Application note | AN41665

Complete soil and sediment analysis

Thermo Scientific ARL PERFORM'X Series Advanced X-Ray Fluorescence Spectrometers

Keywords
ARL PERFORM'X 4200 W, soil, sediment, XRF, X-ray fluorescence

Introduction

Geological samples are formed by constant deposition of inorganic and organic materials over millions of years. As the layers of deposits accumulate, the weight from the additional layers creates pressure and increased temperature creating rocks or other formation. Over time, these formations are eroded and carried away by rain, wind and snow and deposited in streams and lake beds.

Analysis of these materials is of vital importance because it gives not only indications of the mineral bodies present, but also the environmental contaminates.

Elemental analysis of soil and sediment samples encompasses a vast variety of material and matrix types with many elements to be analyzed having concentrations ranging from low parts per million (ppm) levels to major weight percentages of the composition. These attributes make accurate quantitative analysis ideal for wavelength dispersive X-ray fluorescence (WDXRF).

WDXRF is the most commonly used technique for the analysis of geological base materials in particular due to its (a) accuracy (b) precision (c) wide dynamic range of concentrations (from ppm to 100 %) (d) simplicity compared to other analytical techniques (e) automation possibilities to handle high throughput of samples and (f) the widest element range.

To aid in the total analysis of these sample types, our company has produced a factory calibration specifically for geochemical sample analysis. This analysis involves two groups of elements or oxides: majors and minors analysis and the traces analysis.

The analysis of majors and minors should be as accurate as possible. In many processes, these elements are either materials of interest or the largest influential factor on the analysis of other elements in the sample. If pressed pellets are used, there are several sample related effects such as (a) mineralogical (b) particle size and (c) in-homogeneities that influence the accuracy of analysis.

The best method for combating these influences is by using fused bead sample preparation. Fusion is the most accurate method of preparation for XRF samples.

Essentially, the procedure consists of heating a mixture of the sample and a borate flux, namely lithium tetraborate and/or lithium metaborate at high temperature (1000 °C – 1100 °C) so that the flux melts and dissolves the sample.

The overall composition and heating conditions must be set so that the end product after cooling is a one phase glass.

The fusion bead preparation is not appropriate for the analysis of trace elements primarily because of the dilution ratio, making the determination of very low concentrations (1-30 ppm for example) difficult.

For these reasons, a pressed pellet is the most suitable sample preparation method for the analysis of trace elements. The physical effects which influence the accuracy discussed above are also not as significant for trace elements analysis.

Instrument

Thermo Scientific™ ARL™ PERFORM'X Series Spectrometer used in this analysis was a 4200-watt system. This system is configured with 6 primary beam filters, 4 collimators, up to nine crystals, two detectors, helium purge and our 5GN+ Rh X-ray tube for best performance from ultra-light to heaviest elements thanks to its 50 micron Be window. This X-ray tube fitted with a low current filament ensures an unequalled analytical stability month after month.

Designed for demanding laboratories, the ARL PERFORM'X Spectrometer offers dual sample loading and is able to process more than 60 samples per hour, offering rapid and precise analysis of up to 84 elements.

The ARL PERFORM'X Spectrometer offers the ultimate in performance and sample analysis safety. Its unique LoadSafe design includes a series of features that prevent any trouble during sample pumping and loading. Liquid cassette recognition prevents any liquid sample to be exposed to vacuum by mistake. Over exposure safety automatically ejects a liquid sample if X-ray exposure time is too long.

For spectral chamber protection, the ARL PERFORM'X Spectrometer uses a helium shutter designed for absolute protection of your goniometer during liquid analysis under helium operation. In the "LoadSafe Ultra" optional configuration, a special X-ray tube shield provides total protection against sample breakage or liquid cell rupture.

For added analytical capability, the ARL PERFORM'X Spectrometer offers the features of small spot and elemental mapping analysis, allowing for analysis at either 1.5 mm or 0.5 mm sizes. These tools enhance the capabilities of an XRF system by providing additional screening, contamination identification, inclusion analysis and segregation/non-homogeneity mapping.

Calibration ranges and results

Table 1 illustrates the elements and the working concentration ranges used in the fused bead analysis. A working curve is established for each element using the Multi- Variable-Regression incorporated in the innovative Thermo Scientific™ OXSAS™ Software. Theoretical alpha factors are used for all matrix corrections.

Table 1: Concentration ranges of the various oxide types with the standard errors of estimate achieved (fused-beads preparation).

