Portable X-ray fluorescence Spectroscopy

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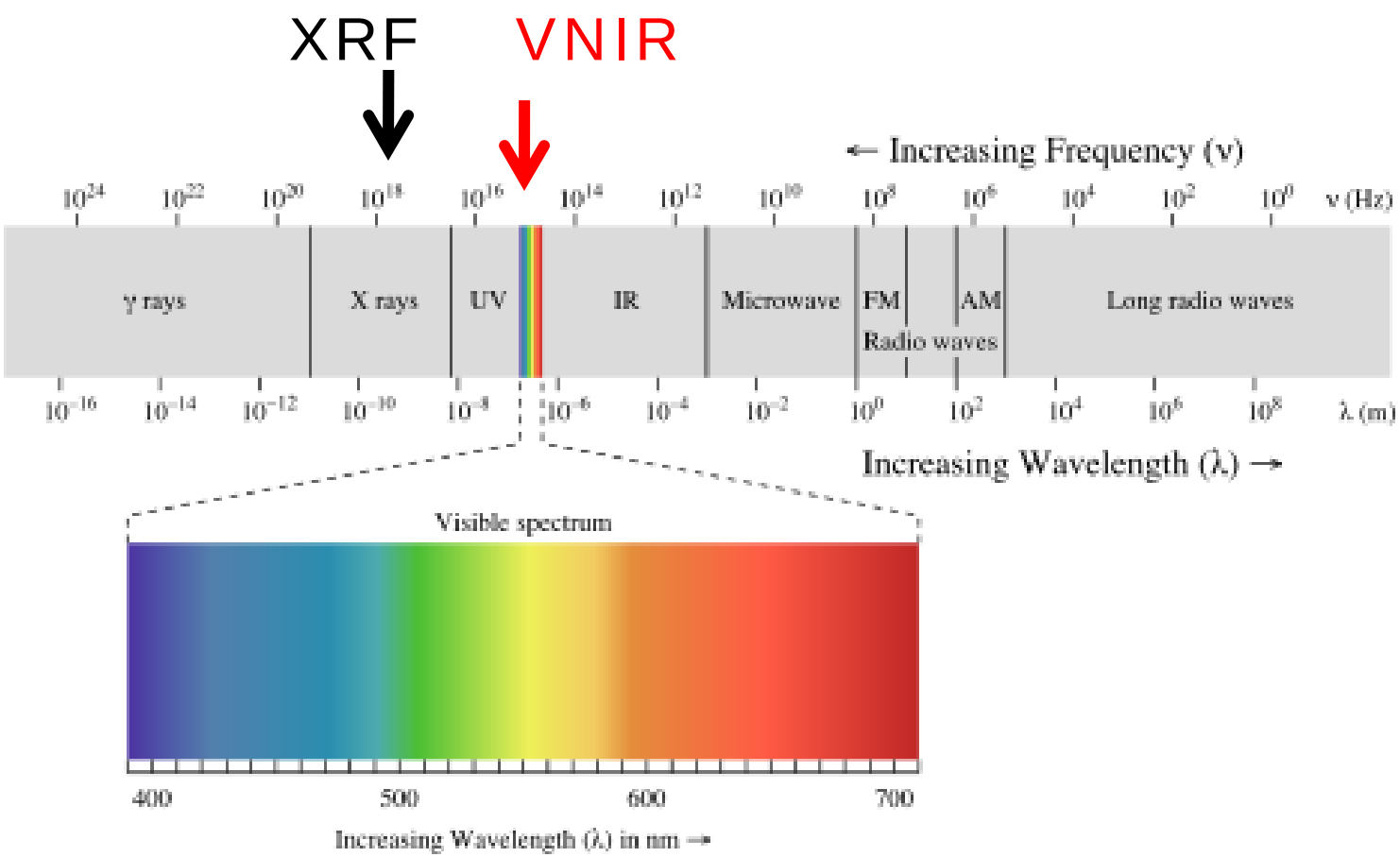
OBJECTIVES

- **Background of the method**
- **Features of the instrument**
- **Applications for soil survey**



