6.2 Hydrofluoric acid (HF), 48%

6.3 Boric acid, (H_3BO_3), granular

7. Procedure

HF Dissolution

7.1 Prepare Na-saturated clay as in method 7A2i, preparation of clay suspension, 7.8 to 7.19.

7.2 Pipette 2 mL of clay suspension into a 25-mL Teflon cup and add 5 mL of HF. A 100 mg of 100-mesh whole-soil sample may be substituted for the clay suspension.

7.3 Pipette a duplicate sample into a weighing dish, dry at 105 °C, and weigh. Use this sample for calculations.

7.4 Place covered Teflon cup in stainless steel retainer and tighten Teflon cap. Place sample in oven at 105 °C for ≈4 h.

7.5 Turn off oven, open door, and let stand overnight to cool.

7.6 Remove sample from oven.

7.7 Under a hood, remove Teflon cup from steel retainer vessel and add 2 to 3 g of H_3BO_3 acid.

7.8 Rinse contents of Teflon cup into a 100-mL Nalgene volumetric flask and adjust to volume with distilled water. Allow to stand overnight.

7.9 Decant ≈20 mL into a 25-mL polyethylene container for elemental analysis by atomic absorption. Refer to methods 7C7a, 6G11a, and 6Q3a.

8. Calculations

Use the MR 2.0 to perform calculations. Inputs are as follows: project number; sample number; tare value; tare + sample value; Al and Fe readings (mg L^{-1}); and K readings (meq L^{-1}). Review data for internal consistency. Request a rerun, if necessary, at this time. Store data on a data disk.

The following example illustrates the conversion calculations of atomic absorption readings or element concentrations of Fe, Al, and K to appropriate oxide forms. The concentrations of Fe and Al (mg L^{-1}) and K (meq L^{-1}) are converted to percent Fe_2O_3, Al_2O_3, and K_2O, respectively. Refer to method 4A5 for air-dry/oven-dry ratio (AD/OD).

Sample weight	=S	=0.1071 g
Fe reading	=[Fe]	=34.2 mg L^{-1}
Fe_2O_3 molecular weight	$=Fe_2O_3$	=159.70
Fe atomic weight	=Fe	=55.85
Al reading	=[Al]	=72.8 mg L^{-1}
Al_2O_3 molecular weight	$=Al_2O_3$	=101.94
Al atomic weight	=Al	=26.98
K reading weight	=[K]	=0.61 meq L^{-1}
K_2O molecular weight	$=K_2O$	=94.19
K atomic weight	=K	=39.10
K equivalent weight	=39	=39
Air-dry/oven-dry ratio	=1.024	=AD/OD
100 mL/1000 mL	=dil. factor	=100/1000
1/1000 mg g^{-1}	=conv. factor	=1/1000
100/1 P/100 pts.	=conv. factor	=100/1

% Fe_2O_3 =

[Fe] x 1/S x 100/1000 x 1/1000 x 100/1 x AD/OD x Fe_2O_3/Fe =

34.2 x 1/0.1071 x 0.1 x 0.001 x 100 x 1.024 x 159.7/111.70

% Fe_2O_3 = 4.68

$\% Al_2O_3$ =

[Al] x 1/S x 100/1000 x 1/1000 x 100/1 x AD/OD x Al_2O_3/Al =

72.8 x 1/0.1071 x 0.1 x 0.001 x 100 x 1.024 x 101.94/53.96

$\% Al_2O_3$ = 13.15%

$\% K_2O$ =

[K] x 1/S x 100/1000 x 1/1000 x 100/1 x AD/OD x K_2O/K x 39 =

0.61 x 1/0.1071 x 0.1 x 0.001 x 100 x 1.024 x 94.19/78.2 x 39 =

$\% K_2O$ = 2.74

9. Report

Report data to nearest whole percent.

10. Precision

Precision data are not available for this procedure. A quality control check sample is routinely run in HF analyses. For 38 observations of the quality control check sample, the mean, standard deviation, and C.V. for percent Fe, Al_2O_3, and K_2O are as follows:

Analyte	Mean	Std. Dev.	C.V.
% Fe	2.8	0.40	14
$\% Al_2O_3$	12.1	1.04	9
$\% K_2O$	2.4	0.38	16

11. References

Berdanier, C.R., W.C. Lynn, and G.W. Threlkeld. 1978. Illitic mineralogy in soil taxonomy: X-ray vs. total potassium. Agron. Absts. 1978 Annual Mtgs.

Soil Conservation Service. 1984. Procedures for collecting soil samples and methods of analysis for soil survey. USDA–SCS Soil Surv. Invest. Rep. No. 1. U.S. Govt. Print. Office, Washington, DC.

Washington, H.S. 1930. The chemical analysis of rocks. 4th ed. John Wiley and Sons, Inc., New York, NY.

Whittig, L.D., and W.R. Allardice. 1986. X-ray diffraction techniques. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:331–362.

OBSOLETE METHODS SECTION V: SSIR NO. 1, PROCEDURES FOR COLLECTING SOIL SAMPLES AND METHODS OF ANALYSIS FOR SOIL SURVEY (1972, 1982, 1984)

SAMPLE COLLECTION AND PREPARATION (1)

Laboratory Preparation of Soil Samples (1B)
Carbonate-Containing Material (1B3)

Procedure

Prepare dialysis membrane sacks from 5½-inch cellulose casing (Visking Company), using large rubber bands to tie the bottoms. Place the sample (as much as 6 kg if very gravelly and highly calcareous) in a dialysis membrane and add about 1 L pH 5, *N* NaOAc buffer. Tie the top of the dialysis membrane around a glass breather tube 4-in long and hang the assembly in a 60-L reservoir of buffer held in a 20-gal plastic garbage can. If carbonate is dissolving, knead the membrane to release bubbles of CO_2. When bubbles of CO_2 no longer form on kneading, open the dialysis membrane and use strong acid to check the coarser material for carbonate coatings (carbonate remains longer in the coarser material). When sample is free of carbonate, desalt it by dialysis against tap water flowing continuously through a large plastic garbage can. Check the ionic concentration inside the membrane by measuring conductivity of a small volume of the supernatant liquid poured out through the breather tube. Continue dialysis until the salt concentration is less than 10 meq/L.

The procedure used to dry the sample depends on whether the particles larger than 2 mm have been removed before buffer treatment. If they have been removed, withdraw excess water from the sample in the membrane with filter candles. Knead the membrane to mix the sample and place it in contact with ethanol to desiccate further. Remove the sample from the membrane and air-dry.

If the buffer-treated sample contains particles larger than 2 mm, wet sieve the sample through a 2-mm sieve. Then dry sieve the material remaining on the sieve (>2 mm) and add the <2-mm fraction from this sieving to the <2-mm fraction separated by the wet sieving. Remove most of the water from the <2-mm fraction with filter candles. Use ethanol to transfer the samples to shallow pans and dry. Ethanol prevents aggregation of clay into durable flakes during drying.

Discussion

The time required for carbonate removal varies greatly, depending on particle size, percentage and type of carbonate, and sample size. Samples from horizons strongly cemented by carbonate have required as long as 2 months. The concentration of alkaline-earth ions in the buffer greatly affects the rate of carbonate removal. Changing the buffer in the reservoir well before the buffer capacity has been exhausted, thereby keeping the alkaline-earth ion concentration low, increases the rate markedly. Desalting usually takes about 4 days.

For carbonate-cemented horizons, the whole sample, not just the <2-mm material, must be buffer treated. Furthermore, for horizons without carbonate cementation, buffer treatment of the whole sample has the advantage of washing the >2-mm skeletal material free of adhering fines and organic material. This problem is considered further in 1B4.

For very gravelly horizons, large samples (several kilograms) are necessary for buffer treatment because of the small amount of <2-mm material. Using large samples also increases precision of the >2-mm percentage.

References

Grossman and Millet (1961).

Carbonate-Indurated Material Containing Coarse Fragments (1B4)

Break the field sample to get several representative subsamples. Remove the carbonate from one subsample by acid treatment and separate the coarse fragments from the fine earth (1B3). Weigh the two fractions. Use the noncarbonate fine earth for the standard characterization and mineralogical measurements (sections 6-7).

Grind another subsample of the whole field sample to pass 80-mesh sieve. Determine the carbonate content (weight) of this whole ground subsample (6E).

These weights can be used to calculate the $CaCO_3$ percentage of the fine earth. Any analytical value based on the noncarbonate fine earth can be converted to the whole-soil basis as well as to the basis of the carbonate-containing fine earth.

PARTICLE-SIZE ANALYSIS (3)

Particles <2 mm (Pipette Method) (3A)

An automated balance system, consisting of a Radio Shack Model II microcomputer interfaced to a Mettler PL2000 electronic balance (for sand) and a Mettler AE160 electronic balance (for silt and clay), is used for determining, storing, and processing sample weights.

Air-Dry Samples (3A1)

Apparatus

- Fleaker, 300 ml (tare to 1 mg)
- Pasteur-Chamberlain filter candles, fineness “F”
- Shaker, horizontal, 120 oscillations per minute
- Cylinders, 1000 ml
- Stirrer, motor-driven
- Stirrer, hand. Fasten a circular piece of perforated plastic to one end of a brass rod.
- Shaw pipette rack
- Pipets, 25 ml automatic (Lowy with overflow bulb)
- Polyurethane foam, pipe-insulating cover
- Shaker with ½-in vertical and lateral movements and 500 oscillations per minute. Accommodates a nest of sieves.
- Wide-mouth glass pill bottles with screw caps, 90 ml (tare to 1 mg)
- Electronic balance (0.1-mg sensitivity)
- Set of sieves. Square-mesh woven phosphor bronze wire cloth. U.S. Series and Tyler Screen Scale equivalent designations as follows:

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

Reagents

- Hydrogen peroxide (H_2O_2), 30 to 35 percent
- Sodium hexametaphosphate $(NaPO_3)_6$. Dissolve 35.7 grams of $(NaPO_3)_6$ and 7.94 grams of Na_2CO_3 per liter of water.
- Demineralized water

Procedure

Removing organic matter.—Place about 10 air-dry soil containing no particles larger than 2 mm in a tared fleaker. Add about 50-ml of demineralized water (referred to subsequently as water) and then add 5 ml of H_2O_2. Cover the fleaker with a watchglass. If a violent reaction occurs, repeat the cold H_2O_2 treatment periodically until no more frothing occurs. Heat the fleaker to about 90 °C on an electric hot plate. Add H_2O_2 in 5-ml quantities at 45-min intervals until the organic matter is destroyed, as determined visually. Continue heating for about 30 min to remove any excess H_2O_2.

Removing cementing agents (optional).—Treat the sample with about 200 ml of 1 *N* sodium acetate buffered at pH 5 to remove carbonates. When CO_2 bubbles are no longer evident, wash free of salts with a filter candle system. Highly calcareous samples may need a second treatment.

Remove siliceous cementing agents by soaking the sample overnight in 0.1 *N* NaOH. Iron oxide cementing agents are removed by shaking overnight in sodium dithionite (6C2). Wash free of salts with filter candle system before proceeding.

Removing dissolved mineral and organic components.—After the H_2O_2 treatment, place the fleaker in a rack and add about 150 ml of water in a jet strong enough a short Pasteur-Chamberlain filter of “F” fineness. Five such washings and filterings are usually enough except for soils containing much coarse gypsum. Remove soil adhering to the filter by gentle back pressure; use finger as policeman. Dry the sample overnight in an oven at 105 °C, cool in a desiccator, and weigh to the nearest milligram. Use the weight of the oven-dry, H_2O_2-treated sample as the base weight for calculating percentages of the various fractions.

Dispersing the sample.—Add 10 ml of sodium hexametaphosphate dispersing agent to the Fleaker containing oven-dry treated sample. Make the volume to approximately 200 ml. Stopper and shake overnight on a horizontal reciprocating shaker at 120 oscillations per minute.

Separating sands from silt and clay.—Wash the dispersed sample with water on a 300-mesh sieve. Silt and clay pass through the sieve into a 1-L cylinder. Use a clamp and stand to hold the sieve above the cylinder. Avoid using jets of water in washing the sample. Gently tap the sieve clamp with the side of the hand to facilitate sieving. Continue washing until the suspension volume in the cylinder is about 800 ml. Sand and some coarse silt remain on the sieve. It is important to wash all particles of less than 20 µ diameter through the sieve. Remove the sieve

from the holder, wash the sands into an evaporating dish with water, and dry at 105 to 110 °C. Bring the silt and clay suspension in the cylinder to 1 L with water and cover with a watchglass.

Pipeting.—First pipette the <20 µ fraction at a 10-cm depth. Vary sedimentation times according to temperature. Next, pipette the <2µ fraction after a predetermined setting time (usually 4½ to 6½ hr). Vary depth according to time and temperature. Use a Lowy 25-ml automatic pipette and regulate filling time to about 12 s. Before each pipeting, stir material in the sedimentation cylinder, and stir the suspension for 30 s with a hand stirrer, using an up-and-down motion. Note the time at completion of stirring. About 1 min before sedimentation is complete, lower the tip of the pipette slowly into the suspension to the proper depth with a Shaw pipette rack. At the appropriate time, fill the pipette and empty into a 90-ml, wide-mouth bottle. Rinse the pipette into the bottle once. Dry in an oven overnight at 105 °C. Cool in a desiccator containing phosphorus pentoxide (P_2O_5). Weigh.

Sieving and weighing the sand fractions.—Transfer the dried sands to a nest of sieves. Shake for 3 min on a shaker that has ½-in vertical and lateral movements and oscillates at 500 strokes per minute. Record the weights of the individual sand fractions.

Calculations

Pipetted fractions:

Percentage of pipetted fractions = (A − B)KD

where:

A = Weight (g) of pipeted fraction

B = Weight correction for dispersing agent (g)

K = 1000/(ml in pipette)

D = 100/(g of H_2O_2-treated oven-dry total sample)

The <20-µ fraction minus the <2-µ fraction equals fine silt.

Sand fractions:

Percentage of sieved fractions = weight (g) of fraction on sieve times D.

Coarse silt fraction:

Obtain by difference. Subtract the sum of the percentages of sand plus the <20-µ fraction from 100.

References

Kilmer and Alexander (1949), Kilmer and Mullins (1954), Tyner (1939), and Grossman and Millet (1961).

Carbonate and Noncarbonate Clay I (3A1a)

Apparatus

- Warburg manometer
- ¼-oz (5-ml) gelatin capsules
- 30-ml plastic cups

Reagents

- Hydrochloric acid (HCl), 6 *N*

Procedure

If carbonate is present, use the glass bottle containing clay residue from regular pipette analysis and determine carbonate as in 6E1b. Use Warburg manometer.

Calculations

$$Cc = \{[(A - B - C) \times Factor]/D\} \times 100$$

where:

Cc = Carbonate clay (pct <2 mm)

A = Upper reading

B = Lower reading

C = Blank

Factor = Factor derived from standard curve and includes pipette volume factor

D = Total sample weight (3A1)

$$Nc = \text{Total clay} - Cc$$

where:

Nc = Noncarbonate clay (pct <2 mm)

Cc = Carbonate clay (pct <2 mm)

References

Shields and Meyer (1964).

Moist Samples (3A2)

If drying affects dispersion of treated sample, oven-drying may be avoided by

removal of a pipette sample to estimate the total weight of the sample. Pipette 50 ml at a depth of 20 cm at time zero while the suspension is still turbulent. Use the oven-dry weight of the aliquot to calculate the total weight of the <0.05-mm fraction. Add this weight to the total weight of the sands to obtain the total weight of the sample.

An optional procedure is to carefully weigh out two identical samples and pretreat to remove organic matter and dissolved mineral matter. The first sample is continued through the standard procedure, excluding oven-drying. The second sample is oven-dried, weighed, and discarded. The oven-dry weight of the second sample is substituted in the calculations for the first sample.

Carbonate and Noncarbonate Clay (3A2a)

Proceed as in 3A1a except use field-moist sample.

FABRIC-RELATED ANALYSES (4)

Bulk Density (4A)

Density is defined as mass per unit volume. Soil density as commonly used differs from most density measurements in that the volume of interparticle space is included but the mass of the liquid phase is excluded. Therefore, soil density has been called bulk density, Db, to distinguish it from the more usual density that is based on intraparticle volume only. Since the volume of a shrinking-swelling soil changes with a change in its water content, subscripts are added to designate the moisture condition when the measurement was made. Thus, Db_m is the bulk density of a moist sample, $Db_{1/3}$ is the bulk density of a clod sample equilibrated at ⅓-bar tension, and Db_d is the bulk density of a dry sample.

Saran-Coated Clods (4A1)

Reagents

- Methyl ethyl ketone
- Dow Saran F310.—The saran resin dissolves readily in acetone or methyl ethyl ketone. In this method, methyl ethyl ketone is used as a solvent because it is less soluble in water than is acetone and there is less penetration of the Saran-solvent solution into a moist clod. However, acetone is adequate for a first (field) coat and is more readily available. Saran-solvent ratios of 1:4 to 1:7 are used, depending on the porosity of the soil to be coated.
- Coating solution.—To prepare the solution, fill a weighted container with a solvent to about three-fourths its volume. From the weight of the solvent, calculate the weight of resin required to obtain a predetermined resin-solvent ratio and add to the solvent. Since the solvent is flammable and its vapors form explosive mixtures with air, mix the components with an air-powered or nonsparking electric stirrer under an exhaust hood. Information on the safe handling and use of methyl ethyl ketone is available in Chemical Safety Data Sheet SD-83, Manufacturing Chemists' Association, Inc., 1825 Connecticut Avenue NW, Washington, D.C. The threshold limits of methyl ethyl ketone are 200 ppm as given in OSHA standards, Part 2, Section 1910.93, table G1.
- If a high-speed stirrer is used, the resin dissolves in about 1 hr. In the field, mix with a wooden stick. Metal cans (1 gal) are satisfactory containers for mixing and storing the plastic. Keep the containers tightly closed to prevent evaporation of the solvent.

Procedure

Collect natural clods (three per horizon) of about 100 to 200 cm^3 in volume (fist-sized). Remove a piece of soil larger than the clod from the face of a sampling pit with a spade. From this piece, prepare a clod by directly cutting or breaking off protruding peaks and material sheared by the spade. If roots are present, they can be cut conveniently with scissors or side cutters. In some soils, clods can be removed directly from the face of a pit with a knife or spatula. No procedure for taking clod samples fits all soils; the procedure must be adjusted to meet the conditions in the field at the time of sampling.

The clods are tied with the fine copper wire or placed in hairnets and suspended from a rope or string, hung out like a clothesline. Moisten dry clods with a fine mist spray. The suspended clods are dipped by raising a container of the dipping mixture upward around each clod, so it is immersed momentarily. The saran-coated clods should be allowed to dry for 30 min or longer. Clods coated in this way can be transported to the laboratory and examined microscopically in an undisturbed state. For convenience, either of two concentrations of plastic solution is usually used—a 1:7 solution for most soil samples or a 1:4 solution for clods that have larger pores. If bulk density at field-moisture content is desired, store the clods in waterproof plastic bags as soon as the coating dries since the coating is permeable to water vapor. Although the coating keeps the clods intact, they may be crushed in transport unless they are packed in rigid containers.

In the laboratory, additional coatings of plastic are applied to make the clod waterproof and to prevent its disruption during wetting. Then, weigh the clod, either in its natural moisture condition or in an adjusted moisture condition (e.g., ⅓-bar tension) in air and in water to obtain its volume by Archimedes' principle. Subsequent changes in moisture condition and volume of the soil sample can be followed by reweighing the coated clod in air and in water. Finally, weigh the oven-dry clod in air and in water.

Be careful not to lose any soil material because the weight of material lost is calculated as soil moisture, and calculated bulk densities depend on the final oven-dry weight of the clod.

Bulk-density values determined by this method are reported on the basis of fine-earth fabric. Weight and volume measurements are made on clod samples that may contain particles >2 mm; however, after the measurements are made, the weight and volume of the coarse fraction are subtracted. The remainder consists of the weight of <2-mm material and the volume of these fine-earth particles and the pore space associated with them.

Sometimes it is necessary to correct bulk density for weight and volume of the plastic coating. The coating has a density of about 1.3 g/cm^3 and it loses 10 to 20 percent of its air-dry weight on oven-drying at 105 °C. Thus, the amount of correction becomes smaller as bulk density of the soil approaches the density of the coating and as moisture content of the soil approaches the weight loss of the coating.

Calculations

$$Db_{1/3} = \frac{wtclod_{od} - wt{>}2\ mm - tcoat_{od}}{volclod_{1/3} - vol{>}2\ mm - vol\ coat}$$

$$Db_{od} = \frac{wtclod_{od} - wt{>}2\ mm - wtcoat_{od}}{volclod_{od} - vol{>}2\ mm - vol\ coat}$$

$$W_{1/3} = \frac{wtclod_{1/3} - wtclod_{od} - (wtclod_{ad} - wtcoat_{od})}{wtclod_{od} - wt{>}2\ mm - wtcoat_{od}} \times 100$$

where:

$Db_{1/3}$ = bulk density of <2-mm fabric at ⅓-bar tension in grams per cubic centimeter

Db_{od} = bulk density of <2-mm fabric at oven-dryness in grams per cubic centimeter

$W_{1/3}$ = the weight percentage of water retained at ⅓-bar tension

wt $clod_{od}$ = weight of oven-dry coated clod

wt $clod_{1/3}$ = weight of coated clod equilibrated at ⅓-bar tension

vol $clod_{od}$ = volume of oven-dry coated clod

vol $clod_{1/3}$ = volume of coated clod equilibrated at ⅓-bar tension

vol >2 mm = volume of material >2 mm separated from clod after oven-drying

wt >2 mm = weight of material >2 mm separated from clodafter oven-drying

wt $coat_{ad}$ = weight of Saran coating before oven-drying

wt $coat_{od}$ = weight of Saran coating after oven-drying

vol coat = volume of Saran coating (estimated)

The field coat (initial coat) of plastic penetrates the clod to some extent. Weight of the field coat, estimated to 1.5 times the weight of each additional coat, is computed by:

$$Wtcoat_{init} = \frac{(Wtclod_B - Wtclod_A)}{3} \times 1.5$$

where:

$Wtcoat_{init}$ = Weight of field (initial) coat

$Wtclod_A$ = Weight of clod with one coat of plastic

$Wtclod_B$ = Weight of clod with three additional coats of plastic

References

Brasher et al. (1966).

Air-Dry (Db_d) (4A1b)

After measuring field-state volume, place clods in a drying room kept at 90 °F. Weigh a few clods each day until they reach a constant weight. Assume then that all the clods are air-dry. Coat them again with Saran and measure "air-dry" volume as described in 4A1a. Determine oven-dry weight and calculate bulk density as described in 4A1.

30-cm Absorption (Db_{30}) (4A1c)

After measuring air-dry volume, remove a patch of the Saran coating from one side of each clod. Next, place the clods on a sand tension table with the exposed side in contact with very fine sand that has been equilibrated to 30-cm water tension. Again weigh a few clods each day until they reach constant weight and assume that all the clods are at 30-cm water tension. Most clods reach equilibrium in 7 to 10 days. Remove the clods from the tension table and coat with Saran until waterproof. Measure volume of the clods and calculate bulk density as described in 4A1.

⅓-Bar Desorption II ($Db_{1/3}$) (4A1e)

Cut a flat surface on the coated field-moist clods with a sharp knife or diamond saw. Seat the clods on saturated ceramic plates with the flat surface in contact with the plates. Place the plates in pans and add water to just cover the surface of the plates. After the clods become wet by capillary movement, place the plates in a pressure cooker and equilibrate at ⅓ bar. After equilibration, carefully remove the clods from the plates and dip in Saran until waterproof. Measure volume of the clods and calculate bulk density as described in 4A1.

⅓-Bar Desorption III ($Db_{1/3}$) (4A1f)

Proceed as in 4A1e except prewet the clods at 10-cm tension on porous bricks (cheesecloth layer between clod and brick) instead of saturating them on ceramic plates.

1/10-Bar Desorption ($Db_{1/10}$) (4A1g)

Proceed as in 4A1d, e, or f except make final desorption at $^1/_{10}$ bar.

Paraffin-Coated Clods (4A2)

Oven-dry (Db_d) (4A2a)

Oven-dry the clods, coat with paraffin, and weigh in water and in air. Calculate bulk density as follows:

$$Db_d\ (g/cc) = \frac{Wtair - Wt{>}2\ mm}{Wtair - WtH_2O - (Wt{>}2\ mm/2.65)}$$

where:

Wtair = Weight in air

Wt>2 mm = Weight of >2-mm fraction in clod

WtH_2O = Weight in water

Nonpolar-Liquid Saturated Clods (4A4)

Procedure

Place a natural clod in a nonpolar liquid of low viscosity, e.g., high-purity kerosene. Evacuate under vacuum until bubbles cease to appear and weigh the clod suspended in the nonpolar liquid. Remove the clod, place it on a sand table under 3-cm tension against the nonpolar liquid to drain off excess nonpolar liquid, and weigh it in air. The difference in weight of the clod in air and suspended in the nonpolar liquid divided by the density of the nonpolar liquid is the clod volume. Determine the oven-dry weight and calculate bulk density as in 4A1. The difference between the clod's initial weight before immersion in the nonpolar liquid and its oven-dry weight is the moisture content.

References

Rennie (1957).

Water Retention (4B)

Pressure-Plate Extraction (4B1)

After measuring the ⅓-bar volume (4A1d), the Saran coating is removed from the flat surface of the clods. The clods are allowed to air-dry (4 to 6 days) and then placed in the drying room 2 or 3 days. They are then placed on a tension table of very fine sand and equilibrated to 5-cm tension as in 4A1d. After about 2 weeks, some of the highly organic clods that have not rewetted are placed in a pan of free water overnight to make certain that wetting is complete. The clods are again desorbed to ⅓-bar as in 4A1d and volume measurements of the clod are made and bulk density is calculated as described in 4A1.

Soil Pieces (4B1b)

Procedure

Make desorption measurements of soil pieces concurrently with the sieved-sample measurements. Cover the sieved samples in retainer rings with small

squares of industrial tissues (Kimwipes). Place the soil pieces (about 2.5 cm in diameter) on the tissues before adding water to the plate. Proceed as in 4B1a. If the soil pieces contain >2-mm material, wet sieve and weigh the oven-dry >2-mm material. Report moisture content as percentage of oven-dry weight of <2 mm material.

References

Young (1962).

Sand-Table Absorption (4B3)

Saran-coated clods that have been equilibrated on a sand table to determine bulk density (4A) can also be used to determine water content at these tensions.

Micromorphology (4E)

Thin Sections (4E1)

Moved-Clay Percentage (4E1c)

Apparatus

- Diamond tile saw
- Thin-section equipment
- Point-counting eyepiece

Reagents

- Aroclor 5460 (Monsanto)
- Polyester resin
- Styrene

Procedure

Impregnate an undisturbed field sample with Aroclor (4E1b). With a diamond saw, cut the clods into pieces about 3 by 1 by 1 cm. Mount about 10 pieces side by side with polyester resin (use a little styrene) to form a block. Cut this assembly to form slices 3 by 1 by 1 cm. Slice all the field sample, composite, and withdraw subsamples of 10 to 15 slices. Stack these slices, tape them together, and mount in plastic (polyester resin plus styrene). Cut a section through the stack parallel to the direction of stacking and along the longer of the two remaining axes. Mount one such section from each stack on a glass slide and prepare a thin section.

To estimate the moved-clay volume, insert a point-counting eyepiece into the microscope and run a transect along each strip. Keep the transect length and the

number of fields in a transect constant. Count the number of points that fall on moved clay. Divide this number by the total number of points to get an estimate of the proportion of moved clay. To convert these volume estimates to weight estimates, multiply by the ratio of the bulk density of the moved clay to the bulk density of the appropriate dry fabric. Assume that the moved clay has a bulk density of 2.00 g per cubic centimeter.

References

Grossman (1964).

Scanning Electron Microscopy (4E2)

Electronically reproduced images of fabric surfaces can be obtained at magnifications ranging from 50 to 30,000 diameters. Depth of focus by this technique is large compared to that by light microscope. Stereoscopic pictures can be taken to give three-dimensional viewing.

Procedure

Take a sample of fabric up to 10 mm in diameter and 2 to 3 mm thick. Coat with a thin metallic layer and insert in the instrument. The image is displayed on a cathode ray tube.

ION EXCHANGE ANALYSES (5)

Cation Exchange Capacity (CEC) (5A)
NH_4OAc, pH 7.0 (Buchner funnel) (5A1)

Reagents

- Ammonium acetate (NH_4OAc), 1 *N*, pH 7.0. Mix 68 ml ammonium hydroxide (NH_4OH), specific gravity 0.90, and 57 ml 99.5-percent acetic acid (CH_3COOH) per liter of solution desired. Cool, dilute to volume with water, and adjust to pH 7.0 with CH_3COOH or NH_4OH. Optionally prepare from NH_4OAc reagent salt and adjust pH.
- Ethanol (CH_3CH_2OH), 95-percent, U.S.P.
- Nessler's reagent (optional). Prepare according to Yuen and Pollard.

Procedure

Weigh 25 g air-dry <2-mm soil (some early work was done with 50-g samples) into a 250-ml Erlenmeyer flask and add 35 to 50 ml NH_4OAc solution. Stopper, shake the flask for several minutes, and allow to stand overnight. Transfer contents of the flask to a Buchner funnel (Coors No. 1) fitted with moist Whatman No. 42 filter paper. Filter, using gentle suction if needed. Leach with 200 ml NH_4OAc, adding small amounts at a time so that leaching requires no less than 1 hour. Transfer leachate from suction flask to volumetric flask and retain for analysis of NH_4OAc-extractable cations (methods 6N2, 6O2, 6P2, 6Q2).

Add 95-percent ethanol in small amounts to the ammonium-saturated soil remaining on the Buchner funnel until the leachate gives a negative test for ammonia with Nessler's reagent or leach with 100 ml ethanol.

References

Peech et al. (1947) and Yuen and Pollard (1952).

Direct Distillation of Adsorbed Ammonia, Kjeldahl (5A1a)

Reagents

- Sodium chloride (NaCl)
- Antifoam mixture. Mix equal parts of mineral oil and n-octyl alcohol.
- Sodium hydroxide (NaOH), 1 *N*
- Hydrochloric acid (HCl), 0.2 *N*, standardized
- Boric acid (H_3BO_3), 4-percent

- Mixed indicator. Mix 1.250 g methyl red and 0.825 g methylene blue in 1 liter 95-percent ethanol
- Brom cresol green, 0.1-percent, aqueous solution

Procedure

Transfer the soil plus filter paper from method 5A1 to a Kjeldahl flask. Add 400 ml water and about 10 g NaCl, 5 drops antifoam mixture, a gram or two of granular zinc, and 40 ml 1 *N* NaOH. Connect the flask with the condenser and distill 200 ml into 50 ml 4-percent H_3BO_3 solution. Titrate the distillate to the first tinge of purple with 0.2 *N* HCl, using 10 drops mixed indicator and 2 drops brom cresol green.

Calculations

CEC (meq/100 g) = (A/B) x *N* x 100

where:

A = Volume HCl (mL)

B = Sample weight (g)

N = Normality of acid

Report on oven-dry basis.

References

Peech et al. (1947).

Displacement of Adsorbed Ammonia, Semimicro Kjeldahl (5A1b)

Reagents

- Sodium chloride (NaCl), acidified, 10-percent. Dissolve 100 g NaCl, reagent-grade, ammonia-free, in 750 ml warm water; add 25 ml 2 *N* hydrochloric acid (HCl) and bring to 1000-ml volume.
- Sodium hydroxide (NaOH), 1 *N*
- Boric acid (H_3BO_3), 2-percent
- Sulfuric acid (H_2SO_4), 0.01 *N*, standardized
- Ethanol, 95-percent
- Mixed indicator. Dissolve 0.1 g methyl red and 0.1 g brom cresol green in 250 ml ethanol.

Procedure

Leach soil from method 5A1 with 240 ml 10-percent acidified NaCl solution, using small increments. Drain completely between each increment. Transfer the leachate to a 250-ml volumetric flask and adjust volume to mark. Pipette a suitable aliquot of the leachate into a micro-Kjeldahl distillation flask and attach to steam-distillation apparatus. Start steam distillation and slowly add 10 ml 1 *N* NaOH. Catch distillate in a 250-ml Erlenmeyer flask containing 10 ml H_3BO_3 and 10 drops of mixed indicator. Distill for 5 minutes after H_3BO_3 turns green, lower receiving flask, and rinse condenser and outlet hose into receiving flask. Titrate the ammonia with 0.01 *N* H_2SO_4 to a red end point, using a blank for comparison.

Calculations

$$\text{CEC (meq/100 g)} = (A/B) \times N \times (C/D) \times 100$$

where:

A = Volume H_2SO_4 (mL)

B = Sample weight (g)

N = Normality of acid

C = Volume leachate (mL)

D = Volume aliquot (mL)

Report on oven-dry basis.

NaOAc, pH 8.2 (5A2)

Centrifuge Method (5A2a)

Reagents

- Sodium acetate (NaOAc), 1 *N*, pH 8.2
- Ethanol, 95-percent
- Ammonium acetate (NH_4OAc), 1 *N*, pH 7.0. Add 57 ml concentrated acetic acid and 68 ml concentrated NH_4OH, specific gravity 0.90, to about 800 ml water. Cool and dilute to 1 liter and adjust to pH 7.0 by adding more NH_4OH or acetic acid.

Procedure

Weigh 5-g samples to an accuracy of 1 percent and place in centrifuge tubes. Add 33 ml NaOAc, stopper the tubes, and shake for 5 minutes. Remove stopper and centrifuge until the supernatant liquid is clear (usually 5 min). Decant the supernatant liquid as completely as possible and discard. Repeat four times, discarding the supernatant liquid each time. After the last saturation, wash the rubber stoppers and use absorbent paper to remove any acetate crystals

remaining on lip of centrifuge tube. Add about 30 ml ethanol to each tube, stopper, shake for 5 minutes, remove stopper, and centrifuge until the supernatant liquid is clear. Decant and discard the supernatant liquid. Continue washing until the electrical conductivity of the supernatant liquid from the last washing is between 55 and 40 µmho per centimeter. Optionally, decrease volume by about 5 ml each washing. Replace the absorbed sodium from the sample by extracting with three 30-ml portions of NH_4OAc solution. Dilute to 100 ml and determine the sodium concentration as described in 6P2a.

Calculations

CEC (meq/100 g) = (A/B) x dilution x 10

where:

A = Na from curve (meq/L)

B = Sample weight (g)

Report on oven-dry basis.

References

Richards (1954).

KOAc, pH 7.0 (5A4)

Procedure

Proceed as in 5A1 except substitute 1 *N* KOAc, pH 7.0, for NH_4OAc. Determine potassium with flame photometer.

$BaCl_2$, pH 8.2 (5A5)

Apparatus

- Leaching tubes
- Flame photometer

Reagents

- Buffer solution. Barium chloride ($BaCl_2$), 0.5 *N*, and triethanolamine (TEA), 0.2 *N*. Adjust to pH 8.2 with HCl. Protect from CO_2 of the air by attaching a drying tube containing soda lime (sodium calcium hydrate) to the air intake.
- Replacement solution. Barium chloride ($BaCl_2$), 0.5 *N*. Add 0.4 ml buffer solution per liter and mix. Protect from CO_2 with soda-lime tube.
- Magnesium nitrate ($Mg(NO_3)_2$), 1 *N*

Procedure

Transfer a 5-g sample to a leaching tube. For field-moist samples use a sample large enough to give an oven-dry weight of about 5 g. Leach with 50 ml $BaCl_2$-TEA solution, controlling the leaching rate to give at least 4 hours of soil-solution contact time. Follow with 100 ml $BaCl_2$ replacement solution, controlling the leaching rate so that the soil and $BaCl_2$ solutions are in contact for a total of 20 to 24 hours. Rinse walls of leaching tube with 15 to 20 ml H_2O, collecting this washing with leachates from $BaCl_2$ solutions. Extractable acidity can be determined by using this solution (6H1a). Place leaching tube on a clean flask and wash with methanol until free of chloride ion. For many samples 100 ml methanol is enough, but more methanol may be needed for some soils, particularly those of heavy texture and containing large amounts of hydrous oxides. Leach with 100 ml 0.001 *N* $BaCl_2$ to remove methanol.

Disconnect leaching tube and flask, rinse underside of leaching tube, place over a 250-ml volumetric flask, and leach with 100 ml 1 *N* $Mg(NO_3)_2$ solution. Control leaching rate to give a soil-solution contact time of 16 hours or more. Rinse walls of leaching tube with 15 to 20 ml H_2O; collect rinse in the $Mg(NO_3)_2$ leachate. Make to volume.

Barium by Flame Photometry (5A5a)

Make standards in 1 *N* $Mg(NO_3)_2$. Determine barium by flame photometry at 489 mμ.

Calculations

$$\text{CEC (meq/100 g)} = (A/B) \times \text{dilution} \times 25$$

where:

A = Ba from curve (meq/L)

B = Sample weight (g)

NH_4OAc, pH 7.0, Leaching Tube (5A6)

Apparatus

- Allihn leaching tubes or 50-ml plastic syringe barrels

Reagents

- Same as in 5A1

Procedure

Prepare the Allihn tubes by placing either filter paper (Reeve Angel No. 934 AH, 3-cm fiber glass) or filter paper pulp on the fritted glass plate. If the syringe barrel is used as a leaching tube, compress the filter paper pulp in the barrel

bottom with the syringe plunger. Place a Gooch perforated plate over the filter paper to permit stirring the soil without damage to the filter. (This plate is not necessary if an adequate pulp pad is used.) Place 5 or 10 g soil and a teaspoon of Celite into the tubes. (Optionally place a layer of Celite under the soil.) Add 25 ml *N* NH_4OAc; stir and leach. Add an additional 25 ml *N* NH_4OAc and let stand overnight. Stop the leaching with a pinch clamp or by stoppering the leaching tube. Add the NH_4OAc directly to the leaching tube or use a constant level device (fig. 6N3-1). A volumetric flask can be substituted for the 250-ml Erlenmeyer flask and tubing.

Make the leachate to volume if a volumetric flask is used or, if tared suction flasks are used, make to the appropriate calibrated weight for 100 ml NH_4OAc. Set aside the leachate for further analysis. Add about 10 ml ethanol to the soil pad, stir, and leach. Leach with 100 ml ethanol and check for NH_4^+ in leachate. If NH_4^+ is present, leach with an additional 100 ml ethanol. Some soils, particularly those containing amorphous material, require as much as 400 ml ethanol to clear the ammonia from the leachate.

Direct Distillation (5A6a)

Transfer soil cake to Kjeldahl flask and determine ammonia as described in 5A1a.

NH_4Cl, pH 7.0, Mechanical Extraction (5A7)

Direct Distillation (5A7a)

Determine ammonia by Kjeldahl distillation as described in 5A1a.

NH_4OAc, pH 7.0, Automatic Extractor (5A8)

Direct Distillation (5A8a)

Reagents

- Sodium chloride (NaCl)
- Antifoam mixture. Mix equal parts of mineral oil and n-octyl alcohol.
- Sodium hydroxide (NaOH), 1 *N*
- Hydrochloric acid (HCl), 0.2 *N*, standardized
- Boric acid (H_3BO_3), 4-percent

Procedure

Transfer the soil plus filter pulp from methods 5A8 or 5A9 to a Kjeldahl flask. Add 400 ml water and about 10 g NaCl, 5 drops antifoam mixture, a gram or two of granular zinc, and 40 ml of 1 *N* NaOH. Connect the flask with the condenser

and distill 140 ml into 50 ml of 4-percent H_3BO_3 solution in 250-ml titrator beaker. Titrate with automatic titrator to end point pH setting of 4.60.

Calculations

CEC (meq/100 g) = (A/B) x *N* x 100

where:

A = Volume HCl (mL)

B = Sample weight (g)

N = Normality of acid

Report on oven-dry basis.

References

Peech et al. (1947).

NH_4Cl, pH 7.0, Automatic Extractor (5A9)

Direct Distillation (5A9a)

Determine ammonia by Kjeldahl distillation as described in 5A8a.

Extractable Bases (5B)

NH_4OAc, pH 7.0, Buchner Funnel (5B1)

Procedure

Analyze the NH_4OAc leachate from method 5A1a for calcium, magnesium, sodium, and potassium (methods 6N2, 6O2, 6P2, 6Q2).

Uncorrected (extractable) (5B1a)

If a soil does not contain soluble salts, the extractable bases are presumed to equal the exchangeable bases. They are, however, reported as extractable bases.

Corrected (exchangeable) (5B1b)

If a soil contains soluble salts, estimate their amount from the saturation extract as follows. Multiply cation concentration in the saturation extract (meq/L) by the saturation percentage (divided by 1000) to convert to milliequivalents per 100 g. Subtract this quantity from the concentration of the extracted cation. This procedure is not valid for calcium and magnesium in the presence of carbonates or for calcium in the presence of gypsum because these salts are soluble in NH_4OAc.

References

Peech et al. (1947).

KCl-Triethanolamine Extraction, pH 8.2 (5B2)

Reagents

- Buffer solution. Potassium chloride (KCl), 1.0 *N*, and triethanolamine (TEA), 0.2 *N*, pH 8.2.

Procedure

Proceed as in 5B1 except leach with 1 *N* KCl buffered at pH 8.2 with triethanolamine. Determine calcium by method 6N4, magnesium by 6O4.

References

North-Central Regional Research Committee (1955).

KCl-Triethanolamine Extraction, pH 8.2 (revised) (5B3)

Reagents

- Buffer solution. Potassium chloride (KCl), 1.0 *N*, and triethanolamine (TEA), 0.2 *N*, pH 8.2.

Procedure

Weigh 10-g samples and transfer to 100-ml beakers. Add 40 ml buffer solution. Stir thoroughly at least three times over a period of not less than 1 hour. Filter the suspension and collect the leachate in a 100-ml volumetric flask.

Analyze the leachate for Ca and Mg by an appropriate method (6N4, 6O4).

Uncorrected (extractable) (5B3a)

If a soil does not contain soluble salts, the extractable bases are presumed to equal the exchangeable bases. They are, however, reported as extractable bases.

Corrected (exchangeable) (5B3b)

If a soil contains soluble salts, estimate their amounts from the saturation extract and correct as in 5B1b.

NH_4OAc, pH 7.0, Leaching Tube (5B4)

Analyze the NH_4OAc leachate from method 5A6 for Ca, Mg, Na, and K (methods 6N2, 6O2, 6P2, 6Q2).

Uncorrected (extractable) (5B4a)

If a soil does not contain soluble salts, the extractable bases are presumed to equal the exchangeable bases. They are, however, reported as extractable bases.

Corrected (exchangeable) (5B4b)

If a soil contains soluble salts, estimate their amounts from the saturation extract and correct as in 5B1b.

NH_4OAc, pH 7.0, Automatic Extractor (5B5)

Corrected (exchangeable) (5B5b)

If a soil contains soluble salts, estimate their amount from the saturation extract as follows. Multiply cation concentration in the saturation extract (meq/L) by the saturation percentage (divided by 1000) to convert to milliequivalents per 100 g. Subtract this quantity from the concentration of the extracted cation. This procedure is not valid for calcium and magnesium in the presence of carbonates that contain those elements, or for calcium in the presence of gypsum, because these compounds are soluble in NH_4OAc.

Base Saturation (5C)

NaOAc, pH 8.2 (5C2)

Divide sum of NH_4OAc-extracted bases by the exchange capacity determined by method 5A2a.

Exchangeable Sodium Percentage (ESP) (5D)

NaOAc, pH 8.2 (5D1)

Divide exchangeable sodium (meq/100 g) by the exchange capacity determined by method 5A2a.

Calcium Saturation (Exchangeable-Calcium Percentage) (5F)

NH_4OAc, pH 7.0 (5F1)

Divide the NH_4OAc-extracted calcium by the exchange capacity determined by method 5A1 or 5A6.

Organic Carbon (6A)

Determine carbon for each horizon that may contain organic matter. Report as carbon percentage by weight of <2-mm material.

To calculate total carbon per unit area, convert these weight percentages to volume percentages. Multiply each value by the bulk density Dbm, where m is usually ⅓ bar or 30 cm, and by the thickness (inches) of that horizon. If coarse fragments are present, further multiply by Cm (4A). Sum the organic-matter percentages and multiply by 0.254 to convert to kilograms of carbon per square meter.

Acid-Dichromate Digestion (6A1)
$FeSO_4$ Titration (6A1a)

Reagents

- Potassium dichromate ($K_2Cr_2O_7$), 1.00 *N* (49.04 g per liter)
- Ferrous sulfate, 1.0 *N*. Dissolve 280 g reagent-grade $FeSO_4 \cdot 7H_2O$ in water, add 80 ml concentrated H_2SO_4, cool, and dilute to 1 liter. Standardize this reagent each day by titrating against 10 ml *N* $K_2Cr_2O_7$ as directed.
- Barium diphenylaminesulfonate indicator, 0.16 percent aqueous solution
- Orthophenanthroline-ferrous complex (optional), 0.025 *M* solution of one of the phenanthroline-ferrous complex indicators
- H_2SO_4, at least 96-percent
- Phosphoric acid (H_3PO_4), 86-percent

Procedure

Transfer 1 g (0.5 g or less if high in organic matter) soil ground to pass an 80-mesh sieve to a 500-ml Erlenmeyer flask. Add 10 ml *N* $K_2Cr_2O_7$. Add 20 ml concentrated H_2SO_4 rapidly, directing the stream into the solution. Immediately swirl vigorously or place in wrist-action shaker for 1 minute. Let the flask stand on a sheet of asbestos for about 30 minutes. Add 200 ml water and 10 ml H_3PO_4. Add 0.5 ml barium diphenylaminesulfonate just before titrating. Titrate by adding $FeSO_4$ drop by drop to a light green end point. If more than 8 ml of the available 10 ml $K_2Cr_2O_7$ are reduced, repeat the determination, using less soil. If orthophenanthroline-ferrous complex is the indicator, it is not necessary to add H_3PO_4.

Calculations

$$\text{Organic carbon (pct.)} = ((A - B)/C) \times N \times (0.30/0.77)$$

where:

A = Volume $FeSO_4$ blank (mL)

B = Volume $FeSO_4$ sample (mL)

C = Sample weight (g)

N = Normality of $FeSO_4$

0.77 = Recovery factor proposed by Walkley (1935)

Report on oven-dry basis.

References

Peech et al. (1947) and Walkley (1935).

CO_2 Evolution, Gravimetric (6A1b)

Apparatus

See figure 6A1b-1.

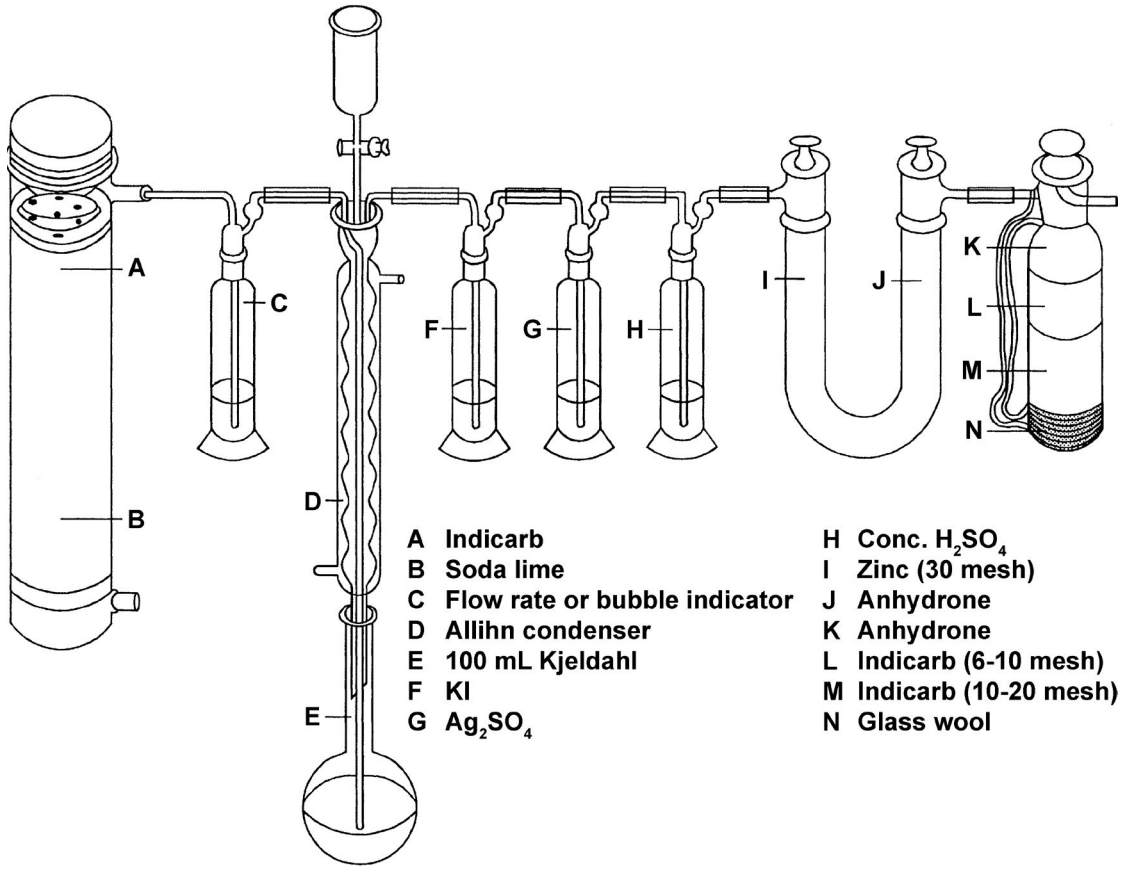


Figure 6A1b-1.—Apparatus for gravimetric organic carbon determination by wet combustion with potassium dichromate (6A1b).

Reagents

- Digestion-acid mixture. Mix 600 ml concentrated H_2SO_4 and 400 ml 85-percent H_3PO_4.
- Potassium dichromate ($K_2Cr_2O_7$), reagent grade
- Potassium iodide (KI). Dissolve 100 g KI in 100 ml water.
- Silver sulfate (Ag_2SO_4), saturated aqueous solution
- Concentrated sulfuric acid (H_2SO_4)
- Other reagents: Indicarb or Mikohbite, soda lime, 30-mesh zinc, and anhydrone (anhydrous magnesium perchlorate)

Procedure

Place a soil sample containing 20 to 40 mg carbon (usually 0.5 to 3 g oven-dry soil) in digestion flask and add 1 to 2 g $K_2Cr_2O_7$. Wash the neck of the flask with 3 ml water and connect the flask to reflux condenser. Attach the weighed Nesbitt bulb to the system and open the valve at the top. Pour 25 ml digestion-acid mixture into funnel, let it enter the flask, and close the stopcock immediately to prevent loss of CO_2. Use digestion-acid mixture to lubricate the funnel stopcock. The tip of the air-delivery tube should extend about 0.5 cm below the surface of the acid during digestion. Adjust the “carrier stream” to a flow rate of one or two bubbles per second and maintain this rate during digestion. Heat with a gas flame of sufficient intensity to bring the sample to boiling in 3 to 4 min. Continue gentle boiling for a total heating period of 10 min (avoid excessive frothing). Heating is too rapid if white fumes of SO_3 are visible above the second bulb of the reflux condenser during boiling. At the end of the digestion period, remove the flame and aerate for 10 min at the rate of six to eight bubbles per second. Then close the stopcock on the Nesbitt bulb, disconnect the bulb from the system, and weigh.

Calculations

$$\text{Organic carbon (pct.)} = ((A - B)/C) \times 27.3$$

where:

A = Final bulb weight (g)

B = Initial bulb weight (g)

C = Sample weight (g)

Report on oven-dry basis.

References

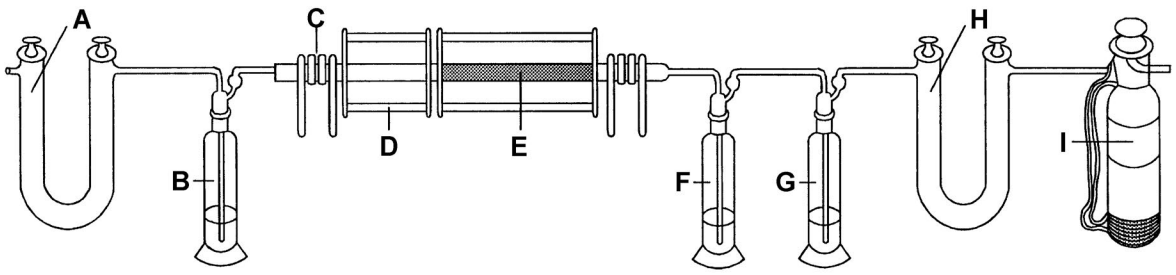
Allison (1960).

Dry Combustion (6A2)

CO_2 Evolution, Gravimetric I (6A2a)

Apparatus

- See figure 6A2a-1.



A Schwartz absorption tube containing 8-20 mesh Caroxite
B Gas washing bottle containing conc. H_2SO_4
C Cooling coils
D Combustion furnace
E Platinum and asbestos catalyst
F Gas washing bottle containing saturated Ag_2SO_4
G Gas washing bottle containing conc. H_2SO_4
H Schwartz absorption tube containing granular zinc in left arm and anhydrous magnesium perchlorate in right arm
I Nesbit absorption bottle containing anhydrous magnesium perchlorate in top layers, 8-20 mesh Caroxite in middle layer, and glass wool in bottom layer

Figure 6A2a-1.—Apparatus for organic carbon determination by dry combustion, carbon dioxide evolution I (6A2a).