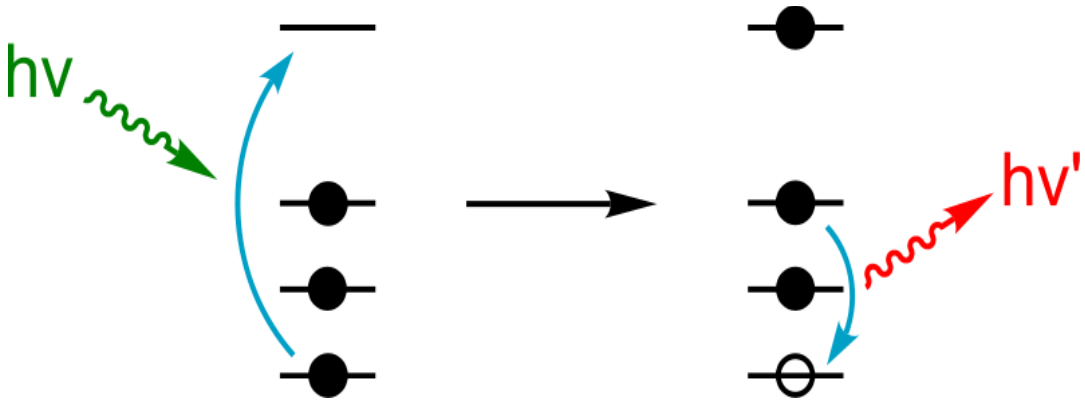
X-ray fluorescence (XRF) is used to detect and measure the concentration of elements in substances.

Fluorescence - phenomena of absorbing incoming radiation and re-radiating it as lower-energy radiation.

VNIR –Measures spectral signatures of materials defined by their reflectance, or absorbance, as a function of wavelength.
Signatures are due to electronic transitions of atoms and vibrational stretching and bending of structural groups of atoms that form molecules and crystals.

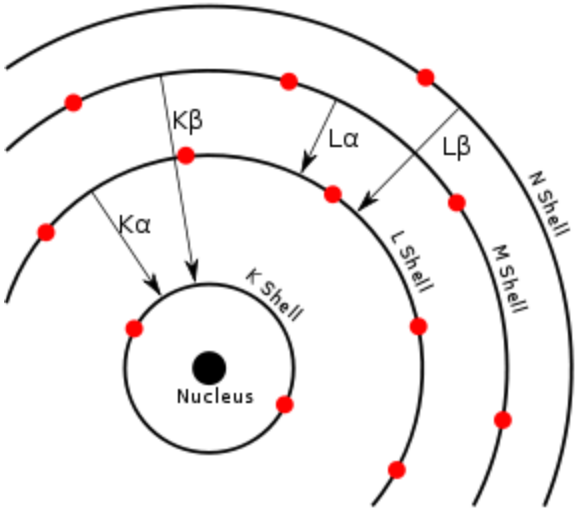
Key Point: Atoms fluoresce at specific energies when excited by X-rays.

Energy source: X-ray tube or radioisotope



X-ray fluorescence (XRF)

When exposed to x-rays, electrons are ejected from inner orbitals



Subsequently, electrons of higher energy orbitals fall into the lower orbitals. A fluorescent photon with a characteristic energy is released.

Facts of Portable XRF

- Excitation source is either:
  - ➡ X-ray tube with target of Ag (silver), Ta (tantalum), Au (gold), Rh (rhodium), W (Tungston)
  - ➡ Radioisotope (e.g., Fe-55, Co-57, Cd-109)
- Energy Dispersive X-ray fluorescence
- Detectors: Proportional counter detector tube, solid state Si-PIN detection system, Silicon Drift Detectors (SDD)
- Analysis covers area of 1 cm^2 to a depth of approximately 2mm
- Minimum set up and calibration required (Factory Calibrated with alloy chip)
- Nondestructive analysis

Advantages of Portable XRF

- Fast results

- Portable and easily transported to job sites; can check on an airplane as baggage or carry-on

- Delivers qualitative and/or quantitative multi-element analysis; simultaneous determination

- Wide range of application
    - Alloy determination / chemical analysis
    - Soil analysis
    - Mineral analysis

- Can be used on many different samples - solids, powders, liquids, etc.