Reagents

- Powdered manganese oxide (MnO_2)

Procedure

Place 0.5 to 1.5 g soil that has been ground to 80 mesh in an Alundum boat containing 0.25 g powdered MnO_2. Insert the boat into the quartz tube of the multiple-unit combustion furnace shown. Before inserting the soil, preheat the long part of the quartz tube to 900 °C or more (1000 or 1100 °C) and clear of CO_2 by passing CO_2-free oxygen through the combustion train until the weighing bottle shows a constant weight. While oxygen is passing slowly through the apparatus, heat to a temperature of 900 °C or higher (15 to 30 min). Continue heating in a streaming oxygen atmosphere for 30 minutes more or until the Nesbitt absorption bulb has reached a constant weight.

Calculations

Report on oven-dry basis as in 6A1b.

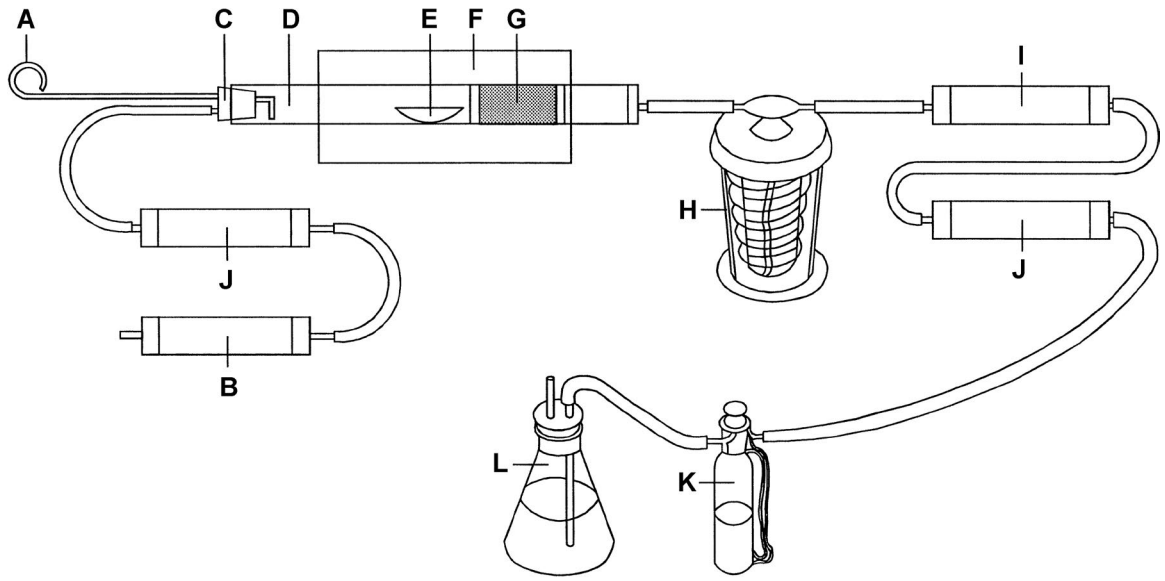
References

Robinson (1930).

CO_2 Evolution, Gravimetric II (6A2b)

Apparatus

- See figure 6A2b-1.



A Push rod
B Drying tube containing Indicarb
C Rubber stopper
D Alundum combustion tube
E Combustion boat
F Combustion furnace
G Cupric oxide wire
H Milligan gas washing bottle containing Conc. H_2SO_4
I Tube containing ZnO_2
J Tube containing Anhydrone
K Nesbit absorption bulb containing Anhydrone and Indicarb
L Bubble counter containing H_2SO_4

Figure 6A2b-1.—Apparatus used for organic carbon determination by dry combustion, carbon dioxide evolution II (6A2b).

Procedure

Heat tube to approximately 950 °C. Sweep with oxygen until weight of Nesbitt bulb is constant. Remove rubber stopper in the oxygen inlet end of the tube and insert the boat containing 0.5 to 1.5 g soil. Reinsert the stopper and use the push rod to move the boat into the hot zone. Heat for 10 minutes, remove bulb, and record weight gain. Remove boat and repeat process with fresh sample, using the same Nesbitt bulb.

Calculations

Report on oven-dry basis as in 6A1b.

References

Robinson (1930) and Post. (Post, G.J. A study of three methods for determination of organic carbon in Ohio soils of several great soil groups and the profile distribution of carbon-nitrogen ratios. M.Sc. thesis. The Ohio State University, 34 pp. 1956.)

CO_2 Evolution III (6A2c)

Apparatus

- LECO 70-second carbon analyzer, model 750-100
- LECO induction furnace, model 521-000

Reagents

- Manganese dioxide
- Antimony
- 1-g standard sample rings containing 0.870 percent carbon
- 1-g standard sample rings containing 0.073 percent carbon
- Metal accelerator
- Iron chip accelerator
- Anhydrone

Procedure

For noncalcareous soils, weigh approximately ½ g of <2-mm soil into crucibles in duplicate. Add to the soil in the crucibles one scoop of copper accelerator and one scoop of iron chip accelerator. Mix by stirring. Add an additional scoop of iron chips to the stirred mixture. Four standard soils containing 0.8, 2.1, 3.5, and 6.5 percent organic carbon are run with each group of soils. Follow LECO instruction manuals for instrument operation. Record readings from digital voltmeter as percent carbon.

References

Tabatabai and Bremner (1970).

Peroxide Digestion (6A3)

Gravimetric Weight Loss (6A3a)

Reagents

- Hydrogen peroxide (H_2O_2), 6-percent

Procedure

Digest soil for several hours in a covered beaker with 6-percent H_2O_2. Remove soluble material by washing three to five times with a Pasteur-Chamberlain clay filter, “F” fineness. Dry the beaker and soil, and weigh.

Calculations

$$\text{Organic matter (pct.)} = ((A + B)/C) \times 100$$

where:

A = Weight loss on heating (g)

B = Weight of dry matter in solution (g)

C = Sample weight (g)

Note that organic matter differs from organic carbon (see 6A1a).

References

North-Central Regional Research Committee on Soils (1955).

Nitrogen (6B)
Kjeldahl Digestion I (6B1)

Reagents

- Concentrated sulfuric acid (H_2SO_4)
- Salt mixture:
  - Potassium sulfate (K_2SO_4), 1000 g
  - Ferrous sulfate (anhydrous) $FeSO_4$, 55 g
  - Copper sulfate (anhydrous) $CuSO_4$, 32 g
  - Hengar granules (selenized)

Procedure

Weigh 5 g soil into 800-ml Kjeldahl flask, add 20 ml distilled water, and let stand overnight. Add 10 g salt mixture, 2 or 3 Hengar granules, and 30 ml H_2SO_4. Digest on Kjeldahl digestion heaters, rotating flasks frequently. Continue digestion 1 hr after mixture is clear.

References

Association of Official Agricultural Chemists (1945).

Ammonia Distillation (6B1a)

Reagents

- Mixed indicator. Methyl red, 0.125-percent, and methylene blue, 0.0825-percent, in 95-percent ethanol.
- Methyl red (optional), 0.25-percent
- Brom cresol green, 0.1-percent aqueous solution
- Boric acid (H_3BO_3), 4-percent
- HCl, standardized, 0.1 *N* or 0.05 *N*

Procedure

Cool digestion flask (6B1) and dilute contents with about 400 ml water. Add 2 to 3 g mossy zinc, 5 drops antifoam mixture, and 70 ml concentrated NaOH solution. Connect flask to condenser and distill ammonia into 25 or 50 ml H_3BO_3 solution. Titrate with standard HCl to purple end point, using 10 drops mixed indicator and 2 drops brom cresol green or 3 drops brom cresol green and 1 drop methyl red.

Calculations

$$N\ (pct) = ((A - B)/C) \times N \times 1.4$$

where:

A = Volume HCl sample (mL)

B = Volume HCl blank (mL)

C = Sample weight (g)

N = Normality of HCl

Report on oven-dry basis.

Ammonia Distillation, Automatic Titrator (6B1b)

Reagents

- Boric acid (H_3BO_3), 4-percent
- HCl, standardized, 0.1 *N* or 0.05 *N*
- Concentrated sodium hydroxide (NaOH) solution, 50-percent
- Antifoam mixture: Equal parts n-octyl alcohol and mineral oil
- Mossy zinc

Procedure

Cool digestion flask (6B1) and dilute contents with about 400 ml water. Add 2 to 3 g mossy zinc, 5 drops antifoam mixture, and 70 ml concentrated NaOH solution. Connect flask to condenser and distill ammonia into 250-ml titrator beaker containing 50 ml H_3BO_3 solution. Titrate with standard HCl to end point pH setting of 4.60 on automatic titrator.

Calculations

$$N\ (pct.) = ((A - B)/C) \times N \times 1.4$$

where:

A = Volume HCl sample (mL)

B = Volume HCl blank (mL)

C = Sample weight (g)

N = Normality of acid

Report on oven-dry basis.

Semimicro Kjeldahl (6B2)

Apparatus

- Aminco-Koegel semimicro rotary digestion rack and steam-distillation apparatus

Reagents

- Concentrated sulfuric acid (H_2SO_4)
- H_2SO_4, 0.01 *N*, standardized
- Sodium hydroxide (NaOH), 50-percent
- Boric acid (H_3BO_3), 2-percent
- Mixed indicator. Mix 0.1 g methyl red and 0.1 g brom cresol green and dissolve in 250 ml ethanol.
- Salt mixture. Mix 790 g potassium sulfate (K_2SO_4), 100 g ferrous sulfate ($FeSO_4$), 100 g copper sulfate ($CuSO_4$), and 10 g selenium metal.

Procedure

Using an analytical balance, weigh on a cigarette paper either 0.500 or 1.000 g oven-dry soil that has been ground to about 0.2 mm. Roll soil in cigarette paper and drop into a 100-ml digestion-distillation flask. Add 2 g salt mixture, 1 ml water, and 5 ml concentrated H_2SO_4. Swirl vigorously and digest, rotating the flask

frequently until fumes are emitted. Continue digestion for at least 1 hour after mixture becomes white. Cool to room temperature and add 15 ml water. Shake until the contents of the flask are thoroughly mixed.

Ammonia Distillation (6B2a)

Procedure

Measure 10 ml 2-percent H_3BO_a with an automatic pipette into a 125-ml flask and add 0.5 ml mixed indicator. Place this flask under delivery tube. Connect digestion-distillation flask containing soil digested according to method 6B2 to the distillation unit by the ground-glass connection. Start steam passing through the system and slowly add 15 ml 50-percent NaOH. Distill for 12 minutes, add 0.5 ml more mixed indicator, and titrate the absorbed ammonia with 0.01 *N* H_2SO_4.

Calculations

$$N\ (pct) = (A/B) \times N \times 1.4$$

where:

A = Volume H_2SO_4 (mL)

B = Sample weight (g)

N = Normality of H_2SO_4

Report on oven-dry basis.

Iron (6C)
Dithionite Extraction (6C1)

Reagents

- Sodium dithionite powder ($Na_2S_2O_4$)
- Hydrochloric acid (HCl), 10-percent

Apparatus

- 8-oz Pyrex nursing bottles or 250-ml flat-bottomed centrifuge bottles

Procedure

Place 4 g soil, ground to 80 mesh, in a nursing or centrifuge bottle. Add 4 g $Na_2S_2O_4$ and 75 ml water. Stopper and shake overnight or for 16 hours. Then adjust the pH to 3.5 to 4.0, if necessary, with 10-percent HCl. Let stand for no less than 1 hour, stirring four or five times. Transfer the suspension to a graduated cylinder, dilute to 200 ml with water, and mix. Centrifuge or filter a part of the suspension and transfer 50 ml of the clear solution to a 250-ml beaker.

References

Kilmer (1960).

Dichromate Titration (6C1a)

Reagents

- Hydrogen peroxide (H_2O_2), 35-percent
- Ammonium hydroxide (NH_4OH), 1:1
- Hydrochloric acid (HCl), 1:1
- Stannous chloride ($SnCl_2$). Dissolve 1 g $SnCl_2$ in 2 to 4 ml concentrated HCl and dilute to 50 ml with water; prepare fresh each time.
- Mercuric chloride ($HgCl_2$), saturated aqueous solution
- Phosphoric acid (H_3PO_4), 85-percent
- Potassium dichromate ($K_2Cr_2O_7$), 0.100 *N*, standard
- Barium diphenylaminesulfonate, 0.16-percent aqueous solution

Procedure

Add 10 to 15 ml H_2O_2 (6C1) to the solution to destroy any excess reducing agent. Cover the beaker with a watchglass and warm on a hot plate until the reaction starts. Set the solution aside until the reaction subsides and then boil for 10 to 15 minutes. Add a slight excess of 1:1 NH_4OH and boil the solution for 15 to 20 minutes to ensure complete removal of H_2O_2. Dissolve $Fe(OH)_3$ by adding 1:1 HCl through the lip of the beaker. Usually 10 to 15 ml are enough. Heat the solution to 90 °C and reduce by adding $SnCl_2$ by drops, stirring until the yellow color just disappears. Add three to four drops more. Cool the solution to room temperature and add 15 ml $HgCl_2$ solution all at once. A light silky precipitate of Hg_2Cl_2 forms if the proper amount of $SnCl_2$ has been added. Dilute the solution to 100 to 150 ml and add 5 ml H_3PO_4. Add 10 drops of barium diphenylaminesulfonate and titrate the solution with standard $K_2Cr_2O_7$ to a violet-blue end point.

Calculations

$$\text{Fe (pct.)} = (A/B) \times N \times (C/D) \times 5.58$$

where:

A = Volume $K_2Cr_2O_7$ (mL)

B = Sample weight (g)

N = Normality of $K_2Cr_2O_7$

C = Volume extract (mL)

D = Volume aliquot (mL)

Fe_2O_3 (pct.) = Fe (pct.) x 1.43

Report on oven-dry basis.

EDTA Titration (6C1b)

Reagents

- Hydrogen peroxide (H_2O_2), 35-percent.
- Ammonium persulfate ($(NH_4)_2S_2O_8$).
- Salicylic acid, 1-percent in 95-percent ethanol
- EDTA, standardized as g iron per ml EDTA. Prepare EDTA as described in 6N1a.
- Iron standard, 0.500 g iron per liter

Procedure

Pipette a 5- to 25-ml aliquot from the centrifuge tube of method 6C1 into a 250-ml beaker. Add 50 ml water to the beaker. Then add by drops 5 ml H_2O_2 and digest over low heat until bubbling from the decomposing H_2O_2 ceases. Remove immediately to avoid precipitation of Fe_2O_3 in samples high in iron. Caution: Add H_2O_2 slowly to prevent liberation of elemental sulfur from any remaining $Na_2S_2O_4$. Keep the volume in the beaker to about 50 ml during the digestion by adding water if necessary. Remove from heat and cool. Adjust the pH between 2.0 and 3.0 with a pH meter, using either concentrated acetic acid or a 20-percent NaOAc solution. Add a few milligrams $(NH_4)_2S_2O_8$ to the solution to ensure total oxidation of iron. Then add 1 ml indicator (1-percent salicylic acid) and titrate with 0.02 *N* EDTA to a pale yellow or colorless end point.

Calculations

Fe (pct.) = (A/B) x V x (C/D) x 100

where:

A = Volume EDTA (mL)

B = Sample weight (g)

V = Titer of EDTA in g Fe/ml EDTA

C = Volume extract (mL)

D = Volume aliquot (mL)

Fe_2O_2 (pct.) = Fe (pct.) x 1.43

Report on oven-dry basis.

References

Cheng, Bray, and Kurtz (1953).

Dithionite-Citrate Extraction (6C2)

Reagents

- Sodium dithionite ($Na_2S_2O_4$)
- Sodium citrate
- Superfloc flocculating agent, 0.2 percent in water

Procedure

Weigh 1 to 4 g of soil (approximately 0.2 g maximum extractable iron) into an 8-oz nursing bottle. Add 2 g sodium dithionite and 20 to 25 g sodium citrate. Make up to 4 oz with water, and shake overnight in a reciprocating shaker. Add 2 ml Superfloc solution to the suspension, make up to 8 oz with water, shake vigorously for 15 s, and allow to settle for at least 1 hr. This extract is used for analysis of iron (6C2b), aluminum (6G7a), and manganese (6D2a).

References

Holmgren (1967).

Orthophenanthroline Colorimetry (6C2a)

Apparatus

- Seligson pipette, 0.1-ml

Reagents

- Orthophenanthroline, 0.25-percent
- Iron solution, 1000 mg per liter, standard
- Sodium dithionite powder ($Na_2S_2O_4$)
- Sodium citrate crystals
- Superfloc flocculating agent, 0.2-percent, in water

Procedure

Add 5 drops Superfloc solution to the dithionite-treated soil suspension (6C2) and make to 8 oz. Shake vigorously for about 15 seconds and allow to settle. Pipette a 0.1-ml aliquot with a Seligson pipette into a 25-ml volumetric flask. Add water to about 10 ml. Using a small scoop, tap a pinch of dithionite and a pinch

of sodium citrate into the flask. Add 0.5 ml 0.25-percent orthophenanthroline and make to volume. Shake and read in a colorimeter at 508 Mμ after 1 hour. To prepare the standards, pipette 5-, 10-, 25-, 50-, 100-, 150-, and 200-ml aliquots of standard iron solution (1000 mg/L) into 8-oz shaking bottles and make to 8 oz after adding reagents as in 6C2. Transfer 0.1-ml aliquots to 25-ml volumetrics and develop color by the above procedure.

Plot the standard curve as milligrams iron per 8-oz bottle against percentage transmission.

Calculations

$$Fe\ (pct.) = (A/B) \times 10^{-1}$$

A = Fe in bottle (mg)

B = Sample weight (g)

$$Fe_2O_3\ (pct.) = Fe\ (pct.) \times 1.43$$

Report on oven-dry basis.

References

Holmgren (1967).

Dithionite-Citrate-Bicarbonate Extraction (6C3)

Reagents

- Sodium bicarbonate ($NaHCO_3$), 1 *M*
- Sodium citrate, 0.3 *M*
- Sodium chloride (NaCl), saturated solution
- Acetone

Procedure

Weigh 4 g soil (1 g clay) into a 100-ml centrifuge tube. Add 40 ml 0.3 *M* Na-citrate and 5 ml 1 *M* $NaHCO_3$. Bring temperature to 80 °C in water bath. Add 1 g solid $Na_2S_2O_4$, stir constantly for 1 minute and occasionally for 15 minutes. Add 10 ml NaCl solution and 10 ml acetone to promote flocculation. Mix, warm in water bath, and centrifuge 5 minutes at 1,600 to 2,200 rpm. Decant clear supernatant into 500-ml volumetric flask and make to volume.

References

Mehra and Jackson (1960).

Potassium Thiocyanate Colorimetry (6C3a)

Apparatus

- Colorimeter

Reagents

- Hydrochloric acid (HCl), 6 *N*
- Potassium thiocyanate (KSCN), 20-percent
- Hydrogen peroxide (H_2O_2), 30-percent

Procedure

Transfer suitable aliquot (0.5 to 3 ppm iron in final solution) to 50 ml-volumetric flask. Add water to 35 ml, 1 drop H_2O_2, 5 ml HCl, and 5 ml KSCN solution. Make to volume and read at 490 mμ in colorimeter.

Calculations

Fe (pct.) = (A/B) x (C/D) x 0.005

where:

A = Fe from curve (mg)

B = Sample weight (g)

C = Volume extract (mL)

D = Volume aliquot (mL)

Fe_2O_3 (pct.) = Fe (pct.) x 1.43

Report on oven-dry basis.

References

Jackson (1956).

Pyrophosphate-Dithionite Extraction (6C4)

Reagents

- Pyrophosphate solution. Dissolve 89.2 g $Na_4P_2O_7 \cdot 10H_2O$ in 800 to 900 ml water. Adjust the pH of this solution to 8.0 by adding hydrogen saturated exchange resin. Decant or filter, wash the resin, and dilute the solution to 1000 ml to make 0.2 *M* $Na_4P_2O_7$.
- Sodium dithionite ($Na_2S_2O_4$)

- Digestion acid. 10 parts concentrated HNO_3, 4 parts concentrated H_2SO_4, and 4 parts concentrated $HClO_4$.

Procedure

Mix 80 ml pyrophosphate solution and 2.0 g solid sodium dithionite in a beaker and add this solution to 4 g soil in a centrifuge tube (pH 8.0 pyrophosphate solution and dithionite combined in this ratio result in a solution having a pH of about 7.3). Continue the extraction for 30 minutes at 50 °C, shaking the suspension in the tube every 5 minutes. Centrifuge the suspension 5 to 10 minutes at 2000 rpm. Dilute the extract to 100 ml (solution A).

Immediately transfer 5 ml solution A to a beaker. Add 1 to 2 ml digestion acid and heat on a hot plate until almost dry to destroy the organic and hydrolyze pyrophosphate to orthophosphate. Allow to cool, dissolve the salts in HCl, and dilute to 100 ml (solution B). Determine iron and aluminum in solution B by appropriate methods, such as 6C3a and 6G1a.

References

Franzmeier, Hajek, and Simonson (1965).

Sodium Pyrophosphate Extraction (6C5)

Reagents

- Sodium pyrophosphate ($Na_4P_2O_7$), 0.1 *M*
- Superfloc solution, 0.4 percent

Procedure

Place 2 g soil into 250-ml centrifuge bottle (polypropylene). Add 200 ml 0.1 *M* $Na_4P_2O_7$, cap, and shake overnight. Add 5 to 10 drops 0.4-percent Superfloc, shake, and centrifuge at 2000 rpm (Int. No. II centrifuge). Transfer the supernatant liquid to a plastic or glass container and reserve for Fe and Al analyses.

The supernatant liquid must be clear in reflected light. If fine colloids are visible, repeat the procedure. If fine colloids are still present, spin the suspension in a super centrifuge until the supernatant liquid is clear. Foam rubber can be used in the centrifuge cups as a cushion for the 250-ml flat-bottom plastic bottles.

References

Bascomb (1968).

Atomic absorption (6C5a)

Apparatus

- Atomic absorption spectrophotometer

Reagents

- Standard Fe solution, 0 to 50 ppm

Procedure

Establish standard curve and match readings from extract to curve readings. Dilute where necessary.

Calculations

$$\text{Fe (pct.)} = A \times (B/C) \times (1/10{,}000) \times \text{dilution}$$

where:

A = Fe (ppm)

B = Volume extract (mL)

C = Sample weight (g)

Report on oven-dry basis.

Ammonium Oxalate Extraction (6C6)

Reagents

- Ammonium oxalate $(NH_4)_2C_2O_4$ 0.2 *M*, pH 3.0
- Adjust the pH of 0.2 *M* $(NH_4)_2C_2O_4$ to 3.0 with 0.2 *M* oxalic acid ($H_2C_2O_4$).
- Superfloc solution, 0.4 percent

Procedure

Place 2 g soil into 250-ml centrifuge bottle (polypropylene). Add 200 ml 0.2 *M* $(NH_4)_2C_2O_4$, cap, and shake immediately in the dark for 4 hours. Add 5 to 10 drops 0.4-percent Superfloc, shake, and centrifuge at 2000 rpm (Int. No. II centrifuge). Transfer the supernatant liquid to a plastic or glass container. Store in the dark and reserve for Fe and Al analyses.

The supernatant liquid must be clear in reflected light. If fine colloids are visible, repeat the procedure. If fine colloids are still present, spin the suspension in a supercentrifuge until the supernatant liquid is clear.

References

McKeague and Day (1966).

Atomic Absorption (6C6a)

Proceed as in 6C5a except use extract from 6C6.

Manganese (6D)

Dithionite Extraction (6D1)

Extract 4.00 g soil as described in 6C1.

Permanganate Colorimetry (6D1a)

Reagents

- Concentrated nitric acid (HNO_3)
- Hydrogen peroxide (H_2O_2), 30-percent
- Phosphoric acid (H_3PO_4), 85-percent
- Sodium para periodate ($Na_3H_2IO_6$) or sodium meta periodate ($NaIO_4$)
- Purified water diluent. Add 100 ml 80-percent H_3PO_4 and 1 g $Na_3H_2IO_6$ to 1 liter water (Mn-free); heat to boiling and digest for 1 hour; stopper with foil-covered stopper. About 85 ml of this diluent is needed for each sample.
- $KMnO_4$, standard

Procedure

Take a 10- to 25-ml aliquot from the dithionite extract and place in a 150-ml beaker. Add 5 ml 30-percent H_2O_2, digest on hot plate, and evaporate until dry. Cool beaker and contents and add 3 ml concentrated HNO_3 and 2 ml 30-percent H_2O_2. Digest on hot plate for 30 minutes, using a close fitting cover glass, then raise cover glass, and evaporate until dry. Take up residue with 10 ml 85-percent H_3PO_4, heat to boiling, remove, and cool to about 50 °C. Dilute with 10 ml water and add 0.2 g $Na_3H_2IO_6$. Cover beaker and heat to boiling. Cool to 50 °C and add 62 ml purified water diluent and 0.1 g $Na_3H_2IO_6$. Digest at 90 °C for 40 minutes or until no further color develops. Transfer the hot solution to a 100-ml volumetric flask, using purified water diluent to rinse the beaker. Cool, make up to volume with the diluent, stopper, and shake. Determine percentage transmittance with a photoelectric colorimeter at 540 mμ. Interpolate concentration from a standard absorbance concentration.

Calculations

$$Mn\ (pct.) = (A/B) \times (C/D) \times 54.9$$

where:

A = MnO_4^- (meq/L)

B = Sample weight (g)

C = Volume extract (mL)

D = Volume aliquot (mL)

$$MnO\ (pct.) = Mn\ (pct.) \times 1.291$$

Report on oven-dry basis.

References

Jackson (1956).

Calcium Carbonate (6E)

HCl Treatment (6E1)

Gas Volumetric (semiquantitative) (6E1a)

This procedure uses a simple leveling device to measure the volume of gas released when the soil is treated with HCl. It has an inherent error caused by the solubility of CO_2 in the HCl solution. Data on file at the laboratory at Lincoln, Nebraska, indicate that the results are about 10 percent (8 to 12 percent) low for $CaCO_3$ equivalents ranging from 40 percent to 6 percent (1-g basis). For 1-percent equivalents, the values are about 20 percent low; and for less than 1 percent, the values have doubtful significance.

References

Association of Official Agricultural Chemists (1945).

Manometric (6E1b)

Apparatus

- Wide-mouth prescription bottles, 3-oz, with bakelite cap; drill $^{7}/_{16}$-in hole in cap for serum bottle stopper. Rubber gasket, 1⅜ in OD x $^{15}/_{16}$ in ID.
- Serum bottle stopper
- Mercury manometer and a 26-gauge hypodermic needle attached to manometer tube
- Gelatin capsule, ¼ oz

Reagents

- Hydrochloric acid (HCl), 6 *N*
- Glycerin

Procedure

Place 2 g of soil in prescription bottle and add 5 ml water. Moisten lip of bottle with a drop of glycerin to ensure a good seal with rubber gasket. Fill gelatin capsule with HCl, put cap in place, and invert to seal cap on capsule. Place capsule in bottle and immediately cap the bottle. In a minute or two the HCl will dissolve the capsule. After 1 hr insert hypodermic needle through serum stopper and read manometer. Compare reading with those for standards prepared by treating aliquots of standard Na_2CO_3 solution in same manner as samples.

Vary sample weight according to $CaCO_3$ content as follows: For <25 percent $CaCO_3$, use 2 g soil; for 25 to 50 percent $CaCO_3$, 1 g soil; and for >50 percent $CaCO_3$, 0.5 g soil. For trace amounts, add a few drops 6 *N* HCl to soil and observe under binocular microscope. Evolution of gas bubbles indicates the presence of $CaCO_3$.

References

Williams (1948).

Gravimetric (weight loss) (6E1c)

Apparatus

- See figure 6E1c-1.

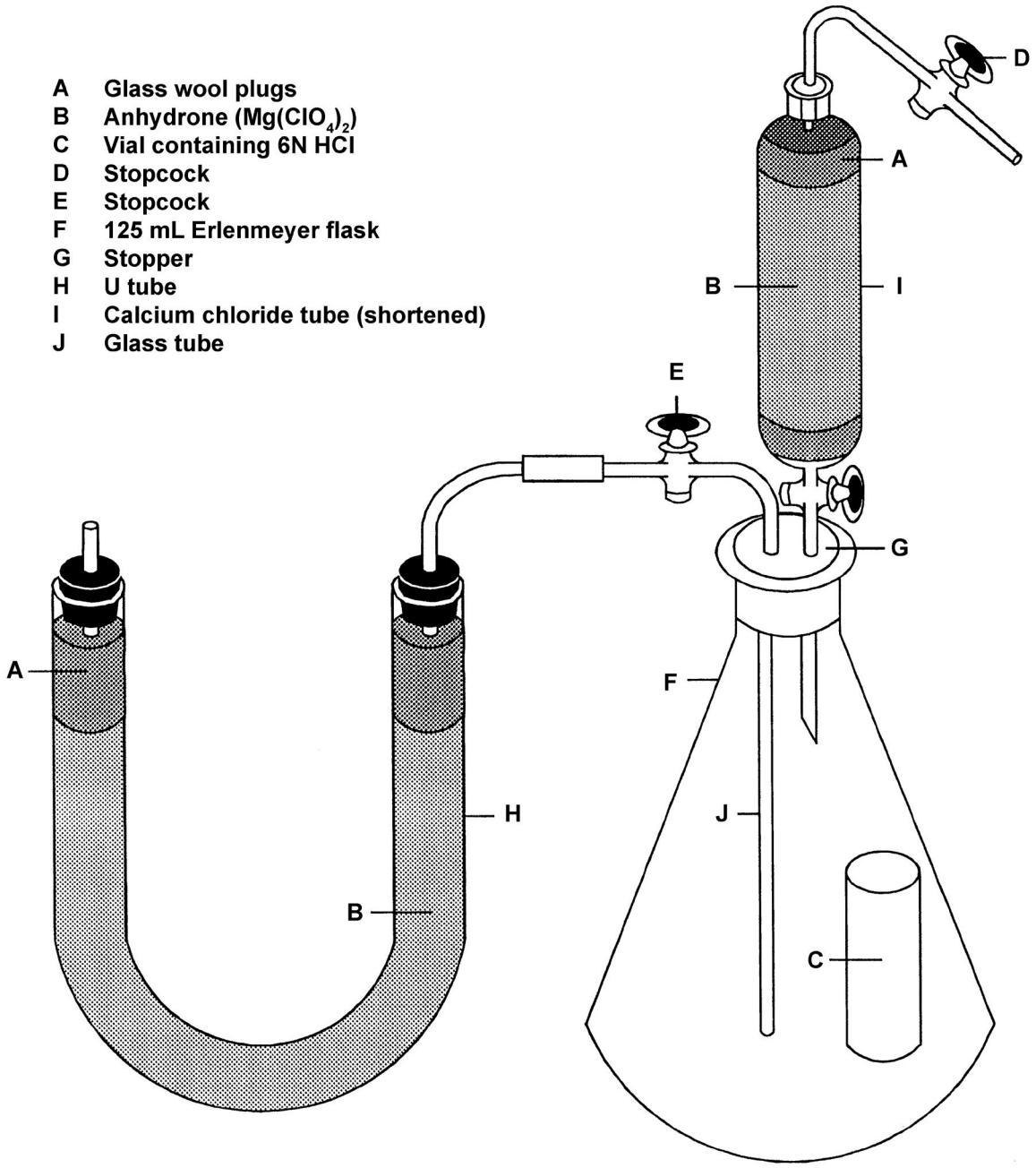


Figure 6E1c-1.—Apparatus used for calcium carbonate determination by weight loss (6E1c).

Reagents

- Hydrochloric acid (HCl), 6 *N*
- Anhydrone ($Mg(ClO_4)_2$)

Procedure

Assemble apparatus as shown in figure 6E1c-1. Place a sample of soil containing less than 1 g $CaCO_3$ equivalent in a 125-ml Erlenmeyer flask. Wash

down the sides of the flask with 10 ml water. Place 7 ml 6 *N* HCl into vial C and then place the vial upright in the flask without spilling any acid. Moisten stopper G with glycerin, sprinkle with a small amount of 180-mesh abrasive to overcome slipperiness, and place the apparatus with stopcocks D and E, tubes I and J, attached firmly in position in the flask. Close stopcocks D and E. Place the apparatus beside the balance. Wait 30 minutes before weighing to allow temperature of the apparatus to equilibrate with temperature of air in the balance. Do all weighing with stopcock D open since a change in temperature of the flask with the stopcock closed results in a change in weight of the apparatus. Use tongs to place apparatus on the weighing pan, open stopcock D, weigh to 0.1 mg, and then immediately close stopcock D. Check the weight 10 minutes later to be certain that the weight of the flask has stabilized. Open stopcock D and then shake apparatus to upset the vial, allowing the acid to react with the carbonates. After 10 minutes, attach the rubber tube from the air-drying vessel to stopcock E. Open stopcock E and apply suction at stopcock D to give 5 to 10 bubbles per second at the base of tube J to sweep out CO_2. Shake the flask after 10 minutes and again after 20 minutes. After 30-minutes sweeping time, stop the suction and close stopcocks D and E. Return apparatus to the balance. Delay weighing for 1 hour to allow the heat generated by absorption of water by the anhydrone to be dissipated. Weigh apparatus with stopcock D open. Check the weight after 10 minutes.

Calculations

$$\text{Carbonate as } CaCO_3 \text{ (pct.)} = ((A - B)/C) \times 228$$

where:

A = Initial weight of flask (g)

B = Final weight of flask (g)

C = Sample weight (g)

Report on oven-dry basis.

References

Erickson et al. (1947).

Gravimetric (weight gain) (6E1d)

Proceed as in 6E1c except add additional trap containing CO_2-absorbing Ascarite to end of gas train. Weigh Ascarite bulb before and after CO_2 evolution. Weight gain equals the CO_2 evolved from the sample. Better results are obtained if the Ascarite is size-graded so that CO_2 passes through the coarser material first. Indicarb can be used in place of Ascarite.

Titrimetric (6E1e)

Reagents

- Hydrochloric acid (HCl), 0.5 *N*, standardized
- Sodium hydroxide (NaOH), 0.25 *N*, standardized
- Phenolphthalein, 1 percent in 60-percent ethanol

Procedure

Place 5 to 25 g soil in a 150-ml beaker, add exactly 50 ml HCl, cover with a watchglass, and boil gently for 5 minutes. Cool, filter, and wash all the acid from the soil with water. Determine the amount of unused acid by adding 2 drops of phenolphthalein and back-titrating with NaOH.

Calculations

$$\text{Carbonate as } CaCO_3\ (\%) = ((50 \times A - B \times C)/D) \times 5$$

where:

A = Normality of HCl

B = Volume NaOH (mL)

C = Normality of NaOH

D = Sample weight (g)

Report on oven-dry basis.

References

Richards (1954).

Warburg Method (6E1f)

Apparatus

- Warburg manometer, mercury filled
- Warburg reaction vessel, 15-ml capacity, with vented stopper for sidearm
- Constant temperature bath

Reagents

- HCl, 1:1. Na_2CO_3 solution for standard curve. Dissolve 1.06 g Na_2CO_3 in water and make to 1 liter. Solution contains 1.06 mg Na_2CO_3 per ml or the equivalent of 1 mg $CaCO_3$ per ml. Obtain standard curve by measuring CO_2 pressure from 1, 2, 4, 6, 8, and 10 ml Na_2CO_3 solution.

Procedure

Weigh 100 mg sample of finely ground soil and transfer to Warburg reaction vessel. Be careful not to get any sample in center well. Pipette 1 ml water into vessel and mix well with sample. Pipette 1 ml 1:1 HCl into sidearm, insert greased stopper, and leave in vent-open position. Attach reaction vessel to manometer and fasten with rubber bands or spring supports. Place reaction vessel in constant temperature bath at 25 °C for 5 to 10 minutes to bring flask contents to temperature of water bath. Remove flask from bath, close stopper vent, and fasten with rubber bands or springs. Tilt flask to allow acid to flow from sidearm into reaction vessel, mix contents, and return vessel to water bath. Let stand for at least 30 minutes before reading manometer. Use the standard curve to convert the difference between the two manometer arm readings (mm) to milligrams $CaCO_3$. Gently tap the manometer holder occasionally to prevent low readings caused by mercury adhering to manometer walls.

Sensitive Qualitative Method (6E2)

Visual, Gas Bubbles (6E2a)

Add few drops 6 *N* H_2SO_4 to soil and observe under binocular microscope. Evolution of gas bubbles indicates the presence of $CaCO_3$.

H_2SO_4 Treatment (6E3)

Gravimetric (weight gain) (6E3a)

Apparatus

- See figure 6A1b-1.

Reagents

- Sulfuric acid (H_2SO_4). Dissolve 57 ml concentrated H_2SO_4 and 92 g of $FeSO_4 \cdot 7H_2O$ in 600 ml water, cool, and dilute to 1000 ml. This solution is approximately 2 *N* in acidity and contains 5-percent $FeSO_4$ as antioxidant. Keep well stoppered.

Procedure

Place a 1- to 5-g sample of oven-dry soil in the digestion flask E and connect condenser D. Weigh the Nesbitt bulb, attach to the system, and adjust the carrier stream to a flow rate of 1 or 2 bubbles per second. Pour 25 ml of the acid solution into the funnel and let it enter the digestion flask E. Close the stopcock immediately. Apply heat slowly and bring contents of flask to a boil in about 4 minutes. Continue gentle boiling for exactly 3 minutes more for a total heating period of 7 minutes. Remove the flame, adjust the carrier stream to 6 or 8 bubbles

per second, and continue aerating for 10 minutes. Disconnect the Nesbitt bulb and weigh.

Calculations

Carbonate as $CaCO_3$ (%) = ((A − B)/C) x 227

where:

A = Final weight of bulb (g)

B = Initial weight of bulb (g)

C = Sample weight (g)

Report on oven-dry basis.

References

Allison (1960).

Gypsum (6F)

Water Extract (6F1)

Indirect Estimate (6F1b)

Add a weighed quantity of soil to enough water to dissolve all the gypsum by overnight shaking. The concentration of sulfate in this dilute soil:water extract should be <10 meq/L. Gypsum can be estimated by method 6F2. If crystals are observed or estimated gypsum content is >5 percent, the <2−mm sample should be ground to approximately 80 mesh. Determine total sulfate in this extract by any appropriate procedure. Also determine Ca and SO_4 in a saturation extract by any appropriate procedure.

Calculations

$$\text{Gypsum} = (SO_4)_{DE} - (SO_4)_{\text{non-gypsum SE}}$$

$$\text{but } SO_{4\ \text{non-gypsum SE}} = (SO_4)_{SE} - (SO_4)_{\text{gypsum SE}}$$

$$\therefore \text{gypsum} = (SO_4)_{DE} + (SO_4)_{\text{gypsum SE}} - (SO_4)_{SE}$$

$(SO_4)_{DE} = SO_4$ in dilute water extract

$(SO_4)_{SE} = SO_4$ in saturation extract

$(SO_4)_{\text{gypsum SE}} = 30$ meq/L if SO_4 and Ca are ≥ 30 meq/L

$= (SO_4)_{SE}$ if $(Ca)_{SE} > (SO_4)_{SE}$

$= (Ca)_{SE}$ if $(Ca)_{SE} < (SO_4)_{SE}$

All quantities are reported in meq/100 g.

Gypsum (%) = Gypsum (meq/100 g) x 0.0861 (g/meq)

References

Lagerwerff, Akin, and Moses (1965).

Ion Chromatograph (6F1c)

Apparatus

- DIONEX Model 2110i ion chromatograph
- Recorder (1 volt input)
- Voltage stabilizer

Reagents

- *M* Na_2CO_3
- 0.003 *M* $NaHCO_3$
- 0.0024 *M* Na2CO_3
- *N* H_2SO_4
- Mixed standard solutions:
    - Fluoride 0.0125 to 5.0 meq/L
    - Chloride 0.01 to 4.0 meq/L
    - Nitrate 0.025 to 10.0 meq/L
    - Sulfate 0.05 to 20.0 meq/L

All solutions are filtered through a polycarbonate membrane having 0.4-µm pore size. Soil extracts are filtered with a disposable filter unit (Millix™) having 0.22-µm pore size.

Procedure

The soil extract is obtained as described in 6F1a. Fill a plastic syringe (3 to 10 cc) with a solution having a concentration within the range of the sulfate standard. Baseline is established using a full-scale µmhos setting of 3 before each determination. This setting is adjusted as needed, keeping in the range used for making the determinations on the mixed standard. Peak height readings are made on the mixed standard using eight concentrations. A curve fitting linear regression equation [$y(meq/L) = a_1 (PKH) + a_0$] is established for the sulfate standards. Sulfate concentration in the soil extracts is determined by this equation.

Calculations

See 6F1b.

Weight Loss (6F2)

Apparatus

- Vacuum desiccator
- Aluminum dish
- Balance, 0.001-g sensitivity

Reagents

- Phosphorus pentoxide (P_2O_5)

Procedure

Place about 10 g of soil in a tared (Wt A) aluminum dish. Saturate sample with water and let stand overnight to air-dry. Place in a vacuum desiccator with P_2O_5 desiccant. Evacuate desiccator and allow to stand 48 hr. Remove dish from desiccator and weigh (Wt B), then place in oven at 105 °C for 24 hr. Allow dish to cool in desiccator and weigh (Wt C).

Calculations

$$\text{Gypsum (\%)} = ((\text{WtB} - \text{WtC}) \times 100) / ((\text{WtB} - \text{WtA}) \times 0.1942)$$

The theoretical crystal water content of gypsum is 20.91 percent. However, Nelson et al. have determined that, in practice, this content averages 19.42 percent.

References

Nelson, Klameth, and Nettleton (1978).

Gypsum Requirement (6F5)

The amount of gypsum needed to replace all of the sodium on the exchange complex with calcium is the gypsum requirement.

Reagents

- Saturated gypsum solution. Place about 25 g gypsum ($CaSO_4 \cdot 2H_2O$) in 5 L water in a large flask, stopper, and shake by hand periodically for 1 hr or more. Let settle and decant through a filter into storage bottle. Determine

calcium concentration by titration of an aliquot with standard EDTA solution using Eriochrome black T as indicator.

- EDTA solution. Dissolve 1.25 g di-sodium ethylenediamine tetraacetate in water and dilute to 1 L. Standardize against solutions containing known concentrations of Ca and Mg.
- Buffer solution. Dissolve 6.75 g ammonium chloride in about 400 ml water. Add 570 ml concentrated ammonium hydroxide and dilute to 1 L with distilled water.
- Eriochrome black T indicator. Dissolve 1 g Eriochrome black T in 100 ml triethanolamine.

Procedure

Weigh 5 g soil into flask, add 100 ml saturated gypsum solution, stopper, and shake for 5 min in mechanical shaker. Filter through folded filter paper, discarding the first few milliliters of filtrate, which may be cloudy. Pipette a 5-ml aliquot of filtrate into a 125-ml Erlenmeyer flask and dilute to 25 or 30 ml with distilled water. Add 10 drops of buffer solution, 2 drops Eriochrome black T indicator, and titrate with standard EDTA solution to blue end point.

Calculations

$$\text{Gypsum requirement (meq/100 g)} = (A - B) \times 2$$

where:

A = Ca concentration of gypsum solution (meq/L)

B = Ca + Mg concentration of filtrate (meq/L)

References

Richards (1954).

Aluminum (6G)

KCl Extraction I (30 min) (6G1)

Reagents

- Potassium chloride (KCl), 1 *N*

Procedure

Weigh 10-g soil samples into 125-ml Erlenmeyer flasks. Add 50 ml 1 *N* KCl to each flask, mix several times, and let stand for 30 minutes. Filter through 5.5-cm Whatman No. 42 filter paper in Buchner funnel, using suction as necessary. Leach each sample as rapidly as possible with about five 9-ml portions of KCl, using the first to help transfer the remaining soil in the Erlenmeyer flasks to the

Buchner funnels. Transfer the extract to 100-ml volumetric flasks and dilute to volume with the extracting solution. Or use Allihn leaching tubes and bring to standard weight in tared suction flasks.

References

Lin and Coleman (1960) and Pratt and Bair (1961).

Aluminon Colorimetry I, Hot Color Development (6G1a)

Reagents

- Thioglycolic acid ($HSCH_2COOH$). Dilute 1 ml purified acid to 100 ml with water.
- Aluminon reagent. Dissolve in separate containers 0.75 g Aluminon (ammonium aurine tricarboxylate), 15 g gum acacia, and 200 g NH_4OAc crystals. To the NH_4OAc solution add 189 ml concentrated HCl, then the gum acacia, and finally the Aluminon. Mix, filter, and dilute to 1500 ml with water. To get the gum acacia in suspension, add slowly to boiling water while stirring constantly.
- Aluminum standard. Add 2.24 g $AlCl_3 \cdot 6H_2O$ per liter of water. This solution should be nearly 250 ppm aluminum. Check concentration of an aliquot containing 10 ppm aluminum by analyzing for chloride.

Procedure

If samples contain less than 5 meq per 100 g aluminum, pipette a 1-ml aliquot of each extract into numbered and calibrated test tubes. If more aluminum is present, dilute before the aliquot is taken. Dilute to approximately 20 ml with distilled water. Add 2 ml dilute thioglycolic acid to each tube, stopper, and shake all the tubes. Pipette 10 ml Aluminon into each tube and dilute to exactly 50 ml. The pH should be between 3.7 and 4.0. Stopper and shake all tubes. Place tubes in a rack and heat in a boiling-water bath for 4 minutes. Cool in running water to room temperature. Transfer samples to reading tubes and measure light transmittance at 535 mμ and compare with a standard curve.

Calculations

$$Al\ (meg/100\ g) = (A/B) \times (C/D) \times (9/5)$$

where:

A = Al from curve (mg/L)

B = Sample weight (g)

C = Volume extract (mL)

D = Volume aliquot (mL)

Report on oven-dry basis.

References

Chenery (1948) and Yoe and Hill (1927).

Aluminon Colorimetry II, HCl Predigestion (6G1b)

Procedure

Proceed as in 6G1a but first add 3 ml *N* HCl to the aliquot and heat for 30 minutes at 80 to 90 °C.

References

Hsu (1963).

Aluminon Colorimetry III, Overnight Color Development (6G1c)

Proceed as in 6G1a except eliminate boiling-water bath, adjust pH to 4.0, and allow color to develop overnight before reading.

Fluoride Titration (6G1d)

Reagents

- Potassium fluoride (KF), 1 *N*. Titrate with NaOH to a phenolphthalein end point. This eliminates the need for a blank correction in the Al titration.
- Sodium hydroxide (NaOH), 0.1 *N*, standardized
- Sulfuric acid (H_2SO_4), 0.1 *N*, standardized
- Phenolphthalein, 0.1 percent

Procedure

Add 6 to 8 drops phenolphthalein to the leachate in the suction flask (6G1). Titrate with standard NaOH to a pink color that persists for 30 seconds or more. Correct for a KCl blank to obtain KCl extractable acidity. Then add 10 ml KF, and titrate with standard H_2SO_4 until the pink color disappears. Set aside while other samples are titrated and then complete to a lasting colorless end point. If there is a considerable amount of Al, add a few more drops of phenolphthalein.

Calculations

$$\text{Acidity (meq/100 g)} = (A/B) \times N \times 100$$

where:

A = Volume NaOH (mL)

B = Sample weight (g)

N = Normality of NaOH

$$Al\ (meq/100) = (A/B) \times N \times 100$$

where:

A = Volume H_2SO_4 (mL)

B = Sample weight (g)

N = Normality of H_2SO_4

References

Yuan (1959).

Atomic absorption (6G1e)

Apparatus

- Perkin-Elmer Model 290 atomic absorption spectrophotometer with nitrous oxide burner attachment

Reagents

- Standard Al solution, 0 to 5 meq per liter

Procedure

Dilute sample to within range of standard curve. Compare absorbance with standard curve.

Calculations

$$Al\ (meq/100\ g) = (A/B) \times dilution \times (C/10)$$

where:

A = Al from curve (meq/L)

B = Sample weight (g)

C = Volume extract (mL)

KCl Extraction II, Overnight (6G2)

Weigh 10 g soil into 125-ml Erlenmeyer flask. Add 50 ml 1 *N* KCl and let stand overnight. In the morning transfer to filter funnels and leach with an additional 50 ml KCl.

Aluminon Colorimetry I (6G2a)

Follow procedure for aluminum analysis described in 6G1a.

NH_4OAc Extraction (6G3)

Prepare soil as described in 5A1.

Aluminon Colorimetry III (6G3a)

Follow method of 6G1c.

NaOAc Extraction (6G4)

Prepare soil as described in 5A2.

Aluminon Colorimetry III (6G4a)

Follow method of 6G1c.

Sodium Pyrophosphate Extraction (6G5)

Prepare extract as described in 6C5.

Atomic Absorption (6G5a)

Apparatus

- Atomic absorption spectrophotometer

Reagents

- Standard Al solution, 0 to 50 ppm or 0 to 160 ppm

Procedure

Establish standard curve and match readings from extract to curve readings. Dilute where necessary.

Calculations

$$Al\ (pct.) = A \times (B/C) \times (1/10{,}000) \times dilution$$

where:

A = Al (ppm)

B = Volume extract (mL)

C = Sample weight (g)

Report on oven-dry basis.

Ammonium Oxalate Extraction (6G6)

Prepare extract as described in 6C6.

Atomic absorption (6G6a)

Analyze extract as described in 6G5a.

NH_4Cl, Automatic Extractor (6G8)

Prepare extract as described in 5A9.

Atomic Absorption (6G8a)

Apparatus

- Atomic absorption spectrophotometer

Reagents

- Standard Al solutions, 0 to 6 meq/L

Procedure

Compare absorbance of samples from 5A9 with that of standards at 309.3 nm, diluting if necessary.

Calculations

$$Al\ (meq/100\ g) = (A/B) \times dilution \times (C/10)$$

where:

A = Al (meq/L)

B = Sample weight (g)

C = Volume extract (mL)

Report on oven-dry basis.

Extractable Acidity (6H)

$BaCl_2$-Triethanolamine I (6H1)

Extractable acidity data are reported on some data sheets as exchange acidity and on others as extractable H^+.

Reagents

- Buffer solution. Barium chloride, 0.5 *N*, and triethanolamine, 0.2 *N*. Add about 90 ml 1 *N* HCl per liter to adjust pH to 8.2. Protect the buffer solution from CO_2 of the air by attaching a drying tube containing soda lime (sodium calcium hydrate) to the air opening at the top of the solution bottle.
- Replacement solution. Barium chloride, 0.5 *N*. Add 5 ml buffer solution per liter. Protect the replacement solution from CO_2 of the air by attaching a drying tube similar to that used for the buffer solution.

Procedure

Weigh 5 g soil into a 125-ml Erlenmeyer flask. Add 15 ml buffer solution and let stand for 30 minutes, swirling occasionally to mix. Use 35 ml buffer solution to transfer all the soil solution to a No. 4 Gooch crucible containing a moist Whatman No. 540 filter paper and filter into a 500-ml suction flask. The rate of filtration should be such that at least 30 minutes is needed to complete the filtering and leaching. Then leach the soil with 100 ml of the replacement solution, adding small amounts at a time. It may be necessary to use a larger amount of buffer solution to leach allophanic soils high in organic matter with extractable acidity of more than 35 meq per 100 g.

Back-Titration with HCl (6H1a)

Reagents

- Hydrochloric acid (HCl), 0.2 *N*, standardized
- Brom cresol green, 0.1-percent aqueous solution
- Mixed indicator. Dissolve 1.250 g methyl red indicator and 0.825 g methylene blue in 1 liter 90-percent ethanol.

Procedure

Run a blank by adding 100 ml replacement solution, 2 drops brom cresol green, and 10 drops mixed indicator to 50 ml buffer solution. Titrate with HCl to a chosen end point in the range from green to purple. Add 2 drops brom cresol green and 10 drops mixed indicator to the leachate and titrate to the same end point chosen for the blank. Calculate exchange acidity (EA) as follows.

Calculations

$$EA\ (meq/100\ g) = ((A - B)/C) \times N \times 100$$

where:

A = Volume HCl blank (mL)

B = Volume HCl sample (mL)

C = Sample weight (g)

N = Normality of HCl

Report on oven-dry basis.

References

Peech et al. (1947).

$BaCl_2$-Triethanolamine II (6H2)

Apparatus

- Sulfur absorption tubes
- Whatman No. 41 filter paper or glass-fiber filter paper cut to fit sulfur absorption tubes

Reagents

- Buffer solution. $BaCl_2$, 0.5 *N*, and triethanolamine, 0.2 *N* as in 6H1.
- Mixed indicator. Dissolve 1.250 g methyl red and 0.825 g methylene blue in 1 liter 90 percent ethanol.
- Celite

Procedure

Stopper bottom of sulfur absorption tubes with medicine-dropper bulbs and fit to a 300-ml suction flask with a rubber stopper. Place Whatman No. 41 filter paper in bottom of absorption tube, cover with ¼ inch of acid-washed sand, and add exactly 25 ml buffer solution. Weigh 10 g soil and mix with teaspoonful of Celite. Add to the absorption tube by means of a funnel. After 30 minutes remove the medicine-dropper bulbs, wash bulbs out with a little water, and add washings to absorption tubes. Leach with 25 ml more buffer solution and then leach with 100 ml replacement solution in small increments. If necessary, use suction to facilitate leaching.