- Little or no sample preparation required

Elements quantified by XRF

hydrogen 1 H 1.0079																		helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122												boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305												aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * *	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]				

*Lanthanide series	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
**Actinide series	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

Limitations of Portable XRF

•Very difficult to detect or quantify lighter elements
e.g., Si, Al, Li, Be, P, B, C

Detection limits is in parts per million (ppm) range and varies with element

•XRF is a surface/near surface technique
Only measures the portion of sample directly in front of window
Measures ALL material in front of analyzing window

•User must understand the dangers of x-rays, know the fundamentals of radiation protection

Factors impacting performance

- Source and energy of x-ray
- Detection system
- Sample preparation/presentation
  - In situ (direct field measurement)
  - Bagged sample (mixed)
  - Prepared sample (dried, sieved, ground, mixed)
- Calibration of instrument – internal vs site specific standards
- Analysis/count time (30 sec to 5 min)
- Chemical/physical matrix effects
- Interelement spectral interferences
- Moisture – esp. >20%

Companies

- Bruker Tracer IV-SD
- Oxford X-MET 5000
- Olympus Innov-X Delta RXF
- Thermo Scientific Niton XL2 GOLDD
- QSX Quickshot

Comparison of Detection Limits for ICP and PXRD

Analyte	SSL Acid Digestion; ICP	InnovX 3-beam; Ta/Au tube
	---------- mg kg-1	----------
Al	31	5000
Ca	9	25
Fe	3	5
K	34	40
Mg	5	10000
Mn	1	4
Na	28	No detection
P	29	600
As	0.0001	2
Cd	0.0001	7
Cr	0.0062	8
Cu	0.0002	6
Hg	0.0001	3
Ni	0.0009	15
Pb	0.0001	3
Zn	0.0006	4

Correlation of X-ray Fluorescence and ICP Spectroscopy for Elemental Determination In Composted Products

Element	n	ICP-XRF r^2
Cu	34	0.95
As	7	0.84
Zn	65	0.81
Mn	63	0.67
Fe	38	0.67
Ca	56	0.51
K	53	0.14

Weindorf, et al., 2008. Compost Science and Utilization. 16(2): 79-82.

Recovery of NIST Standard Reference Material 1646-esturaine Sediment

Element	Certified	PXRF	Recovery
	------- mg kg^{-1} --------		%
As	11.6	11	95
Cd	0.36	4	1111
Co	10.5	575	5476
Cr	76	59	78
Cu	18	22	122
Hg	0.63	2	3175
Mn	375	318	85
Ni	32	16.3	51
Pb	28	29	103
Ti	5100	5092	100
Zr	138	127	92

Weindorf et al., 2011, Environ. Monit. Assess.

Utility for Soil Survey

- **Geographic profiling of elemental constituents in profiles**
- **Target elemental concentration in calcic, gypsic, spodic, placic horizons**
- **Mapping/spatial variability of contaminants across landscape**
- **Assist in selection of sites for sample collection**

New York City Soil Survey
Rich Shaw

Innov-X Delta Standard XRF Environmental Analyzer
NYC Soil Survey office, Staten Island, NY
Cost: $30,875; Acquired Oct 2010

Main Objective for purchase: screening soil for community gardens in NYC

Current Applications:

•Differentiating serpentinitic from non-serpentinitic soils in glacial till using Cr & Ni contents (CSI grad student project)

•Determine atmospheric additions of trace metals in urban woodland soils (CSI grad student project)

•Assess contamination levels of tidal marsh soils, anthropogenic soils; examining correlation between artifacts & trace metals; looking at geographic distribution (hot spots) of trace metals; spatial variability of metal content

Current Procedure:
Air-dry and sieve sample; analyze through sample bag

Will compare with:
•**EPA XRF method 6200 of grinding the soil sample** with mortar & pestle
•Wet chemistry

Evaluation of Portable X-ray Fluorescence for Gypsum Quantification in Soils

David C. Weindorf, et al., Soil Sci 2009

- Time saving advantage; total Ca readings in 30 sec.

- Conversion of Ca content to % gypsum requires absence of calcite

- Matrix effects due to morphology and size of crystals; requires multiple readings across landscape and/or within a soil profile to average out variability and obtain a more consistent gypsum estimate,

- Yet, laboratory limits scope of sampling because of costs of laboratory analyses.

- Finally, an inherent advantage is having the gypsum quantified by the field staff who work in these soils and have a strong sense of expected trends, variability across the landscape, and correlations with different vegetative communities.

Conclusions

- PXRF is viewed by EPA as a screening method
- The principal advantage is rapid field analysis and ease of use.
- Expensive cost
- Detection limits affected by several factors, some controlled by the user.
- Proper training about limitations and safety is essential
- Multiple applications in soils survey for element specific measurements