Back-Titration with HCl (6H2a)

Reagents

- Same as in 6H1a.

Procedure

Titrate with standard HCl, using either 2 drops brom cresol green and 10 drops methyl red or 10 drops mixed indicator. Use same end point as that chosen for a blank run by leaching sand and Celite with 50 ml buffer solution and 100 ml replacement solution.

Calculations

Use same calculation as in 6H1a.

KCl-Triethanolamine (6H3)

Back-titration with NaOH (6H3a)

Procedure

Leach 10 g soil with 50 ml KCl-triethanolamine solution and follow by washing with 50 ml unbuffered 1 *N* KCL. Add a known volume of standard acid to leachate and washings and back-titrate with standard alkali (NaOH). Titrate an equal volume of acid to the same end point for a blank.

Calculations

$$EA\ (meq/100\ g) = ((A - B)/C) \times N \times 100$$

where:

EA = Extractable acidity

A = Volume NaOH sample (mL)

B = Volume NaOH blank (mL)

C = Sample weight (g)

N = Normality of NaOH

References

North-Central Regional Research Committee (1955).

$BaCl_2$-Triethanolamine III (6H4)

Apparatus

- 60-ml plastic syringe barrels
- Buffer solution. Barium chloride, 0.5 *N*, and triethanolamine, 0.2 *N*. Add 1 *N* HCl (about 90 ml/L) to adjust pH to 8.2. Protect the buffer solution from CO_2 of the air by attaching a drying tube containing soda lime (sodium calcium hydrate) to the air opening at the top of the solution bottle.
- Replacement solution. Barium chloride, 0.5 *N*. Add 5 ml of above buffer solution per liter. Protect the replacement solution from CO_2 of the air by attaching a drying tube similar to that used for the buffer solution.
- "Celite" filter pulp

Procedure

Prepare syringe barrels as leaching tubes by forcing a 1-g ball of filter pulp into bottom of barrel with syringe plunger. Measure 1.5 g celite and 5 g soil sample into tube. Attach pinch clamp to delivery tube of syringe barrel and add approximately 25 ml buffer solution to sample. Let stand 30 min, stirring occasionally. Remove pinch clamp and filter with low suction into titrator beaker using a total of 50 ml buffer solution followed by 100 ml replacement solution.

References

Peech et al. (1947).

Back-Titration with HCl, Automatic Titrator (6H4a)

Reagents

- Hydrochloric acid (HCl), 0.33 *N*, standardized

Procedure

Titrate the leachate contained in the 250-ml beaker to an end-point pH setting of 4.60 with automatic titrator. Carry reagent blank through procedure.

Calculations

$$EA\ (meq/100\ g) = ((A - B)/C) \times N \times 100$$

where:

EA = Extractable acidity

A = Volume HCl blank (mL)

B = Volume HCl sample (mL)

C = Sample weight (g)

N = Normality of HCl

Report on oven-dry basis.

Carbonate (6I)

Saturation Extract (6I1)

Acid titration (6I1a)

Reagents

- Sulfuric acid (H_2SO_4), 0.05 *N*, standardized
- Phenolphthalein

Procedure

Pipette an appropriate aliquot of saturation extract into a 250-ml Erlenmeyer flask or a porcelain crucible. The electrical conductivity ($EC \times 10^3$) of the saturation extract (8A1a) can be used to determine the aliquot to be used for carbonate, bicarbonate, and chloride determinations. Where $EC \times 10^3$ is 1.0 or less, use a 10-ml aliquot; if 1.0 to 10.0, use a 5-ml aliquot; if more than 10.0, use a 2-ml aliquot.

Make volume to 50 ml (10 ml for porcelain crucible) with water. To the 50 ml in the Erlenmeyer flask, add a drop or two of phenolphthalein. If a pink color is produced, titrate with 0.05 *N* H_2SO_4, adding a drop every 2 or 3 seconds until the pink color disappears. Use this solution to determine bicarbonate (6J1a).

Calculations

$$\text{Carbonate (meq/L)} = (A/B) \times N \times 2000$$

where:

A = Volume H_2SO_4 (mL)

B = Volume aliquot (mL)

N = Normality of H_2SO_4

References

Association of Official Agricultural Chemists (1945) and Richards (1954).

Bicarbonate (6J)

Saturation Extract (6J1)

Acid Titration (6J1a)

Reagents

- Sulfuric acid (H_2SO_4), 0.05 *N*, standardized
- Methyl orange, 0.01-percent aqueous solution

Procedure

Use solution remaining from carbonate titration (6I1a). To the colorless solution from this titration or to the original solution if no color is produced with phenolphthalein, add 4 drops methyl orange and continue titration to the methyl orange end point without refilling the burette. Retain this solution for the chloride determination (6K1a). Make a blank correction for the methyl orange titration.

Calculations

$$\text{Bicarbonate (meq/L)} = ((A - (2 \times B))/C) \times N \times 1000$$

where:

A = Total volume H_2SO_4 (mL)

B = Volume H_2SO_4 from 6I1a (mL)

C = Volume aliquot (mL)

N = Normality of H_2SO_4

References

Association of Official Agricultural Chemists (1945) and Richards (1954).

Chloride (6K)

Saturation Extract (6K1)

Mohr Titration (6K1a)

Reagents

- Potassium chromate (K_2CrO_4) indicator. Dissolve 5 g K_2CrO_4 in water and add a saturated solution of $AgNO_3$ until a permanent slight red precipitate is produced, filter, and dilute to 100 ml.
- Silver nitrate ($AgNO_3$), 0.05 *N*, standardized
- Sodium bicarbonate ($NaHCO_3$), saturated solution (optional)
- Nitric acid (HNO_3), 0.1 *N* (optional)

Procedure

To the solution from the bicarbonate titration (6J1a) add 6 drops K_2CrO_4 indicator and titrate with $AgNO_3$ to a reddish-orange end point. Make a correction with a blank of 50 ml water containing the indicators of both titrations. The laboratory at Riverside, California, modifies this procedure by adding saturated $NaHCO_3$ solution to a pink end point and neutralizing to a colorless end point with HNO_3 before adding the indicator.

Calculations

$$\text{Chloride (meq/L)} = ((A - B)/C) \times N \times 1000$$

where:

A = Volume $AgNO_3$ sample (mL)

B = Volume $AgNO_3$ blank (mL)

C = Volume aliquot (mL)

N = Normality of $AgNO_3$

References

Association of Official Agricultural Chemists (1945).

Potentiometric Titration (6K1b)

Apparatus

- Silver Billet combination electrode, No. 39187
- Zeromatic pH meter (expanded scale)

Reagents

- Standard silver nitrate ($AgNO_3$), 0.025 *N*
- Buffer solutions. Either potassium acid phthalate or trisodium citrate and citric acid. To prepare phthalate buffer, weigh 37.5 g potassium acid phthalate and bring to a volume of 500 ml with water; 4 ml of this buffer added to a 46-ml solution brings the pH to about 4. To prepare trisodium citrate buffer, weigh 43.8 g trisodium citrate and 43.3 g citric acid into 500-ml volumetric flask and bring to volume with water. Add a small amount of toluene to the solution for storage; 10 ml of this buffer added to a 40-ml solution brings pH to about 4.

Procedure

Standardize the pH meter by adjusting the needle to a convenient setting (about 0.8) on the expanded scale when the electrode is immersed in buffer solution (4

or 10 ml made to 50 ml) without chloride. To titrate the sample, pipette an aliquot containing as much as 2.0 meq chloride into a beaker and add 4 ml buffer. Make to 50 ml. Immerse the electrode and burette tip into the beaker and titrate with $AgNO_3$ to the end point previously established for the buffer without chloride.

Calculations

$$\text{Chloride (meq/L)} = (A/B) \times N \times 1000$$

where:

A = Volume $AgNO_3$ (mL)

B = Volume aliquot (mL)

N = Normality of $AgNO_3$

Sulfate (6L)

Saturation Extract (6L1)

Gravimetric, $BaSO_4$ Precipitation (6L1a)

Reagents

- Concentrated hydrochloric acid (HCl)
- Barium chloride ($BaCl_2$), 10-percent
- Methyl orange, 0.01-percent

Procedure

Pipette an aliquot of saturation extract into a 250-ml beaker. Dilute to approximately 100 ml with water. Add 2 drops methyl orange and 0.5 ml concentrated HCl to the beaker. Heat to boiling and add $BaCl_2$ solution by drops, stirring constantly until precipitation is complete. Let stand on hot plate for several hours. Remove from heat and let samples stand overnight. Filter through Gooch crucibles, which have been ignited and weighed. Dry in 105 °C oven and ignite in muffle furnace at 1200 °F (650 °C) for 30 minutes. Cool in desiccator and weigh.

Calculations

$$SO_4 \text{ (meq/L)} = (A/B) \times 8.568$$

where:

A = $BaSO_4$ (mg)

B = Volume aliquot (mL)

References

Richards (1954).

EDTA Titration (6L1b)

Apparatus

- Repipet, automatic dilutor, pipette range 0.1 to 1.0 ml
- Titration assembly including a 10-ml burette with magnetic stirrer

Reagents

- Thymol blue indicator, 0.04-percent
- Nitric acid (HNO_3), 0.4 *N*
- Calcium nitrate ($Ca(NO_3)_2$), 0.05 *N*. Dissolve 5.90 g $Ca(NO_3)_2 \cdot 4H_2O$ in 1 liter CO_2-free water. EC is 5.15 ±0.15 mmhos per cm at 25 °C.
- Acetone, reagent grade, boiling range 55.5 to 57.5 °C
- Ethanol, 95-percent, reagent grade
- Hydrochloric acid (HCl), 0.01 *N*
- EDTA solution, 0.02 *N*. Standardize against $CaCl_2$.

Procedure

Pipette an aliquot containing 0.01 to 0.05 meq SO_4 from soil-water extracts and transfer to a 100-ml beaker. Bring volume to 7.5 ±0.5 ml with water. Add 2 drops 0.04-percent thymol blue and 0.4 *N* HNO_3 drop by drop until color changes from yellow to distinct red. Add 2 ml 0.05 *N* $Ca(NO_3)_2$, 20 ml acetone, and stir. Allow 30 minutes for the precipitate to flocculate. Place a 9.0-cm Whatman No. 42 filter paper in a 5.0-cm fluted funnel and fit snugly with water. Wash the sides of filter paper with 5 ml 95-percent ethanol from a wash bottle. Transfer the precipitate and supernatant to the filter paper with alcohol. Rinse the beaker twice and wash filter paper three times, using 3 to 5 ml ethanol per rinse. Allow the alcohol in the filter paper to evaporate. Wash the funnel stem thoroughly with water. Place the beaker that contained the $CaSO_4$ precipitate under the funnel and wash the filter paper with 3 to 5 ml portions of 0.01 *N* HCl until approximately 25 ml is leached. Proceed as in 6N1a, except eliminate carbamate and add an extra drop 4 *N* NaOH to neutralize the 25 ml 0.01 *N* HCl.

The amount of sulfate is determined from the Ca^{++} content in the $CaSO_4$ precipitate.

Calculations

$$SO_4 \text{ (meq/L)} = (A/B) \times N \times 1000$$

where:

A = Volume EDTA (mL)

B = Volume aliquot (mL)

N = Normality of EDTA

References

Bower and Wilcox (1965); Lagerwerff, Akin, and Moses (1965); and Nelson (1970).

NH_4OAc Extraction (6L2)

Obtain extract by method 5B1.

Gravimetric, $BaSO_4$ Precipitation (6L2a)

Proceed as in 6L1a. A greater quantity of acid will be needed to lower the pH. Otherwise the procedures are the same.

Nitrate (6M)

Saturation Extract (6M1)

Phenoldisulfonic Acid Colorimetry (6M1a)

Reagents

- Phenoldisulfonic acid. Dissolve 25 g phenol in 150 ml concentrated H_2SO_4, add 75 ml fuming H_2SO_4 (13 to 15 percent SO_3), and heat at 100 °C for 2 hours.
- Standard potassium nitrate (KNO_3), 0.010 *N*
- Silver sulfate (Ag_2SO_4), 0.020 *N*
- Ammonium hydroxide solution (NH_4OH), 1:1, approximately 7 *N*
- Calcium oxide (CaO)

Procedure

First determine the chloride concentration in an aliquot of saturation extract as directed in 6K1a. Pipette another aliquot containing 0.004 to 0.04 meq of nitrate into a 25-ml volumetric flask. Add an amount of Ag_2SO_4 equivalent to the amount of chloride present, dilute to volume, and mix. Separate the precipitate by centrifuging the suspension in a 50-ml centrifuge tube. Transfer the solution to another centrifuge tube, flocculate any suspended organic matter by adding about 0.1 g CaO, and clear by centrifuging again. Pipette a 10-ml aliquot into an 8-cm evaporating dish. Evaporate the aliquot to dryness, cool, and dissolve the residue in 2 ml phenoldisulfonic acid. After 10 minutes, add 10 ml water and transfer to a 100-ml volumetric flask. Make alkaline by adding NH_4OH, dilute to volume, and mix. Measure light transmission through a 460 mμ filter of solution in an optical cell against that of water in a similar cell.

Prepare a calibration curve by pipetting 0-, 0.2-, 0.4-, 0.8-, 1.2-, and 1.6-ml aliquots of standard KNO_3 into evaporating dishes and treating as for sample except for additions of Ag_2SO_4 and CaO and the clarifying procedure.

Calculations

$$NO_3\ (meq/L) = (A/B) \times 1000$$

where:

A = NO_3 from curve (meq/L)

B = Volume aliquot (mL)

References

Richards (1954).

Diphenylamine (Qualitative) (6M1b)

Use this procedure to test for nitrates if there is a significant excess of cations over anions in the extract. A quantitative measurement can be made if there is a positive indication of NO_3 (6M1a).

Reagents

- Diphenylamine in H_2SO_4. Dissolve 0.05 g diphenylamine in 25 ml concentrated sulfuric acid. Store in polyethylene dropper bottle.

Procedure

Place a drop of extract in a spot plate and add 3 or 4 drops diphenylamine reagent. Nitrate is present if a blue color develops.

References

Treadwell and Hall (1943).

Calcium (6N)

Saturation Extract (6N1)

EDTA titration (6N1a)

Reagents

- Sodium hydroxide (NaOH), approximately 4 *N*
- Calcium chloride ($CaCl_2$), 0.02 *N*. Dissolve calcite crystals in HCl and make to volume.
- Murexide. Thoroughly mix 0.5 g ammonium purpurate with 100 g powdered potassium sulfate (K_2SO_4).

- EDTA solution, 0.02 *N*. Standardize against $CaCl_2$.
- Sodium diethyldithiocarbamate, 1-percent

Procedure

Pipette an aliquot containing 0.02 to 0.20 meq of calcium into a beaker. Add 5 drops carbamate, 1 drop NaOH for each 5-ml aliquot, and a suitable amount (15 to 20 mg for a 10-ml aliquot) of murexide, mixing after each addition. A magnetic stirrer is helpful. Titrate with EDTA to a lavender end point. A blank containing NaOH, murexide, carbamate, and a drop or two of EDTA helps to distinguish the end point. If the sample is overtitrated with EDTA, it can be back-titrated with standard $CaCl_2$. Retain solution for magnesium determination (6O1a).

Calculations

$$Ca\ (meq/L) = (A/B) \times N \times 1000$$

where:

A = Volume EDTA (mL)

B = Volume aliquot (mL)

N = Normality of EDTA

References

Cheng and Bray (1951).

NH_4OAc Extraction (6N2)

Prepare NH_4OAc extract as described in 5A1. EDTA-alcohol extraction.

EDTA-Alcohol Separation (6N2a)

Reagents

- Standard calcium chloride ($CaCl_2$), 5 mg per ml. Dissolve calcite crystals in HCl and make to volume.
- Ethanol, 95-percent
- Standard EDTA. Dissolve 1.25 g disodium ethylenediaminetetraacetate in water and dilute to a volume of 1 liter. Standardize against solutions containing known amounts of calcium and magnesium. Run the standards through the separation procedure before titrating.
- Sodium hydroxide (NaOH), 10-percent aqueous solution
- Calcon. Dissolve 1 g Calcon (Eriochrome Blue Black R) in 100 ml triethanolamine.

Procedure

Pipette 25-ml aliquots from the pH 7, NH_4OAc extracts obtained in the total exchange-capacity method (5A1) into 100-ml beakers and evaporate to dryness at moderate heat. Cool and add 3 ml *N* HNO_3 to dissolve the residue. Transfer the solution quantitatively to 50-ml conical centrifuge tubes with ethanol, using a wash bottle with a fine delivery tip. Add 1 ml 6 *N* H_2SO_4. While mixing the contents of the tube by swirling, add approximately 34 ml 95-percent ethanol. Cover the tubes and let stand overnight. The next morning remove the covers and centrifuge the tubes at about 2000 rpm (Int. No. II centrifuge) for 15 minutes. Decant the alcohol solution into 250-ml Erlenmeyer flasks and retain for the magnesium determination. Use the $CaSO_4$ precipitate for calcium determination.

Break up the $CaSO_4$ precipitate with a small steam of water from a wash bottle and transfer the precipitate and solution to 250-ml Erlenmeyer flasks. Dilute the solution to a total volume of about 100 ml. Place the sample on a magnetic stirrer, add 5 ml 10-percent NaOH, 2 drops Calcon indicator solution, and titrate with the standard EDTA solution to the blue color of a blank carried through the procedure. The pH of the solution should be about 12.5. The color change is from red to clear blue. Titrate until the color in the sample and in the blank are the same.

Calculations

$$\text{Ca (meq/100 g)} = (A/B) \times N \times (C/D) \times 100$$

where:

A = Volume EDTA (mL)

B = Sample weight (g)

N = Normality of EDTA

C = Volume extract (mL)

D = Volume aliquot (mL)

References

Barrows and Simpson (1962).

Oxalate Precipitation I, $KMnO_4$ Titration (6N2b)

Reagents

- Oxalic acid ($C_2H_2O_4$), 5-percent aqueous solution
- Brom cresol green, 0.04-percent aqueous solution
- Ammonium hydroxide (NH_4OH), 1 *N*
- Sulfuric acid (H_2SO_4), 1 *N*
- Standard potassium permanganate ($KMnO_4$), 0.05 *N*

- Wash solution, saturated calcium oxalate ($CaC_2 2O_4$)
- Asbestos. Digest asbestos in 1 *N* HNO_3 solution containing just enough $KMnO_4$ to give a deep purple color. Add more permanganate if the color disappears; digest for 24 hours or until the permanganate color is permanent. Destroy the excess permanganate with oxalic acid and wash thoroughly on a Buchner funnel.

Procedure

Transfer an aliquot of the filtrate (5A1) to a 400-ml Pyrex beaker and evaporate to complete dryness. Cool, cover the beaker with a watchglass, and slowly add through the lip 10 ml concentrated HNO_3 and 2 ml concentrated HCl. Warm until the reaction has subsided and no more brown fumes are given off. Rinse the watchglass into the beaker. Evaporate to dryness at low heat to prevent spattering and continue to heat for about 10 minutes to dehydrate the salts. Then place the beaker in an electric muffle furnace at about 150 °C, heat to 390° ±10°, and hold at this temperature for about 20 minutes. Remove the beaker from the muffle furnace and cool. Treat the residue with 3 ml 6 *N* HCl, evaporate to dryness at low heat, and continue heating for about 30 minutes longer to dehydrate silica. Cool and dissolve the residue in 0.1 *N* HNO_3, using a rubber policeman to loosen the residue.

Add 5 ml oxalic acid, heat the contents of the beaker almost to boiling, and add 1 ml brom cresol green. Adjust the pH of the hot solution to approximately 4.6 by slowly adding 1 *N* NH_4OH, stirring constantly. Let digest at about 80 °C for 1 hour or until the supernatant liquid is clear. Collect the CaC_2O_4 precipitate on a compact asbestos pad in a Gooch crucible or in a Whatman No. 42 filter paper in filter funnel. Rinse the beaker four times with water or water saturated with CaC_2O_4 and pour the washings into the crucible. Wash the precipitate five more times with water saturated with CaC_2O_4.

Remove the Gooch crucible from its holder, rinse the outside, and replace crucible in the beaker. If filter paper is used, pierce the paper and wash most of the precipitate into the beaker with 3.6 *N* H_2SO_4. Wash off excess H_2SO_4 with water and place filter paper on watchglass. Add 100 ml water and 7 ml concentrated H_2SO_4. Heat to 90 °C and stir until CaC_2O_4 is dissolved. Titrate with standard $KMnO_4$ solution to a pink color. Add filter paper to solution and titrate to a permanent pink color.

Calculations

$$\text{Ca (meq/100 g)} = (A/B) \times N \times (C/D) \times 100$$

where:

A = $KMnO_4$ (mL)

B = Sample weight (g)

N = Normality of $KMnO_4$

C = Volume extract (mL)

D = Volume aliquot (mL)

Report on oven-dry basis.

References

Peech et al. (1947).

Oxalate Precipitation II, $KMnO_4$ Titration (Fe, Al, and Mn removed) (6N2c)

Proceed as in 6N2b but after muffle treatment and before oxalate precipitation, remove iron, aluminum, and manganese by the following procedure.

Reagents

- Hydrochloric acid (HCl), 6 *N*
- Ammonium hydroxide (NH_4OH), 2 *N*
- Bromine water, saturated
- Ammonium chloride (NH_4Cl), 6 *N*
- Concentrated nitric acid (HNO_3)

Procedure

Dissolve salts and oxides by adding 5 ml 6 *N* HCl and heating on a hot plate until all salts and oxides are in solution. Add 75 to 100 ml water and heat the solution until it is nearly boiling. Immerse the pH electrodes into the hot solution and precipitate the hydroxides of iron, aluminum, and titanium by slowly adding 2 *N* NH_4OH until the meter indicates a pH of 6.2 to 6.4. Add 2 more drops of NH_4OH to neutralize the acidifying effect of the 15 ml saturated bromine water, which is slowly added next to precipitate manganese hydroxide. Since bromine water lowers the pH of the solution, readjust it to 6.2 to 6.4 with 2 *N* NH_4OH. Heat the solution with precipitate until it just begins to boil (1 or 2 min on a Bunsen burner) and remove from the heat.

Place on a hot plate at a temperature of 80 to 90 °C for 1 hour. Filter when the breaker has cooled enough to handle easily. Use an 11-cm Whatman No. 42 filter paper or its equivalent. Collect the filtrate in a beaker of the same size as those used for precipitating calcium. Wash and police the beaker containing the precipitate with hot 2-percent NH_4Cl. Wash the precipitate on the filter with the same solution. Five washings are usually enough. To the filtrate add 10 ml concentrated HNO_3 and evaporate to dryness; add 5.0 ml 6 *N* HCl, take to dryness, and use high heat to dehydrate silica. Proceed with the calcium precipitation (6N2b).

References

Washington (1930) and Fieldes et al. (1951).

Oxalate Precipitation, Cerate Titration (6N2d)

Proceed as in 6N2b except substitute the following for the permanganate titration.

Reagents

- Ammonium hexanitrate cerate ($(NH_4)_2Ce(NO_3)$) in molar perchloric acid ($HClO_4$), 0.1 *N*. Add 85 ml 70- to 72-percent perchloric acid to 500 ml water. Dissolve 56 g ammonium hexanitrate cerate in the acid solution and dilute to 1 liter.
- Ammonium hexanitrate cerate in molar perchloric acid, 0.05 *N*. Follow the directions for the preparation of the 0.1 *N* solution but use only 28 g cerate.
- Perchloric acid ($HClO_4$), 2 *N*. Add 170 ml 70 to 72-percent perchloric acid to 500 ml water and dilute to 1 liter.
- Nitro-ferroin indicator solution. Dilute a solution of nitro-orthophenanthroline ferrous sulfate with water to a convenient working strength. Two to four drops of the solution should give a sharp color change at the end point.
- Standardize the cerate solutions against accurately weighed quantities of primary standard grade sodium oxalate. Convenient weights of sodium oxalate are 0.10 to 0.11 g for the 0.05 *N* solution and 0.10 to 0.18 g for the 0.1 *N* cerate solution. Dissolve the sodium oxalate in 100 to 150 ml 2 *N* perchloric acid and titrate as directed in the following procedure.

Procedure

Dissolve the filtered and washed (use water) calcium oxalate in 100 to 200 ml 2 *N* perchloric acid. If a paper filter has been used, macerate it before titration. Add 2 to 4 drops of nitro-ferroin indicator solution and titrate with 0.05 *N* or 0.1 *N* cerate solution, depending upon the amount of oxalate present. The solution changes from red to colorless at the end point.

Calculations

$$\text{Ca (meq/100 g)} = (A/B) \times N \times (C/D) \times 100$$

where:

A = Volume cerate (mL)

B = Sample weight (g)

N = Normality of cerate

C = Volume extract (mL)

D = Volume aliquot (mL)

Report on oven-dry basis.

NH_4Cl-Ethanol Extraction (Calcareous Soils) (6N3)

Apparatus

- See figure 6N3-1.

Reagents

- Ammonium chloride (NH_4Cl), 1 *N*, in 60-percent ethanol. To make 9 liters of extraction solution, dissolve 482 g NH_4Cl in 2,835 ml water and add 5,985 ml 95-percent ethanol. Adjust pH to 8.5 with 140 to 145 ml NH_4OH.
- Celite

Procedure

Fill extraction tube with water, set tube upright in holder, and let most of the water drain out. Close screw clamp and place filter paper on plate with a stirring rod. Let remainder of the water drain out of tube. The filter paper provides enough tension to keep the bottom part of the tube filled with water. Place tube on the rack and add about 1½ teaspoons washed sand. Place an extra perforated plate (inverted) on top of the sand and cover the plate with more sand. Place heaping teaspoon of Celite on the sand and pour about 20 ml extraction solution into the tube. Pour remainder of 400 ml extraction solution into a 500-ml Erlenmeyer flask. Add soil sample slowly and then stir with a rod to mix soil and Celite. Allow sample to settle and then place filter paper on top of the soil column. Put upper tube in place, stopper, and let stand overnight.

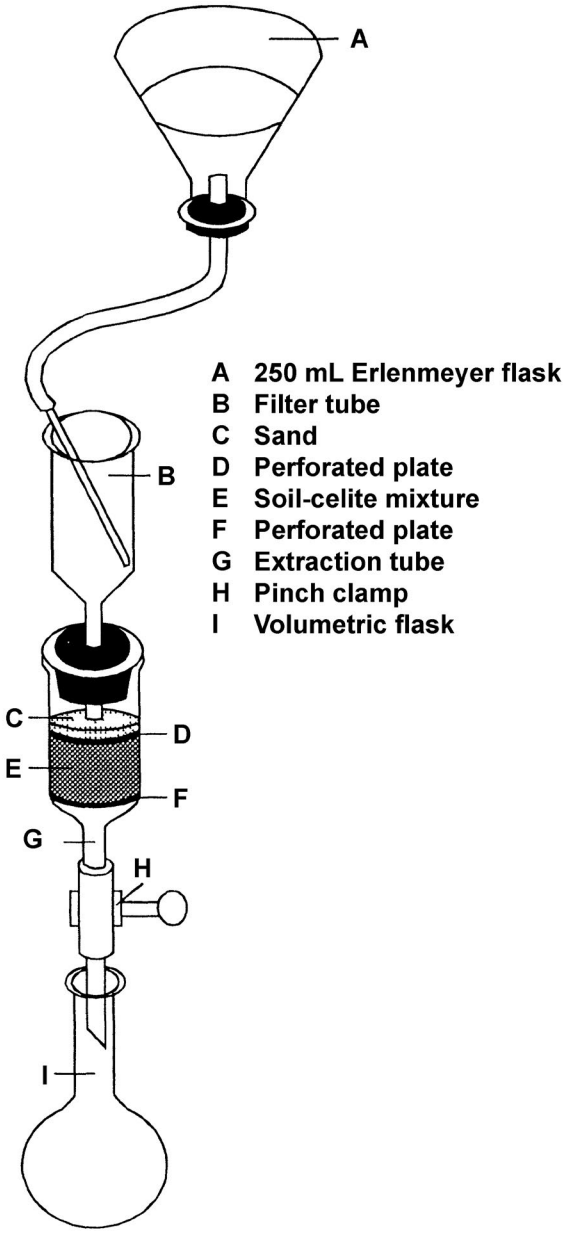


Figure 6N3-1.—Apparatus for ammonium chloride-ethanol extraction for calcium (6N3).

In the morning, place a 500-ml volumetric flask under the delivery tip and open screw clamp on lower extraction tube slowly. When level of liquid is a few milliliters above the soil, invert the 500-ml Erlenmeyer flask containing remainder of extraction solution (delivery tube in place), place glass tip in the upper tube, and open the pinch clamp. Use the screw clamp on lower tube to adjust flow rate through soil column. When all the extraction solution has passed through the soil column, remove volumetric flask, make to volume with water, and mix.

EDTA Titration (6N3a)

Pipette a 50-ml aliquot for determination of Ca and Mg into a 100-ml beaker and evaporate to dryness. Add 10-ml concentrated HNO_3 and 1 or 2 ml concentrated HCl. Cover with watchglass, place on hot plate, and heat until no more brown fumes are evolved. Remove cover glass, rinse into beaker, and evaporate solution to dryness. Take up residue with 3 ml *N* HNO_3. Quantitatively transfer solution with ethanol to a 50-ml conical centrifuge tube and proceed with determination of Ca according to 6N2a.

References

Tucker (1954).

KCl-Triethanolamine Extraction (6N4)

Prepare extract as in method 5B2.

Oxalate-Permanganate Titration (6N4a)

Proceed as in 6N2b.

EDTA Titration (6N4b)

Reagents

- Sodium hydroxide (NaOH), 4 *N*
- EDTA 0.02 *N*. Dissolve 3.723 g disodium dihydrogen ethylenediamine tetraacetate in water and dilute to 1 liter. Standardize the solution against standard $CaCl_2$ prepared in the TEA buffer solution.
- Ammonium purpurate (murexide) indicator. Thoroughly mix 0.5 g ammonium purpurate with 100 g powdered potassium sulfate.
- Eriochrome Black T (Erio T) indicator. Dissolve 0.5 g Erio T in 100 ml of triethanolamine.

Procedure

Pipette a 5-ml aliquot of extract from method 5B3 into a 100-ml beaker. Add 20 ml water, 5 drops 4 *N* NaOH, and 50 mg murexide. Titrate with standard EDTA using a 10-ml microburet. Approach the end point slowly (orange-red to lavender or purple). Save the solution for the Mg^{++} determination.

Calculations

$$Ca\ (meq/100\ g) = (A/B) \times N \times (C/D) \times 100$$

where:

A = Volume EDTA (mL)

B = Sample weight (g)

N = Normality of EDTA

C = Volume extract (mL)

D = Volume aliquot (mL)

References

Bower and Wilcox (1965).

Atomic Absorption (6N4c)

Proceed as in 6N1b except use sample from KCl-TEA extraction.

HF Dissolution (6N5)

Obtain extract as in 7C3.

Atomic Absorption (6N5a)

Apparatus

- Diluter
- Atomic absorption spectrophotometer

Reagents

- Standard Ca solutions, 0 to 30 meq/L

Procedure

Dilute HF extracts from 7C3 and Ca standards fivefold to twentyfold with water. Compare absorbance of samples with that of standards at 442.7 nm.

Calculations

Ca (pct.) = (A x 10 x dilution x 20.04 mg/meq) / B

where:

A = Ca (meq/L)

B = Sample weight (mg)

CaO (pct.) = Ca (pct.) x 1.40

Report on oven-dry basis.

Magnesium (6O)

Saturation Extract (6O1)

EDTA Titration (6O1a)

Reagents

- Buffer solution. Mix 33.75 g NH_4Cl with 285 ml concentrated (15 *N*) NH_4OH, add 5 g disodium Mg-versenate, and dilute to 500 ml.
- Eriochrome Black T indicator. Dissolve 0.5 g Eriochrome Black T (F241) and 4.5 g hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in 100 ml 95-percent ethanol or dissolve 1.0 g Eriochrome Black T in 100 ml triethanolamine.
- EDTA 0.02 *N*. Standardize with magnesium solution.

Procedure

To the sample just titrated for calcium (6N1a), add 3 or 4 drops concentrated HCl, stir until the murexide is destroyed, add 1 ml $NH_4Cl \cdot NH_4OH$ buffer solution, 1 or 2 drops Eriochrome Black T indicator, and complete the titration for magnesium, using EDTA. The end point should be a clear blue with no tinge of red.

Calculations

Mg (meq/100 g) = (A/B) x *N* x (C/D) x 100

where:

A = Volume EDTA (mL)

B = Sample weight (g)

N = Normality of EDTA

C = Volume extract (mL)

D = Volume aliquot (mL)

Report on oven-dry basis.

References

Cheng and Bray (1951).

NH_4OAc Extraction (6O2)

Prepare NH_4OAc extraction as described.

EDTA Titration, Alcohol Separation (6O2a)

Reagents

- Buffer solution. Dissolve 67.5 g NH_4Cl in about 400 ml water. Add 570 ml concentrated NH_4OH and dilute to 1 liter with water.
- Hydroxylamine hydrochloride ($NH_2OH•HCl$), 5-percent aqueous solution. Prepare fresh solution every 10 days.
- Potassium ferrocyanide ($K_4Fe(CN)_6•3H_2O$), 4-percent aqueous solution
- Triethanolamine, U.S.P.
- Eriochrome Black T. Dissolve 1 g Eriochrome Black T (Superchrome Black TS) in 100 ml triethanolamine.
- Standard magnesium solution, 5.0 mg per milliliter. Transfer 2.500 g unoxidized reagent-grade magnesium metal to a 500-ml volumetric flask. Add 150 ml water and 20 ml concentrated HCl. When in solution, make to volume with water and mix. Dilute an aliquot of this solution to get a solution containing 0.5 mg magnesium per milliliter.
- EDTA, 0.02 *N*. Standardize with magnesium standard solution.

Procedure

Place the Erlenmeyer flasks containing the alcohol solution retained from the $CaSO_4$ separation (6N2a) on a hot plate and evaporate the alcohol at moderate heat. Do not evaporate to complete dryness. Cool and dilute to 100 ml with water and add 5 ml buffer solution and 10 drops each of hydroxylamine hydrochloride, potassium ferrocyanide, and triethanolamine. Stir and let stand 5 to 10 minutes. Place the sample on the stirrer, add 2 drops Eriochrome Black T, and titrate with standard EDTA to the ice-blue end point. The color change is from red through wine to ice blue. A blank carried through this procedure usually requires 0.3 to 0.8 ml EDTA to get the proper ice-blue color. Correct for a blank carried through this procedure and use the corrected titration to calculate the magnesium in the sample.

Calculations

$$\text{Mg (meq/100 g)} = (A/B) \times N \times (C/D) \times 100$$

where:

A = Volume EDTA (mL)

B = Sample weight (g)

N = Normality of EDTA

C = Volume extract (mL)

D = Volume aliquot (mL)

Report on oven-dry basis.

References

Barrows and Simpson (1962).

Phosphate Titration (6O2b)

Reagents

- Sodium hydroxide (NaOH), 0.1 *N*, standardized. Protect from CO_2 of the air with a soda lime trap.
- Sulfuric acid (H_2SO_4), 0.1 *N*
- Ammonium hydroxide (NH_4OH), concentrated
- Diammonium hydrogen phosphate ($(NH_4)_2 HPO_4$), 10-percent solution
- Brom cresol green, 0.1-percent aqueous solution
- Hydrochloric acid (HCl), 1:1
- Carbon-dioxide-free water. Boil water in a 5-liter round-bottom boiling flask for about 15 minutes. Cool and protect from CO_2 of the air with a soda lime trap.

Procedure

Transfer the filtrate from the calcium determination (6N2b, 6N2c, or 6N2d) to a 400-ml beaker, add 10 ml concentrated HN_3, cover with a 3.5-inch Speedyvap watchglass and evaporate to dryness. Dissolve the residue in 5 ml 1:1 HCl and transfer to a 250-ml Erlenmeyer flask, policing twice and rinsing the beaker twice after final policing. The volume of solution should be about 75 ml or more. Using 3 to 4 drops brom cresol green indicator, neutralize the solution with concentrated NH_4OH added by drops. Add 5 ml 10-percent $(NH_4)_2HPO_4$ and 10 ml concentrated NH_4OH. Heat the solution just to boiling, cool, stopper, and let stand overnight.

Filter through a 9-cm Whatman No. 40 filter paper, pouring the solution down a stirring rod. Rinse the flask five times with 1 *N* NH_4OH and pour the rinsings onto the filter. Wash the precipitate on the filter five more times with 1 *N* NH_4OH. Place the wet filter paper with precipitate on a watchglass and let dry at no more

than 40 °C until free of ammonia. Place the dry filter in the original flask, add 5 drops brom cresol green and 10 ml 0.1 *N* H_2SO_4 or more if necessary to dissolve the precipitate. The solution should be yellow. After most of the precipitate has dissolved, add 50 ml CO_2-free water, stopper the flask, and shake vigorously until the filter paper is macerated. Remove the stopper and rinse it and the flask walls with CO_2-free water. Back-titrate with standard 0.1 *N* NaOH to pH 4.5. To determine the correct end point, prepare a color standard by pipetting 5 ml potassium dihydrogen phosphate (2-percent solution) into a 250-ml Erlenmeyer flask, adding 65 ml water, 5 drops brom cresol green, and a macerated filter paper.

Calculations

$$\text{Mg (meq/100 g)} = ((A - B)/C) \times N \times (D/E) \times 100$$

where:

A = Volume NaOH blank (mL)

B = Volume NaOH sample (mL)

C = Sample weight (g)

N = Normality of NaOH

D = Volume extract (mL)

E = Volume aliquot (mL)

Report on oven-dry basis.

References

Peech et al. (1947).

Gravimetric, Magnesium Pyrophosphate (6O2c)

Reagents

- Diammonium hydrogen phosphate ($(NH_4)_2HPO_4$), 10-percent solution
- Nitric acid (HNO_3), concentrated
- Ammonium hydroxide (NH_4OH), concentrated
- Ammonium hydroxide (NH_4OH), 1:1
- Hydrochloric acid (HCl), 6 *N*

Procedure

Continue analysis on filtrate from oxalate precipitation (6N2b). This filtrate will probably fill a 150-ml beaker. Place cover glass on filtrate and heat at a low temperature. When volume has been reduced, add 20 ml concentrated HNO_3. Evaporate to complete dryness and wash cover glass and sides of beaker with

water. Dissolve residue in 5 ml 6 *N* HCl and then dilute to about 75 ml. Add 2 or 3 drops brom cresol green and bring pH to 4.6 with 1:1 NH_4OH. Add 5 ml 10-percent diammonium hydrogen phosphate (make up fresh each time). Add 10 ml concentrated NH_4OH, stir solution vigorously until a precipitate forms, and let stand overnight.

On the next day filter on a 11.0-cm Whatman No. 42 filter paper, rinse beaker five times with 1 *N* NH_4OH, and pour washings into the filter. Wash the precipitate in the filter five more times with 1 *N* NH_4OH. Place filter in oven to dry (2 to 3 hours) and evolve NH_4OH to prevent any explosion in the muffle furnace. Place crucibles (Coors 000) with filters containing magnesium precipitate in muffle furnace. Raise temperature gradually to 1000 °C and hold at 1000 °C for 1 hour. Allow muffle furnace to cool down and remove crucibles. Place in desiccator and dry over phosphorus pentoxide (P_2O_5). Weigh $Mg_2P_2O_7$ and record.

Calculations

$$Mg\ (meq/100\ g) = (A/B) \times (C/D) \times 1.797$$

where:

A = $Mg_2P_2O_7$ (mg)

B = Sample weight (g)

C = Volume extract (mL)

D = Volume aliquot (mL)

NH_4Cl-Ethanol Extraction (Calcareous Soils) (6O3)

Proceed as in 6N3.

EDTA Titration (6O3a)

Proceed as in 6N3a except determine magnesium in alcohol extract by method 6O2a.

KCl-Triethanolamine Extraction (6O4)

Prepare extract as described in 5B2 or 5B3.

Phosphate Titration (6O4a)

Proceed as in 6O2b except use extract from 5B2 or 5B3.

EDTA Titration (6O4b)

Reagents

- Concentrated hydrochloric acid (HCl)
- Concentrated ammonium hydroxide (NH_4OH)
- EDTA 0.02 *N*. Dissolve 3.723 g disodium dihydrogen ethylenediaminetetraacetate in water and dilute to a volume of 1000 ml. Standardize the solution against standard $MgCl_2$.
- Eriochrome Black T (Erio T) indicator. Dissolve 0.5 g Erio T in 100 ml triethanolamine.

Procedure

Add 4 or 5 drops concentrated HCl to the solution used for the calcium determination (6N4b). Set aside until the murexide turns colorless. Add 15 to 20 drops concentrated NH_4OH. This should bring the pH between 10.0 and 10.3. Add 1 drop Erio T and titrate with EDTA to a clear blue end point.

Calculations

$$\text{Mg (meq/100 g)} = (A/B) \times N \times (C/D) \times 100$$

where:

A = Volume EDTA (mL)

B = Sample weight (g)

N = Normality of EDTA

C = Volume extract (mL)

D = Volume aliquot (mL)

Report on oven-dry basis.

Atomic Absorption (6O4c)

Proceed as in 6O1b except use samples from the KCl-TEA extract.

HF Dissolution (6O5)

Obtain extract as in 7C3.

Atomic Absorption (6O5a)

Apparatus

- Diluter

- Atomic absorption spectrophotometer

Reagents

- Standard Mg solutions, 0 to 10 meq/L

Procedure

Dilute HF extracts from 7C3 and Mg standards fivefold to twentyfold with water. Compare absorbance of samples with that of standards at 285.2 nm.

Calculations

Mg (pct.) = (A x 10 x dilution x 12.16 mg/meq) / B

where:

A = Mg (meq/L)

B = Sample weight (mg)

MgO (pct.) = Mg (pct.) x 1.66

Report on oven-dry basis.

Sodium (6P)

Saturation Extract (6P1)

Flame Photometry (6P1a)

Apparatus

Beckman Model DU spectrophotometer with flame attachment.

Reagents

- Standard sodium solutions, 0.0 to 2.0 meq per liter
- Concentrated hydrochloric acid (HCl)
- Hydrochloric acid (HCl), 6 *N*
- Hydrochloric acid (HCl), 0.4 *N*
- Concentrated nitric acid (HNO_3)

Procedure

Pipette an aliquot of appropriate size (5 to 25 ml) of the saturation extract into a 100-ml beaker and evaporate to dryness on a hot plate. Treat the residue with 1 ml concentrated HCl and 3 ml concentrated HNO_3 and again evaporate to dryness on the hot plate. Repeat the acid treatment on the residue. Add 5 ml 6 *N* HCl to the residue and bring to dryness. Then raise the temperature to

high for 20 minutes to render the silica insoluble. Wash and filter the residue into 50-ml volumetric flasks, using 0.4 *N* HCl. Determine flame luminosity of samples appropriately diluted and compare with luminosity of standard solutions made up with 0.4 *N* HCl. The evaporation and dehydration steps are used only where there is enough silica to clog the burner. If they are not used, merely dilute the sample.

Calculations

Na (meq/L) = A x dilution

where:

A = Na from curve (meq/L)

NH_4OAc Extraction (6P2)

Flame Photometry (6P2a)

Proceed as in 6P1a except make standard solutions in NH_4OAc. The evaporation and dehydration steps can be eliminated.

Calculations

Na (meq/100 g) = (A/B) x dilution x (C/10)

where:

A = Na from curve (meq/L)

B = Sample weight (g)

C = Volume extract (mL)

Report on oven-dry basis.

References

Fieldes et al. (1951).

HF Dissolution (6P3)

Obtain extract as in 7C3.

Atomic Absorption (6P3a)

Apparatus

- Diluter
- Atomic absorption spectrophotometer

Reagents

- Standard Na solutions, 0 to 20 meq/L in HF and boric acid

Procedure

Dilute HF extracts from 7C3 and Na standards fivefold to twentyfold with water. Compare absorbance of samples with that of standards at 589 nm.

Calculations

Na (pct.) = (A x dilution x 23.00 mg/meq) / B

where:

A = Na (meq/L)

B = Sample weight (mg)

Na_2O (pct.) = Na (pct.) x 1.35

Report on oven-dry basis.

Potassium (6Q)

Saturation Extract (6Q1)

Flame photometry (6Q1a)

Apparatus

- Beckman Model DU spectrophotometer with flame attachment

Reagents

- Standard potassium chloride (KCl) solutions ranging from 0.0 to 1.0 meq per liter

Procedure

Proceed as in 6P1a. Determine flame luminosity of potassium at 768 mμ and compare with that of the standard solutions.

Calculations

K (meq/L) = A x dilution

where:

A = K from curve (meq/L)

References

Fieldes et al. (1951).

NH_4OAc Extraction (6Q2)

Flame Photometry (6Q2a)

Proceed as in 6Q1a except make up standards in NH_4OAc solution.

Calculations

$$K\ (meq/100\ g) = (A/B) \times dilution \times (C/10)$$

where:

A = K from curve (meq/L)

B = Sample weight (g)

C = Volume extract (mL)

Report on oven-dry basis.

Sulfur (6R)

$NaHCO_3$ Extract, pH 8.5 (6R1)

Methylene Blue Colorimetry (6R1a)

References

Kilmer and Nearpass (1960).

HCl Release (Sulfide) (6R2)

Apparatus

- Nitrogen tank (water pumped)
- Scrubber. 250-ml Erlenmeyer flask equipped with three-hole rubber stopper to accommodate entry and exit for sweep gas, and a 4-foot glass tube to serve as a manometer.
- Reaction flask. 250-ml Erlenmeyer equipped with three-hole rubber stopper to accommodate entry and exit for sweep gas, and a burette for adding acid. Reaction flask sits on a magnetic stirrer.
- Collection bottles. Two 500-ml bottles (No. 8 rubber stopper), each fitted with a two-hole rubber stopper to accommodate entry and exit tubes for sweep gas. The entry tubes should be detachable below the rubber stopper. Attach a pinch clamp to the exit tube to help control the flow rate of gases.

Procedure

Place 10 ml zinc acetate solution in collection flask. Add water to 150 ml volume and place flask in train. Add moist sample (collected as in 1A2b) in tared reaction flask (250-ml Erlenmeyer), introduce N_2 gas (unless sample is run immediately), stopper, and weigh. Determine moisture content on a separate sample. Place flask in collection train. Sweep with N_2 gas for about 5 minutes. Reduce flow until pressure drops enough so that 50 to 60 ml of 6 *N* HCl can be added to reaction flask. Adjust flow of N_2 to about 4 bubbles per second in collection flask and turn on stirrer. Collect sample for 45 to 60 minutes. Second collection bottle should be a blank. Cut flow, disconnect entry tube but leave in collection bottle, remove collection bottles, and stopper until ready to titrate.

Iodine Titration (6R2a)

Apparatus

- Iodine applicator, approximately a 50-ml reservoir with stopcock delivery in a two-hole rubber stopper (No. 8). Fit a glass tube for air exit through the stopper.
- Burette for thiosulfate
- Magnetic stirrer

Reagents

- Iodine 0.1 *N*, standardized
- Sodium thiosulfate 0.1 *N*, standardized
- Starch indicator
- Hydrochloric acid (HCl), 6 *N*

Procedure

Mix an aliquot of standardized iodine solution and 5 ml of 6 *N* HCl in iodine applicator. Place applicator on bottle and add acidified iodine. Wash contents of applicator, quantitatively, into bottle. Remove applicator, stopper bottle, and swirl so that iodine enters the top of the entry tube from collection train. Any white precipitate of ZnS should dissolve off entry tube. Remove stopper and titrate with standardized thiosulfate until iodine color becomes faint. Add 1 or 2 ml starch indicator and titrate until blue color changes to clear. The end point is abrupt.

Stopper bottle and again swirl so that solution passes through the entry tube. Blue color should reappear. Again titrate to the end point. Magnetic stirrer can be used to mix the sample.

Calculations

$$S\ (meq/100\ g) = ((A - B)/C) \times N \times 100$$

where:

A = Volume thio for blank (mL)

B = Volume thio for sample (mL)

C = Sample weight (g)

N = Normality of thio

References

Pierce and Haenisch (1955); Johnson and Ulrich (1959); and Chapman and Pratt (1961).

SO_2 Evolution (6R3)

KIO_3 Titration (6R3a)

Apparatus

- LECO induction furnace model 521
- LECO automatic sulfur titrator model 532
- LECO crucibles and lids
- Oxygen tank and regulator
- LECO starch dispenser and 0.2-ml scoop

Reagents

- Potassium iodate (KIO_3)
- Potassium iodide (KI)
- Arrowroot starch
- Hydrochloric acid (HCl) 7.7 *N*
- Hydrochloric acid (HCl) 0.18 *N*
- Magnesium oxide, (MgO)
- Iron-chip accelerator
- Copper metal accelerator

Procedure

Into a tared crucible, weigh approximately ½ g of 60-mesh soil, recording gross weight. Where high sulfur content might be present, either ¼ or $^1/_{10}$ g sample should be run. Add 2 scoops of MgO and a scoop of iron chips. Mix thoroughly.

Add a half scoop of copper accelerator and a scoop of iron chips. Magnesium oxide scoops are heaping; all others are level. A cover is placed on the crucible, which is placed on the pedestal and raised into the combustion tube for ignition. The LECO instruction manual is followed in setting up the furnace and titrator. The timer is set to 8 min and grid tap switch to midposition. These settings should be adjusted as needed to get complete fusion of the mixture in the crucible; however, plate current should not exceed 350 mA. When the burette reading does not change for 2 min and plate current has achieved 300 to 350 mA, the titration is complete and the titer is recorded. A blank is run using all ingredients except soil. Sulfate removal before analysis may be desirable in some instances. Sample is leached with 50 ml of 7.7 *N* HCl followed by 500 ml of distilled water.

Calculations

The KIO_3 burette is direct reading in percent for a 1-g sample containing up to 0.2 percent sulfur, provided the KIO_3 concentration is 0.444 g/L. With 1.110 g KIO_3/L, multiply burette readings by 5 (½-g sample, 0.005 to 1.00-percent sulfur range).

References

Smith (1974).

Phosphorus (6S)

Perchloric Acid Digestion (6S1)

Perchloric acid is extremely hazardous and subject to explosion if improperly handled. Do not attempt this procedure unless the hazards are well understood and the laboratory is specially equipped to handle perchloric acid digestion.

Reagents

- Perchloric acid ($HClO_4$), 60-percent
- Concentrated nitric acid (HNO_3)
- Concentrated hydrochloric acid (HCl)

Procedure

Weigh 2.000 g oven-dry soil, ground to approximately 100 mesh, into a 300-ml Erlenmeyer flask, add 30 ml 60-percent $HClO_4$, and boil until the soil is white. Continue boiling 20 minutes longer to ensure complete extraction. Soils high in organic matter should be pretreated with HNO_3 and HCl to destroy the readily oxidized organic matter.

Molybdovanadophosphoric Acid Colorimetry (6S1a)

Apparatus

- Spectrophotometer

Reagents

- Solution I. Dissolve 20 g ammonium molybdate ($(NH_4)_6Mo_7O_{24}•4H_2O$) in 250 ml water.
- Solution II. Dissolve 1.25 g ammonium metavanadate (NH_4VO_3) in 300 ml boiling water, cool, and add 425 ml 60-percent $HClO_4$. Mix solutions I and II and dilute to 1 liter in a volumetric flask. Store in a brown bottle.
- Standard phosphorus solution. Weigh out 0.2194 g oven-dry KH_2PO_4 and dilute to 1 liter. This solution contains 50 ppm phosphorus.
- Concentrated nitric acid (HNO_3) for samples high in organic matter only. Concentrated hydrochloric acid (HCl) for samples high in organic matter only

Procedure

Transfer the extract into 250-ml volumetric flasks, bring to volume, and let residue settle out. Pipette a 25-ml aliquot into a 50-ml volumetric flask, add 10 ml molybdovanadate reagent, bring to volume, and mix.

After 10 minutes, the color is fully developed on most samples and can be read at 460 mμ. Prepare a standard curve covering the range 0 to 5 ppm phosphorus in 50 ml solution. Plot on semilog paper.

Calculations

$$\text{Total P (pct.)} = (A/400) \times (250/B)$$

where:

A = P from curve (ppm)

B = Volume aliquot (mL)

Comments

The color developed is molybdovanadophosphoric acid and is very stable, lasting 2 weeks or more.

To destroy organic matter in samples high in organic matter, add 15 ml HNO_3 and 5 ml HCl. When brown fumes stop coming off, add $HClO_4$, and follow the usual procedure.

Sediment disturbance during aliquot removal makes it impossible to take more than one aliquot a day. If more aliquots are necessary, remove the

sediment by filtering the suspension into a 250-ml volumetric flack, using Whatman No. 50 filter paper.

Comparison of results by Na_2CO_3 fusion and by perchloric acid on lava samples indicates that extraction may not be complete for some silicate minerals. Extraction by $HClO_4$ should be complete on common phosphate minerals.

The volume of molybdo-vanadate reagent added is not critical but must be constant. The presence of chlorides slows down color development but does not interfere otherwise.

References

Sherman (1942); Kitson and Mellons (1944); and Jackson (1956).

Adsorption Coefficient (6S2)

Apparatus

- Automatic extractor, 24 place
- Syringes, 60 cc polypropylene. Use one sample tube and one extraction syringe per sample.

Reagents

- Extractant. Dissolve 4.5 g ammonium fluoride (NH_4F) and 85.6 g ammonium chloride (NH_4Cl) in about 4 L of distilled water, add 92 ml glacial acetic acid and 10 ml concentrated HCl, make to 8 L and mix.
- Sulfuric-molybdate-tartrate solution. Dissolve 100 g ammonium molybdate [$(NH_4)_6Mo_7O_{24}•4H_2O$] and 2.425 g antimony potassium tartrate [$K(SbO)C_4H_4O_6•½H_2O$] in 500 ml distilled water, heating if necessary but not to exceed 60 °C. Slowly add 1,400 ml concentrated H_2SO_4 and mix well. Cool, dilute to 2 L with water, and store in refrigerator in polyethylene or Pyrex bottle.
- Ascorbic acid solution. Dissolve 88.0 g ascorbic acid in distilled water, dilute to 1 L, mix, and store in glass bottle in refrigerator.
- Phosphorus stock standard, 100 ppm. Weigh 0.4394 g dried monobasic potassium phosphate (KH_2PO_4) into a 1-L volumetric flask, dissolve, and make to volume with extractant solution.
- Phosphorus working standards, 2 to 10 ppm. Pipette 2, 4, 6, 8, and 10-ml aliquots of phosphorus stock standard into a series of 100-ml volumetric flasks and make to volume with extractant solution. The standards contain 2, 4, 6, 8, and 10 ppm P.

- Saturate stock solution. Dissolve 4.394 g dried monobasic potassium phosphate (KH_2PO_4) in distilled water and make to 1 L.
- Saturate working solution. Pipette 20- and 80-ml aliquots of saturate stock solution into two 1-L volumetric flasks. The resulting solutions contain 20 and 80 ppm P.
- Color solution. Measure 40 ml ascorbic solution and 80 ml sulfuric-molybdate-tartrate solution into 2 L of distilled water. Bring to 4 L, mix, and store in refrigerator.

Apparatus

- Colorimeter
- Automatic extractor
- Shaker

Procedure

A. Saturation

Weigh three 2-g subsamples of oven-dried soil into 50-ml Erlenmeyer flasks. To the first add 2 ml distilled water. To the second add 2 ml 20 ppm P solution. To the third add 2 ml 80 ppm P solution. Let stand for 1 hr then place in oven at 60 °C and dry overnight.

B. Extraction

To each of the dried samples in the 50-ml Erlenmeyer flasks, add 20 ml extractant reagent, and shake for 20 min (Burrell shaker). Extract samples using the automatic extractor.

C. Developing the color

Standard curve. Using 50-ml Erlenmeyer flasks, pipette aliquots from the phosphorus working standards as follows:

Flask 1—2 ml extractant

Flask 2—2 ml 2 ppm P

Flask 3—2 ml 4 ppm P

Flask 4—2 ml 6 ppm P

Flask 5—2 ml 8 ppm P

Flask 6—2 ml 10 ppm P

Samples. For each sample extracted in part B, pipette 2 ml of extract into clean 50-ml Erlenmeyer flasks corresponding with sample numbers. To all flasks,

standards, and samples, add 25 ml of color solution, swirl to mix, and let stand for 15 min to allow color to develop. After color has developed fully, transfer to colorimeter tubes.

D. Reading the color

Using a wavelength setting of 880 µm, set colorimeter to 100 percent transmittance (T) with No. 1 standard containing 2 ml extractant. Read percent transmittance of remaining standards and samples. Generally, the standard curve is around the following values:

(ppm)	%T
0	100
2	77
4	59
6	45
8	33
10	24

E. Calculations

1. Develop standard curve by the least squares analysis using concentration of standards as a f(ln%t). This results in the equation:

   Concentration = m(ln%t) + b

2. Use this equation to determine solution concentrations of unknowns (leachate). Concentration of leachate x 10 is desorbed P in ppm of dry soil.
3. P retained of that added = P added (desorbed P at that conc. minus desorbed P at zero P addition).
4. Pa (adsorption coefficient) is the slope of the least square regression of P retained as a function of phosphorus added, f(P added).

Example

P	T	Added P	T
(ppm)	(%)	(ppm)	(%)
0	100		
2	77		
4	59		
6	45	0	84
8	33	20	73
10	24	80	45

1. Conc.= −7.023(ln%t)+32.5158
2. Concentration
   =−7.023 (ln84)+32.5158=1.40
   =−7.023 (ln73)+32.5158=2.38
   =−7.023 (ln45)+32.5158=5.78
   Desorbed P (ppm) of dry soil
   = 1.40x10=14.0
   = 2.38x10=23.8
   = 5.78x10=57.8
3. P (ppm) retained of that added
   = 0−(14.0−14.0)=0
   = 20−(23.8−14.0)=10.2
   = 80−(57.8−14.0)=36.2
4. y=0.4478(P added)+0.5083
   Pα= 0.4478

References

Mehlich (1978).

Boron (6T)

Saturation Extract (6T1)

Carmine Colorimetry (6T1a)

Refer to USDA Handbook 60, method 17 (p. 100) and method 73b (p. 142).

Silicon (6V)

HF Dissolution (6V1)

Obtain extract as in 7C3.

Atomic Absorption (6V1a)

Apparatus

- Diluter
- Atomic absorption spectrophotometer

Reagents

- Standard Si solutions, 400 and 800 mg/L in HF

Procedure

Dilute HF extracts from 7C3 and Si standards fivefold to twentyfold with water. Compare absorbance of samples with that of standards at 252 nm.

Calculations

$$\text{Si (pct.)} = (A \times 10 \times \text{dilution}) / B$$

where:

A = Si (mg/L)

B = Sample weight (g)

$$SiO_2 \text{ (pct)} = (\text{pct}) \times 2.14$$

Report on oven-dry basis.

MINERALOGY (7)

Instrumental Analyses (7A)

Preparation (7A1)

The treatment to be used in preparing samples depends on analysis objective and sample composition.

Carbonate Removal (7A1a)

Reagents

- Sodium acetate (NaOAc), *N*, pH 5.0. Dissolve 82 g NaOAc, 27 mL glacial acetic acid L^{-1}, adjust to pH 5.0.

Procedure

Place 5 g soil in a 90-ml centrifuge tube, add 40 ml *N* NaOAc, pH 5.0, and heat at 95 °C for 30 minutes, stirring occasionally. Centrifuge at 1600 rpm for 5 minutes and decant supernatant liquid. Repeat if necessary until carbonates are removed. Wash twice with *N* NaOAc, pH 5.0. Save decantates for calcium and magnesium analysis. One washing is enough to prepare neutral or basic noncalcareous soils for optimum hydrogen peroxide treatment.

References

Jackson (1956).

Organic-Matter Removal (7A1b)

Reagents

- Hydrogen peroxide (H_2O_2), 30- to 35-percent

Procedure

Transfer sample to a 250-ml tall breaker, using a minimum of water, and add 5 ml H_2O_2. When frothing subsides, heat at 90 °C. Continue to watch for frothing. Add 5- to 10-ml aliquots of H_2O_2 each hour until 25 to 30 ml H_2O_2 has been used. Wash five times, removing water by filter candles. Transfer to a 90-ml centrifuge tube.

References

Kilmer and Alexander (1949).

Iron Removal (7A1c)

Reagents

- Sodium bicarbonate ($NaHCO_3$), *N*
- Sodium citrate ($Na_3C_6H_5O_7$), 0.3 *M*
- Sodium dithionite ($Na_2S_2O_4$) powder

Procedure

If iron reduction is intended, add 5 ml *N* $NaHCO_3$ and as much as 40 ml 0.3 *M* sodium citrate. Heat to 70 °C (not above 80 °C) in a water bath and add 1 to 2 g $Na_2S_2O_4$, stir for 1 minute, and then stir intermittently for 15 minutes. Decant supernatant liquid and save for iron analysis. Repeat treatment as needed if soil is high in iron. Wash twice with 0.3 *M* sodium citrate.

References

Aguilera and Jackson (1953) and Mehra and Jackson (1960).

Disaggregation and Particle-Size Fractionation (7A1d)

Reagents

- Sodium bicarbonate ($NaHCO_3$), pH 9.5 to 10.0
- Sodium metaphosphate ($NaPO_3$). Prepare as in 3A1.

Procedure

Use $NaHCO_3$ solution or sodium hexametaphosphate-sodium bicarbonate as a dispersing agent. Use hexametaphosphate carefully with amorphous materials since phosphates may be precipitated. A dilute HCl treatment may be useful for some highly allophanic soils. Do not use mechanical blenders for disaggregation if silt and sand are to be studied because they fracture large quartz grains. Separate sand from silt with a 300-mesh sieve and further separate the sands, using a nest of sieves (3A1). Separate clay (<2 µ) from silt by centrifuging at 750 rpm for 3 minutes (International No. 2 centrifuge with No. 240 head and solution depth of 10 cm). If silt and sand are to be studied, save these fractions in small vials after drying and weighing. If interested in separating fine clay (<0.2 µ) from the coarse clay (0.2 µ to 2 µ), centrifuge at 2400 rpm for 30 minutes with a solution depth of 10 cm. Adjust time according to temperature. Add 50-ml aliquots of clay suspension after each centrifugation until the required amount of clay is obtained. Make each suspension of coarse and fine clay to known volume and determine its concentration and the concentration of the whole clay.

References

Kilmer and Alexander (1949) and Jackson (1956).

Particle-Size Distribution Analysis (PSDA) Pretreatment (7A1e)

Mineralogical analysis can be performed on samples from the particle-size distribution analysis (3A1). These samples have undergone peroxide digestion and sodium metaphosphate dispersion.

X-Ray Diffraction (7A2)

The minerals in soil clays of greatest interest are mostly flaky or platy, e.g., kaolinite, illite (mica), vermiculite, chlorite, and montmorillonite. They are most readily identified and distinguished from one another by observing the effect of different treatments on the interplanar spacings along the axis perpendicular to the platy surfaces. X-ray diffraction produces peaks on a chart corresponding to the various angles (2R) of goniometer from which the crystallographic spacing of the mineral or minerals can be calculated by Bragg's law. Tables of spacings corresponding to angles have been published in U.S. Geological Survey Circular 29 (Switzer et al., 1948).

The pretreatment used to distinguish montmorillonite from vermiculite and chlorite and to identify illite is saturation of the exchange complex of the clay with magnesium and treatment with ethylene glycol or glycerol. With this treatment, montmorillonite has a distinctive interplanar spacing of 17 Angstroms (17 Å) to 19 Å. Chlorite and vermiculite keep a 14 Å spacing and mica a spacing of 10 Å. To distinguish vermiculite from chlorite and to identify kaolinite, which has a 7 Å spacing, the pretreatment consists of saturating the clay with potassium and heating on a glass slide at 500 °C. Intermediate heat treatments, 110 and 250 °C, can be used to study interlayering in the collapsing minerals or other special problems. After the 500 °C treatment, vermiculite and montmorillonite collapse completely to 10 Å, kaolinite becomes amorphous, and chlorite still shows 14 Å and sometimes 7 Å peaks. Interstratified forms of these minerals are indicated by spacings intermediate between those of the individual components.

Clay suspensions are dried as thin films so that the plates are parallel to one another (preferred orientation). This results in greater x-ray diffraction peak intensities. For identification and semiquantitative estimation of nonplaty minerals such as quartz, feldspars, and crystalline iron and aluminum oxides, randomly oriented dry-powder samples can be used. This dry-powder method was used for nearly all analyses, including clay fractions, before 1951.

Various techniques are used to prepare the ion-saturated clays and to improve their parallel orientation. Details can be obtained from the soil survey laboratories.

References

Brindley (1951), Brown (1961), Brunton (1955), Grim (1953), Jackson (1956), and Switzer et al. (1948).

Thin Film on Glass, Solution Pretreatment (7A2a)

Reagents

- Potassium chloride (KCl), *N*
- Magnesium acetate ($Mg(OAC)_2$), *N*
- Magnesium chloride ($MgCl_2$), *1 N*
- Glycerol, 10-percent in ethanol by volume

Procedure

Place an aliquot containing 50 mg clay in a 50-ml centrifuge tube. Add a few ml 1 *N* KCl, centrifuge, and discard the clear supernatant. Combine sediments if necessary to get 50 mg in the tube. Wash four times by suspending and centrifuging in 20-ml portions *N* KCl. After the last washing with *N* KCl, wash with water until some of the clay remains suspended after centrifuging. Add a few drops of acetone or centrifuge at higher speed, or both, to flocculate the clay. Discard the supernatant. Clays are now free of chloride. Suspend the sediment in water and adjust the volume of the suspension to yield the desired weight of clay per slide. For most clays 50 mg per slide (27 by 46 mm) gives maximum intensity of reflection with minimum peeling of clay films. For amorphous clays, 25 mg per slide is adequate if glass slides are dried in a low-humidity atmosphere.

For magnesium saturation and glycerol solvation, place an aliquot containing 100 mg clay in a 50-ml centrifuge tube. Wash twice with *N* $Mg(OAC)_2$ acetate and then three times with *N* $MgCl_2$. Wash the suspension free of chloride or until clay disperses. Place 2.5 ml clay suspension containing 50 mg clay on a glass slide (25 mg clay if the clay is amorphous). Solvate the remaining clay in the test tube with glycerol (about ½ ml of 10-percent glycerol in ethanol per 50 mg clay). Mix well and pipette 50 mg clay onto the glass slide. The slide should be moist but not wet. Or prepare the glycerol slide by adding 10-percent glycerol, a drop at a time, to the slides until the clay film is moist.

Thin Film on Glass, Resin Pretreatment (7A2b)

Reagents

- Potassium-charged resin (Dowex 50W-X8)
- Magnesium-charged resin (Dowex 50W-X8)
- Glycerol, 10-percent in ethanol by volume

Procedure

Add ¼ teaspoon K-charged resin to 50 mg clay in a 1-ml volume in a 50-ml centrifuge tube. Mix and transfer a 1-ml aliquot to a glass slide (27 by 46 mm). Take the aliquot from the top of the suspension to avoid removing the resin.

Magnesium-clay and Mg-glycerol-clay slides can be prepared using a Mg-charged cation exchange resin. Add ½ teaspoon Mg-charged resin to the clay suspension (100 mg clay in a 4-ml volume) in a 50-ml centrifuge tube. Mix with the suspension, remove 1-ml aliquot, and place it on a glass slide. Add approximately ½ ml 10-percent glycerol in ethanol to the tube. Mix and transfer a 1-ml aliquot to a glass slide or use a Mg-clay slide for both Mg and Mg-glycerol solvated slides. Record a diffraction pattern for the Mg-saturated clay film. After solvating the clay film with 10-percent glycerol solution, record a second x-ray pattern.

References

Rex (1967).

Thin Film on Glass, Sodium Metaphosphate Pretreatment (7A2c)

Shake soil overnight in sodium metaphosphate solution (3A2). Centrifuge to separate the clay or siphon off the clay. Pipette about 50 mg clay to a glass slide (47 by 26 mm). Concentrate the clay suspension if necessary. Scan the clay film at room temperature, again after heating to 500 °C. The clay film is Na^+ saturated. The sodium metaphosphate peaks do not interfere with peaks of the more common clay minerals in this quick check method.

Thin Film on Tile, Solution Pretreatment (7A2d)

Apparatus

- Ceramic tile (porous precipitate drying plate, sawed into 27- by 46- by 7-mm blocks)

Procedure

Prepare clay suspensions as in 7A2a except dry the suspensions on ceramic tile blocks. Clay suspensions dry in a few seconds on tile, preventing particle-size segregation. Partly immerse the Mg-saturated clay films in a 10-percent glycerol solution. The porous tile rapidly transfers the glycerol to the clay film. Blot off excess glycerol before recording the x-ray pattern.

Thin Film on Tile, Resin Pretreatment (7A2e)

Prepare clay suspensions as in 7A2b. Dry on ceramic tile blocks as in 7A2d. Solvate with glycerol as in 7A2d.

Thin Film on Tile, Sodium Metaphosphate Pretreatment (7A2f)

Prepare the sample as in 7A2c. Pipette the clay onto ceramic tile blocks as in 7A2d. Follow method 7A2c for the other treatments. Or solvate with glycerol as in 7A2d.

Powder Mount, Diffractometer Recording (7A2g)

Distinguishing dioctahedral and trioctahedral minerals requires random orientation of the sample. There is no completely satisfactory method for preparing a random mount, but several techniques are used.

Pack the sample in a box mount against a glass slide. When the box is full, tape the back of the box. Invert the box and remove the slide to expose the sample to x-rays. For more random packing, sprinkle the dry sample (ground to <100 mesh) on double stick tape fixed on a glass slide or on a thin film of Vaseline on a glass slide. Scan the sample by x-ray and measure the reflections with a Geiger, proportional, or other counter.

Quick checks for whole samples, particularly for nonlayered minerals, can be made with a modified powder mount. Form the sample into a thick slurry, apply to a glass slide, and let dry. This is for convenience rather than random orientation.

Powder Mount, Camera Recording (7A2h)

Photographic plates are still the best means of identifying minerals. Mount the sample in the center of a circular x-ray camera. Record the x-ray reflections on photographic film placed in a cylindrical film holder inside the camera. All diffraction peaks are recorded simultaneously.

Thin Film on Glass, $NaPO_3$ Pretreatment II (7A2j)

Apparatus

- Hypodermic syringe (1.0 cc)
- Glass slides 24 x 46 mm or 14 x 19 mm
- International No. 2 centrifuge with a No. 240 head
- 100-ml centrifuge tubes (plastic)

Reagents

- Glycerol-water mixture (1:8 glycerol-water)
- Sodium hexametaphosphate solutions

Procedure

Shake approximately 5 g oven-dried soil (<2 mm) overnight with 5 ml sodium hexametaphosphate solution (3A1) and 35 ml of water in a 100-ml centrifuge tube, centrifuge at 750 rpm for 3 min for a 10-cm suspension depth, and decant clays. Draw about 0.5 cc of clay suspension into the syringe. Expel approximately 0.2 cc of the clay suspension onto an area approximately 20 x 27 mm in a band across the middle of a 46- x 27-mm slide or expel approximately 0.1 cc of clay suspension, containing approximately 6 mg of clay, onto and covering the 14- x

19-mm slide. Prior to the deposition of the clay suspension, one small drop of glycerol-water mixture is placed on the slide which is to be solvated. Prepare four slides for x-ray diffraction: (1) Na^+—room temperature, (2) Na^+—solvated, (3) Na^+—heated 2 hr at 300 °C, and (4) Na^+—heated for 2 hr at 500 °C.

Powder Mounts (7A2k)

Two procedures are used for random orientation of mineral separates. In the first procedure, double-stick tape is affixed to a glass slide, a surplus of the sample is sprinkled onto the tape, the excess material is removed, and the slide is scanned by x-ray analysis. In the second procedure, a <2-mm soil sample is ground finer than 100 mesh prior to slide preparation. A thin film of Vaseline is applied to a glass slide, the 100-mesh sample is added, the excess removed, and the slide is scanned by x-ray analysis.

For quick check of a <2-mm sample, particularly for nonlayered minerals, a small portion is ground to less than 100 mesh and placed on a glass slide. Water is applied a little at a time until a thick slurry is formed. The slurry is allowed to dry and the slide is scanned by x-ray analysis. This method is also applicable for specific mineral separates, very fine sands or silts.

References

Brown (1961) and Jackson (1956).

Differential Thermal Analysis (7A3)

Differential thermal analysis (DTA) is a measurement of the difference in heat absorbed by or evolved from a sample of soil material and a thermally inert material as the two are heated simultaneously at a constant rate. Thermocouples are in contact with two platinum pans; one pan contains an unknown and the other pan contains an inert material of similar composition. If a reaction occurs, a difference in temperature is registered on a strip chart recorder or photographically. The magnitude of the difference depends on the nature of the reaction and amount of reacting substance in the unknown. The temperature at which the reaction occurs identifies the substance if enough is known about the sample to predict the possibilities.

Apparatus

- Columbia scientific instrument (CSI) system 200
- Mortar and pestle
- Analytical balance
- Desiccator

Reagents

- Reference sample, calcined kaolinite, 2 to 20 µ
- Ethyl alcohol, 95 percent
- Magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$

Procedure

The decanted clay from 7A2i or 7A2j is air-dried, ground in alcohol to approximately 100 mesh, and stored in a desiccator with $Mg(NO_3)_2 \cdot 6H_2O$. A 3− to 7−mg sample is placed on a small platinum pan in the sample holder. The temperature of the kaolinite reference sample and clay sample is increased at a rate of 20 °C per minute to a maximum of 900 °C. The sample can be heated in air or nitrogen.

The common endothermic reactions studied or recorded are loss of structural water in gibbsite, goethite, and kaolin and loss of carbon dioxide in carbonates. Change of state or rearrangement of crystal lattices can be either exothermic or endothermic. Oxidation reactions such as burning of carbon and oxidation of ferrous iron are exothermic.

Loss of structural hydroxyls can be measured quantitatively by calibrating areas of peaks of known mixtures of standard minerals, as is done commonly to determine the percentage of kaolin and gibbsite in soils. The standard curves are prepared by running the known mixtures under the same conditions as the unknowns. Kaolin has an endotherm at 500 to 600 °C and gibbsite, at 310 °C. Each worker should prepare a set of standard curves.

Endotherms at about 120 °C indicate surface-adsorbed water. Montmorillonite produces a double peak at a low temperature if saturated with a divalent cation. The proportion of this mineral can be estimated if samples are kept in an atmosphere with a high (70 to 80 percent) relative humidity for 24 hr or more before analysis. Allophane has a broad endotherm at about 160 °C.

Samples can be any well-powdered material, whole-soil, or separated fractions. Organic matter is objectionable because it produces irregular exothermic reactions that obscure the important peaks. If a clay separate is used, it must be washed free of hygroscopic salts or salts containing water of crystallization.

References

Grim (1968), McKenzie (1957), and Tan and Hajek (1977).

Thermal Gravimetric Analysis (7A4)

CSI Stone Model 10002B (7A4a)

Thermal gravimetric analysis is the detection and measurement of weight changes in a sample of soil material as the sample is being heated or cooled over a specific temperature range.

Apparatus

- CSI Stone Model lOOOB used in conjunction with an RC−202 recorder−controller. Furnace is water cooled, with a rapid cooling Kanthal element. Furnace is capable of operation at temperatures of up to 1,200 °C.

Procedure

Prepare sample as described in 7A3 and place in balance pan suspended above thermocouple assembly. Heat sample at rate of 20 °C/min to desired temperature. If a weight loss occurs, it is registered on a strip chart recorder. The magnitude of the weight loss depends on the reaction and the amount of reacting substance in the unknown. The temperature at which the reaction occurs usually identifies the substance.

Infrared Analyses (7A5)

Soil or clay samples (7A2j) are incorporated into a potassium bromide (KBr) pellet for infrared analyses. Sample concentration in the pellet ranges from 0.1 to 1 percent.

Reagents

- Potassium bromide, spectroscopic grade

Apparatus

- Infrared spectrometer. Perkin Elmer Model 283.
- Pellet die
- Hydraulic press
- Analytical balance

Procedure

Mix 0.30 g KBr and 1 mg of sample in mortar and pestle. Transfer the mixture to the pellet die, and place die in hydraulic press. Apply 8 tons of pressure for 1 min. Place pellet in instrument holder and scan for 12 min. Peaks produced on chart recorder are used to identify the substance.

References

J.L. White in Dixon and Weed (1977).

Optical Analyses (7B)

Grain Studies (7B1)

Grain Mounts, Canada Balsam (7B1b)

For Canada balsam, heat slide plus balsam for 15 min at 125 °C. Add mineral grains, stir, heat for an additional 5 min, place cover glass in position and press firmly, remove slide from hot plate, and cool.

The refractive index of Canadian balsam is close to that of quartz, which helps to distinguish quartz from other colorless minerals, particularly the feldspars. Other available commercial media cover the refractive index range of 1.53 to 1.55. Piperine with a refractive index of 1.68, which is close to that of many of the common heavy minerals, is best for mounting them.

Electron Microscopy (7B2)

Electron microscopy gives information on particle size and morphology of clay-size particles. Evidence of clay formation or weathering can also be seen. Positive identification of halloysite often depends on observation of rolled structures under the electron microscope.

Procedure

Place a drop of dilute clay suspension on a 200-mesh copper grid. After drying, insert this grid in the microscope.

Total Analysis (7C)

Chemical (7C1)

The procedures follow the standard procedures for rock analysis set forth by Hillebrand and Lundell (1929) and modified by Robinson (1920) and by Shapiro and Brannock (1956).

X-Ray Emission Spectrography (7C2)

X-ray emission spectrography is elemental analysis by measuring the x-ray fluorescence produced by bombarding a sample with high-energy x-rays. Each element yields fluorescent radiation of unique wave lengths, one of which is selected for measurement by using an analyzing crystal that diffracts according to Bragg's law. The intensity of the fluorescent radiation is generally proportional to the amount of the element present, but this is affected by sample homogeneity, particle size, and the absorption and enhancement of radiation by any other elements present in the sample (matrix effects). These effects can be overcome or compensated for by (1) comparing the intensities with those of standards of similar composition prepared in a similar manner, (2) fusing both samples and

standards in borax or lithium borate to eliminate particle-size effects and to reduce matrix effects, and (3) making matrix corrections by calculating the absorption-enhancement coefficient of the sample for the particular radiation being measured.

References

Vanden Heuvel (1965).

Surface Area (7D)
Glycerol Retention (7D1)

Apparatus

- Weighing cans

Reagents

- Glycerol, 2-percent

Procedure

Oven-dry a clay sample (about 0.2 g) at 110 °C for 2 hours. Cool and weigh. Add 5 ml 2-percent glycerol solution and mix. Heat in oven containing free glycerol at 110 °C to constant weight. Record weight.

Calculations

To calculate the percent of glycerol retained, subtract weight of oven-dry sample from weight of glycerol and oven-dry sample, divide by weight of oven-dry sample, and multiply by 100. For the surface area of noncollapsible minerals (m_2/g), multiply glycerol retained by 19.1.

References

Kinter and Diamond (1958).

MISCELLANEOUS (8)

Saturation Extract, Mixed (8A)
Saturation Extract (8A1)

Apparatus

- Richards or Buchner funnels
- Filter rack or flask
- Filter paper
- Vacuum pump
- Extract containers such as test tubes or 1-oz bottles

Procedure

Transfer the saturated soil paste to a filter funnel with a filter paper in place and apply vacuum until air begins to pass through the filter. Collect the extract in a bottle or test tube. If carbonate and bicarbonate are to be determined on the extract, add 1 drop of 1000 ppm sodium hexametaphosphate solution for each 25 ml of extract to prevent precipitation of calcium carbonate on standing.

References

Richards (1954).

Conductivity of Saturation Extract (8A1a)

Apparatus

- Conductivity bridge
- Conductivity cell

Procedure

Determine temperature of the saturation extract obtained by methods 8A1 or 8B1. Draw the extract into the cell and read the meter. Correct for temperature and cell constant using Table 1 (Table 15; Richards, 1954) and report as electrical conductivity, mmhos per centimeter at 25 °C. If the instrument fails to balance, dilute the extract 1:9 with distilled water and redetermine. The conductivity of the diluted extract is approximately one-tenth the conductivity of the saturation extract.

References

Richards (1954).

Conductivity of Saturation Extract (Quick Test) (8A1b)

Apparatus

- Extractor, miniature Richards-type (fig. 8a1b-1)

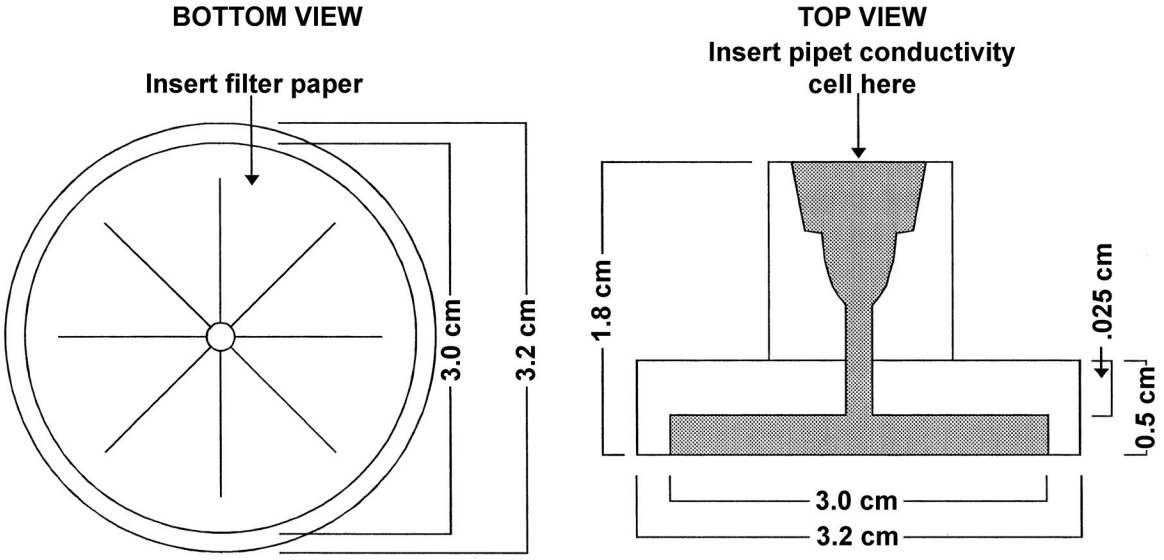


Figure 8a1b-1.—Miniature Richards-type extractor made of polymethyl methacrylate (Lucite).

- Conductivity cell, micropipet
- Filter paper, glass fiber, 3.0 cm
- Vacuum pump

Procedure

Add 1 tablespoon soil to a 100-ml beaker or container. Make a saturated paste as in 8A. Place filter paper in recess of extractor and moisten with water. Insert the tip of the pipette conductivity cell through the other end of the extractor and into the paste. Apply suction to the cell until full. Proceed as in 8A1a.

Bureau of Soils Cup, Resistance (8A2)

Apparatus

- Wheatstone bridge
- Bureau of Soils electrode cup

Procedure

Rinse the soil cup with water, dry, and fill with soil paste (8A). Jar cup to remove air bubbles, strike off excess paste so the cup is level full, and connect cup to the bridge. Record resistance (ohms) and temperature of soil paste (°F).

Calculations

Convert resistance of the soil paste in ohms to percentage of soluble salt by using the tables and formulas on pages 346–349, Soil Survey Manual.

References

Richards (1954) and Soil Survey Staff (1951).

Saturated, Capillary Rise (8B)

Apparatus

- Sand table. Mariotte bottle.
- Filter paper
- Polyethylene dish with lid

Procedure

Weigh 250 g air-dry soil into cups made from Whatman No. 52 (15-cm) filter paper and place them on a sand table wetted at 5-cm tension with water. The sand table used consists of two nested plastic dishpans. The outer pan holds distilled water, which is kept at a constant level by a Mariotte bottle. The inner pan, containing medium to fine (35 to 80 mesh) pure quartz sand, rests on rubber stoppers and is suspended in the distilled water. Its perforated bottom is covered with a fine cloth-mesh screen that permits water to move upward by capillarity through the sand to the table surface. The sand on the table surface is then smoothed and covered with an absorbent paper towel. Lightweight porous firebricks can be used in place of the sand table.

Keep the samples on the sand table 16 to 18 hours, remove them, and weigh. Water adsorption drops rapidly after an initial wetting of 2 hours and the rate becomes very slow after 6 to 9 hours. Moisture moves toward the top and center of the sample, which is wetted last, ensuring retention of soluble salts in the soil. Calculate moisture at saturation from the wet- and dry-soil weights, correcting for the wet and dry filter paper weights. Add air-dry moisture percentage to moisture at saturation and report on oven-dry basis. After the wet weighing, transfer the sample to a pint polyethylene refrigerator dish, mix briefly with a spatula, and determine the pH. Keep a lid on the dish whenever possible to reduce evaporation.

References

Longenecker and Lyerly (1964).

Saturation Extract (8B1)

Proceed as in 8A1, using the saturated paste obtained by method 8B.

Conductivity of Saturation Extract (8B1a)

Proceed as in method 8A1a except use saturation extract obtained by method 8B1.

Reaction pH (8C)

Soil Suspensions (8C1)

Water dilution (8C1a)

Procedure

For 1:1 dilution add an equal weight of water to 20 or 30 g soil in a 50-ml beaker or paper cup. Stir at regular intervals for about an hour. Measure pH of the soil suspension with a glass electrode, stirring well just before immersing the electrodes in the suspension. For other dilutions vary the amount of soil, keeping the volume of water constant.

KCl (8C1c)

Procedure

Proceed as in method 8C1a except use *N* KCl instead of water.

$CaCl_2$ (8C1e)

Proceed as in 8C1a except use 0.01 *M* $CaCl_2$. This procedure can be combined with 8C1a by adding an equal volume of 0.02 *M* $CaCl_2$ to the soil suspension prepared for the water pH. Stir twice at 15-minute intervals before reading. The soil-solution ratio will be 1:2, but the pH difference between 1:1 and 1:2 suspensions is negligible.

References

Schofield and Taylor (1955) and Peech (1965).

LITERATURE CITED

Aguilera, N.H., and M.L. Jackson. 1953. Iron oxide removal from soils and clays. Soil Sci. Soc. Amer. Proc. 17:359–364.

Allison, L.E. 1960. Wet combustion apparatus and procedure for organic and inorganic carbon in soil. Soil Sci. Soc. Amer. Proc. 24:36–40.

American Society for Testing and Materials. 1970. Book of ASTM standards. pp. 212–219.

Association of Official Agricultural Chemists. 1945. Official and tentative methods of analysis, 6th ed. 932 pp. Washington, D.C.

Barrows, H.L., and E.C. Simpson. 1962. An EDTA method for the direct routine determination of calcium and magnesium in soils and plant tissue. Soil Sci. Soc. Amer. Proc. 26:443–445.

Bascomb, C.L. 1968. Distribution of pyrophosphate extractable iron and organic carbon in soils of various groups. J. Soil Sci. 19:251–268.

Bower, C.A., and L.V. Wilcox. 1965. Soluble salts. *In* Methods of soil analysis, Monog. 9. v. 2, pp. 933–951. Amer. Soc. Agron., Madison, Wis.

Brasher, B.R., D.P. Franzmeier, V.T. Valassis, 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.

Brindley, G.W., ed. 1951. X−ray identification and crystal structures of clay minerals. 345 pp. Mineralogical Society, London.

Brown, G., ed. 1961. The x−ray identification and crystal structures of clay minerals. 544 pp. Mineralogical Society (Clay Minerals Group), London.

Brunton, G. 1955. Vapor pressure glycolation of oriented clay minerals. Amer. Min. 40:124–126.

Cady, J.G. 1965. Petrographic microscope techniques. *In* Methods of soil analysis, Monog. 9. v. 2, pp. 604–631. Amer. Soc. Agron., Madison, Wis.

Chapman, H.D., and P.F. Pratt. 1961. Methods of analysis for soils, plants, and waters. Univ. of Calif., Div. of Agr. Sci. 309 pp.

Chenery, E.M. 1948. Thioglycollic acid as an inhibitor for iron in the colorimetric determination of aluminum by means of aluminon. Analyst 73:501–502.

Cheng, K.L., and R.H. Bray. 1951. Determination of calcium and magnesium in soil and plant material. Soil Sci. 72:449–458.

Cheng, K.L., R.H. Bray, and T. Kurtz. 1953. Determination of total iron in soils by disodium dihydrogen ethylenediaminetetraacetate titration. Anal. Chem. 25:347–348.

Erickson, A.E., L.C. Li, and J.E. Gieseking. 1947. A convenient method for estimating carbonates in soils and related materials. Soil Sci. 63:451–454.

Fieldes, M., P.J.T. King, J.P. Richardson, and L. Swindale. 1951. Estimation of exchangeable cations in soils with the Beckman flame spectrophotometer. Soil Sci. 72:219–232.

Fieldes, M., and K.W. Parrott. 1966. The nature of allophane in soils. III. Rapid field and laboratory test for allophane. New Zealand J. Sci. 9:623–629.

Franzmeier, D.P., B.F. Hajek, and C.H. Simonson. 1965. Use of amorphous material to identify spodic horizons. Soil Sci. Soc. Amer. Proc. 29:737–743.

Franzmeier, D.P., and S.J. Ross, Jr. 1968. Soil swelling: Laboratory measurement and relation to other soil properties. Soil Sci. Soc. Amer. Proc. 32:573–577.

Fry, W.H. 1933. Petrographic methods for soil laboratories. U.S. Dept. Agr. Tech. Bull. 344. 96 pp.

Grim, R.E. 1953. Clay mineralogy. 384 pp. McGraw-Hill, New York.

Grim, R.E. 1968. Clay mineralogy. 596 pp. McGraw-Hill, NY.

Grossman, R.B. 1964. Composite thin sections for estimation of clay-film volume. Soil Sci. Soc. Amer. Proc. 28:132–133.

Grossman, R.B., B.R. Brasher, D.P. Franzmeier, and J.L. Walker. 1968. Linear extensibility as calculated from natural-clod bulk density measurements. Soil Sci. Soc. Amer. Proc. 32:570–573.

Grossman, R.B., and J.L. Millet. 1961. Carbonate removal from soils by a modification of the acetate buffer method. Soil Sci. Soc. Amer. Proc. 25:325–326.

Hillebrand, W.F., and G.E.F. Lundell. 1929. Applied inorganic analysis, with special reference to the analysis of metals, minerals and rocks. 929 pp. John Wiley and Sons, New York.

Holmgren, G.G.S. 1967. A rapid citrate-dithionite extractable iron procedure. Soil Sci. Soc. Amer. Proc. 31:210–211.

Holmgren, G.G.S. 1968. Nomographic calculation of linear extensibility in soils containing coarse fragments. Soil Sci. Soc. Amer. Proc. 32:568–570.

Hsu, P.H. 1963. Effect of initial pH, phosphate, and silicate on the determination of aluminum with aluminon. Soil Sci. 96:230–238.

Jackson, M.L. 1956. Soil chemical analysis. Advanced course. Private publication, Madison, WI.

Jackson, M.L. 1958. Soil chemical analysis. Prentice-Hall, Inc., Englewood Cliffs, NJ.

Johnson, C.M., and A. Ulrich. 1959. Analytical methods for use in plant analysis. Calif. Agr. Exp. Sta. Bull. No. 766. 78 pp.

Kilmer, V.J. 1960. The estimation of free iron oxides in soils. Soil Sci. Soc. Amer. Proc. 24:420–421.

Kilmer, V.J., and L.T. Alexander. 1949. Methods of making mechanical analyses of soils. Soil Sci. 68:15–24.

Kilmer, V.J., and J.F. Mullins. 1954. Improved stirring and pipetting apparatus for mechanical analysis for soils. Soil Sci. 77:437–441.

Kilmer, V.J., and D.C. Nearpass. 1960. The determination of available sulfur in soils. Soil Sci. Soc. Amer. Proc. 24:337–339.

Kinter, E.B., and S. Diamond. 1958. Gravimetric determination of monolayer−glycerol complexes of clay minerals. Proc. 5th Natl. Conf. on Clays and Clay Minerals, Natl. Acad. Sci. Natl. Res. Council Publ. 566, pp. 318–333.

Kitson, R.E., and M.E. Mellons. 1944. Colorimetric determination of phosphorus as molybdivanadophosphoric acids. Indus. and Engr. Chem. 16:379.

Krumbein, W.C., and F.J. Pettijohn. 1938. Manual of sedimentary petrography. 549 pp. D. Appleton−Century Co., New York.

Lagerwerff, J.V., G.W. Akin, and S.W. Moses. 1965. Detection and determination of gypsum in soils. Soil Sci. Soc. Amer. Proc. 29:535–540.

Lin, C., and N.T. Coleman. 1960. The measurement of exchangeable aluminum in soils and clays. Soil Sci. Soc. Amer. Proc. 24:444–446.

Lockwood, W.N. 1950. Impregnating sandstone specimens with thermosetting plastics for studies of oil-bearing formations. Bull. Amer. Assoc. Petrol. Geol. 34:2001–2067.

Longenecker, D.E., and P.J. Lyerly. 1964. Making soil pastes for salinity analysis: A reproducible capillary procedure. Soil Sci. 97:268–275.

McKeague, J.A., and J.H. Day. 1966. Dithionite and oxalate extractable Fe and Al as aids in differentiating various classes of soils. Can. J. Soil Sci. 46:13–22.

McKenzie, R.C. 1957. The differential thermal investigation of clays. Mineralogical Society, London.

Mehlich, A. 1978. New extractant for soil test evaluation of phosphorus, potassium, magnesium, calcium, sodium, manganese, and zinc. Comm. Soil Sci. Plant Anal. 9:477–492.

Mehra, O.P., and M.L. Jackson. 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. Proc. 7th Natl. Conf. on Clays and Clay Minerals. pp. 317–327. Permagon Press, New York.

Milner, H.B. 1962. Sedimentary petrography, 4th ed. v. 2. pp. 643 and 715. Macmillan Co., New York.

Nelson, R.E. 1970. Semimicro determination of sulfate in water extracts of soils. Soil Sci. Soc. Amer. Proc. 34:343–345

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.

North-Central Regional Research Committee on Soils. 1955. Loess-derived gray-brown podzolic soils in the Upper Mississippi River Valley. Univ. of Ill. Bull. 587. 80 pp.

Peech, M. 1965. Lime requirement. *In* Methods of soil analysis. Monog. 9. v. 2. pp. 927–932. Amer. Soc. Agron., Madison, Wis.

Peech, M., L.T. Alexander, L.A. Dean, and J.F. Reed. 1947. Methods of soil analysis for soil fertility investigations. U.S. Dept. Agr. C. 757. 25 pp.

Pierce, W.C., and E.L. Haenisch. 1955. Quantitative analysis. pp. 141–143. John Wiley and Sons, New York.

Pratt, P.F., and F.L. Bair. 1961. A comparison of three reagents for the extraction of aluminum from soils. Soil Sci. 91:357–359.

Reed, F.S., and J.L. Mergner. 1953. The preparation of rock thin sections. Amer. Miner. 38:1184–1203.

Rennie, P.J. 1957. Routine determination of the solids, water, and air volumes within soil clods of natural structure. Soil Sci. 84:351–365.

Rex, R.W. 1967. Authigenic silicates formed from basaltic glass by more than 60 million years contact with sea water, Sylvania Guyot, Marshall Islands. Clays Clay Miner. 15:195–203.

Richards, L.A., ed. 1954. Diagnosis and improvement of saline and alkali soils. U.S. Salinity Laboratory, U.S. Dept. Agr. Handb. 60. 160 pp.

Robinson, W.O. 1930. Method and procedure of soil analysis used in the division of soil chemistry and physics. U.S. Dept. Agr. C. 139. 19 pp.

Rogers, A.F., and P.F. Cherry. 1933. Thin-section mineralogy. MSGR−Hill Book Co., New York.

Schofield, R.K., and A.W. Taylor. 1955. The measurement of soil pH. Soil Sci. Soc. Amer. Proc. 19:164–167.

Shapiro, L., and W.W. Brannock. 1956. Rapid analysis of silicate rocks. U.S. Geol. Survey Bull. 1036−C:19–56.

Sherman, M.S. 1942. Calorimetric determination of phosphorus in soils. Indus. and Engr. Chem. 14:182.

Shields, L.G., and M.W. Meyer. 1964. Carbonate clay: Measurement and relationship to clay distribution and cation exchange capacity. Soil Sci. Soc. Amer. Proc 28:416–419.

Smith, R.M., W.E. Grube Jr., T. Arkle Jr., and A. Sobek. 1974. Mine spoil potentials of soil and water quality. EPA Environmental Protection Technology Series. 670/2-74-070:43–48.

Soil Survey Staff. 1951. Soil survey manual. U.S. Dept. Agr. Handb. 18. 503 pp.

Switzer, G., J.M. Axelrod, M.L. Lindberg, and E.S. Larsen. 1948. Tables of d spacings for angle 2Ɵ. U.S. Dept. Interior. Geological Survey. Circular 29. Washington, DC.

Tabatabai, M.A., and J.M. Bremner. 1970. Use of the Leco 70-second carbon analyzer for total carbon analysis of soils. Soil Sci. Soc. Amer. Proc. 34:608–610.

Tan, K.H., and B.F. Hajek. 1977. Thermal analysis of soils. *In* J.B. Dixon and S.B. Weed (eds.) Minerals in soil environments. 2nd ed. SSSA Book Series 1. SSSA, Madison, WI. p. 865–884.

Treadwell, F.P., and W.B. Hall. 1943. Analytical chemistry, Vol. 1: Qualitative analysis, 9th ed. John Wiley and Sons, New York.

Tucker, B.M. 1954. The determination of exchangeable calcium and magnesium in carbonate soils. Austral. J. Agr. Res. 5:706–715.

Tyner, E.H. 1939. The use of sodium metaphosphate for dispersion of soils for mechanical analysis. Soil Sci. Soc. Amer. Proc. 4:106–113.

Vanden Heuvel, R.C. 1965. Elemental analysis by x−ray emission spectrography. *In* Methods of soil analysis. Monog. 9. v. 2. pp. 771–821. Amer. Soc. Agron. Madison, Wis.

Walkley, A. 1935. An examination of methods for determining organic carbon and nitrogen in soils. J. Agr. Sci. 25:598–609.

Washington, H.S. 1930. The chemical analysis of rocks, 4th ed. pp. 168–172. John Wiley and Sons, New York.

White, J.L. 1977. Preparation of specimens for infrared analysi. *In* J.B. Dixon and S.B. Weed (eds.) Minerals in soil environments. Soil Sci. Soc. Amer. Madison, WI. p. 847–860

Williams, D.E. 1948. A rapid manometric method for the determination of carbonate in soils. Soil Sci. Soc. Amer. Proc. 13:127–129.

Yoe, J.H., and W.L. Hill. 1927. An investigation of the reaction of aluminum with the ammonium salt of aurinetri-carboxylic acid under different experimental conditions, and its application to the colorimetric determination of aluminum in water. J. Amer. Chem. Soc. 49:2395–2407.

Young, K.K. 1962. A method of making moisture desorption measurements on undisturbed soil samples. Soil Sci. Soc. Amer. Proc. 26:301.

Young, K.K., and J.D. Dixon. 1966. Overestimation of water content at field capacity from sieved-sample data. Soil Sci. 101:104–107.

Yuan, T.L. 1959. Determination of exchangeable hydrogen in soils by a titration method. Soil Sci. 88:164–167.

Yuen, S.H., and A.G. Pollard. 1952. The determination of nitrogen in agricultural materials by the Nessler reagent. I, Preparation of the reagent. J. Sci. Food and Agr. 3:441–447.

APPENDIX

Figure 1.—Laboratory data sheet for Hayter silt loam, McCreary County, KY.

Figure 2. —Profile description of Hayter silt loam, McCreary County, KY.

Figure 1.—Laboratory data sheet for Hayter silt loam, McCreary County, KY.

SOIL Hayter silt loam SOIL Nos. S63Ky-74-6 LOCATION McCreary County, Kentucky

SOIL SURVEY LABORATORY Beltsville, Maryland LAB Nos. 63776-63781

Depth (in)	Hori-Zon	1Blb	Size class and particle diameter (mm)									3A1						
		Total			Sand					Silt					3B2 >2, Vol pct. of whole soils	Coarse fragments 3B1		
		Sand (2-0.05)	Silt (0.05-0.002)	Clay (< 0.002)	Very Coarse (2-1)	Coarse (1-0.5)	Med. (0.5-0.25)	Fine (0.25-0.1)	Very Fine (0.1-0.05)	(0.05-0.02)	Int. III (0.02-0.002)	Int. II (0.2-0.02)	(2-0.1)			>2, Wt pct. of whole soils	2-20	20-75
																	pct. of <--- ---> <75 mm	
		<---------- Pct. of < 2 mm ---------->																
1/2-5	Ap2	15.0	59.0	26.0	3.8	1.9	0.6	1.6	7.1	15.7	43.3	23.9	7.9		23	36	21	--
5-10	B1	15.0	57.4	27.6	3.0	1.9	0.6	1.1	8.4	14.6	42.8	23.7	6.6		36	52	22	4
10-19	B21	15.6	57.0	27.4	3.4	1.9	0.6	1.5	8.2	14.7	42.3	24.0	7.4		34	47	17	2
19-34	B22t	14.3	57.0	28.7	3.4	2.1	0.8	1.2	6.8	13.4	43.6	20.9	7.5		26	37	12	--
34-48	B23t	15.9	53.7	30.4	4.8	2.9	1.0	1.6	5.6	9.2	44.5	15.7	10.3		47	59	16	18
48-60	B3t	24.1	50.8	25.1	8.1	4.9	1.7	2.8	6.6	9.5	41.3	17.8	17.5		51	62	27	7

Depth (in.)	6A1a Organ-Ic Carbon	6B2a Nitro-gen	C/N		Carbo-nate as $CaCO_3$	6Cla Ext. iron as Fe	Bulk density				Water content						pH	
								4Ale 1/3 bar	4A1h6 Oven drt	4D1 LE		4B1c 1/3 bar	4B2 15 bar	4C1 WRD			8C1c (1:1) KCl	8C1a (1:1) H_2O
	Pct.	Pct.				Pct.	g/cc	g/cc	g/cc	Pct.	Pct.	Pct.	Pct.	in/in			IN.	
1/2-5	1.86	0.180	10			2.9		1.36	1.39	0.7		26.6	12.0	0.15			4.4	4.9
5-10	.87	.100	9			2.9		1.35	1.39	0.6		26.8	11.5	0.13			3.9	4.6
10-19	.35	.058	6			2.3		1.54	1.61	0.9		21.6	11.1	0.11			3.9	5.4
19-34	.21					2.4		1.57	1.63	0.9		21.5	12.0	0.11			3.9	5.4
34-48	.22					2.5		1.60	1.63	0.3		21.7	12.4	0.08			3.8	5.4
48-60	.10					2.9		1.68	1.75	0.6		18.4	10.1	0.07			3.8	5.3

Depth (in.)	Extractable bases			5B1a	6H2a	CEC			6G1d							Base saturation	
	6N2d Ca	6O2b Mg	6P2a Na	6Q2a K	Ext. acidity	5A3a cations			A1							5C3 Sum cations	
	<---------- meq/100g ---------->															Pct.	Pct.
1/2-5	4.3	1.5	0.1	0.5	12.8	19.2			0.4							33	
5-10	1.6	1.1	0.1	02	10.8	13.8			1.5							22	
10-19	1.8	1.6	0.1	02	7.8	11.5			0.7							32	
19-34	1.4	2.4	0.1	.2	7.8	11.9			1.0							34	
34-48	1.5	3.2	Tr.	.2	7.6	12.5			1.2							38	
48-60	1.1	3.0	Tr.	.2	6.9	13.0			1.2							33	

Figure 2.—Profile description of Hayter silt loam, McCreary County, KY.

Soil type:	Hayter silt loam
Soil no.:	S63Ky-74-6
Location:	McCreary County, Kentucky, North off Hwy. 759 about 2 miles east of U.S. Hwy. 27.
Vegetation and land use:	Hickory, persimmon, yellow poplar.
Slope and land form:	50 percent.
Drainage:	Well drained.
Parent material:	Colluvium from sandstone and shale.
Sampled by and date:	D.P. Franzmeier, E.J. Pedersen, C.R. Gass, L. Manhart, G. Chapman; October 15, 1963.
Described by:	J.H. Winsor, C.K. Losche.
Horizon and Beltsville Lab. No.	
01	1-½ to 0 inches. Hardwood leaf litter.
Ap1	0 to ½ inch. Very dark grayish brown (10YR 3/2) silt loam; moderate fine granular structure; very friable; 12 percent sandstone fragments (> 3 in. diameter); many roots; pH 7.0.
Ap2 63776	½ to 5 inches. Brown (10YR 4/3) silt loam; weak medium granular structure; very friable; 12 percent sandstone fragments; many roots; pH 5.0.
B1 63777	5 to 10 inches. Brown (7.5YR 4/4) silt loam; weak to moderate fine subangular blocky structure; friable; 25 percent sandstone fragments; many roots; pH 5.0.
B21 63778	10 to 19 inches. Brown (7.5YR 4/4) silt clay loam / silt loam; moderate medium blocky structure; friable; 25 percent sandstone fragments; common roots; pH 5.0.
B22t 63779	19 to 34 inches. Brown to dark brown (7.5YR 4/4, 3/2) silty clay loam; moderate medium blocky structure; friable; common clay films; 20 percent sandstone fragments; few roots; pH 5.0.
B23t 63780	34 to 48 inches. Brown (7.5YR 4/4) silty clay loam; moderate medium subangular blocky structure; friable to firm; 30 percent sandstone fragments; common clay films; few roots; pH 5.0.
B3t 63781	48 to 60 inches. Brown (7.5YR 5/4) silty clay loam; weak to moderate medium subangular blocky structure; friable to firm; common clay films; 35 percent sandstone fragments; few roots; pH 5.0.

Notes: Colors are given for moist soil. The B21 and B23t layers were sampled for the Bureau of Public Roads. Reaction was determined by Soiltex.