Elements	Range % Ignited Samples	Typical SEE (%) Ignited Samples
Na_2O	0.4-10.4	0.1
MgO	0.2-97.3	0.22
Al_2O_3	0.2-89.2	0.16
SiO_2	0.3-99.7	0.23
P_2O_5	0.06-40.0	0.11
SO_3	0.05-46.2	0.05
K_2O	0.03-15.4	0.03
CaO	0.03-94.4	0.32
TiO_2	0.02-3.8	0.03
Cr_2O_3	0.02-17.4	0.03
MnO	0.02-8.0	0.01
Fe_2O_3	0.03-94	0.15

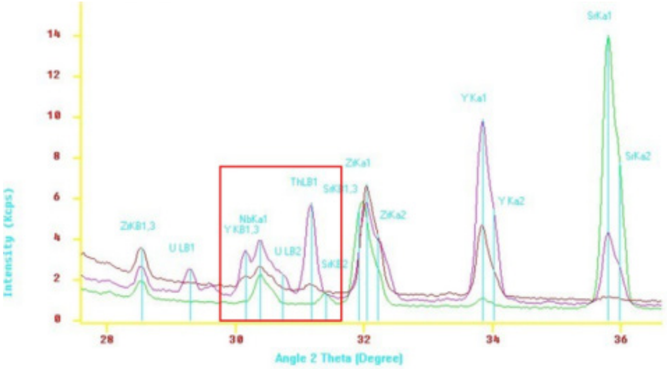
Table 2: Typical limits of detection in 40s obtained on various oxides (fusions with 1:11 dilution).

Elements	Average Conc %	St. Dev. (%)	LoD mpm
Na_2O	0.053	0.005	120
MgO	0.014	0.0021	63
Al_2O_3	0.015	0.0019	60
SiO_2	0.003	0.0017	50
P_2O_5	0.005	0.0005	15
SO_3	0.271	0.0009	27
K_2O	0.002	0.0007	21
CaO	0.002	0.006	18
TiO_2	0.005	0.003	10
Cr_2O_3	0.001	0.0004	12
MnO	0.0003	0.0003	10
Fe_2O_3	0.003	0.0003	10

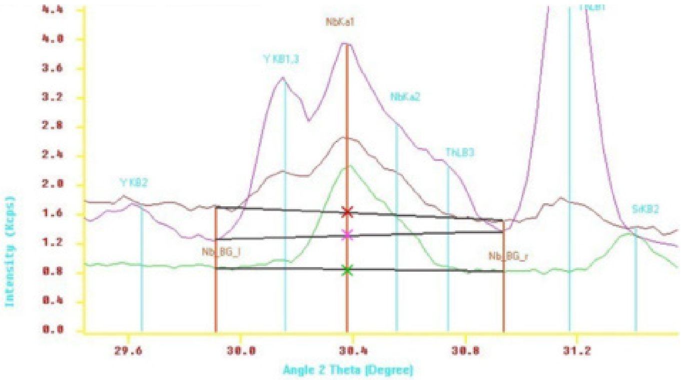
The trace element analysis consists of the measurement of 30 additional elements for quantification. These elements are all represented in the PPM concentration range. Table 3 lists the elements, analytical ranges standard estimates of error (SEE), typical limits of detection (LoD), precision and analysis times used to achieve these results using a calibration for pressed pellets.

Table 3: Data for a pressed pellets calibration on rocks and minerals (LoD = limit of detection; LoQ = limit of quantification, usually 3x LoD). The precision shown for the concentration level and the counting time listed.

Elements	Line	Analytical Range [PPM]	Number of samples	SEE [PPM]	LoD [PPM]	Precision [PPM]	Concentration [PPM]	Analysis time [s]
Ag	Kα	LoQ-35	5	5	2.5	2.1	8	20
As	Kβ	LoQ-600	13	7	2	2.5	116	10
Ba	Lα	LoQ-1000	12	6	2	4.2	252	10
Bi	Lα	LoQ-50	7	2	0.8	0.6	10	20
Ce	Lβ	LoQ-200	10	10	3.8	4	57	30
Cd	Kα	LoQ-42	9	3	2.5	3.1	8	20
Cr	Kα	LoQ-1300	12	6	0.6	1.1	35	6
Co	Kα	LoQ-80	13	2	0.6	1.2	9	20
Cu	Kα	LoQ-3000	13	12	0.5	0.6	80	6
Se	Kα	LoQ-600	2			0.3	2	6
Ti	Kα	LoQ-8000	13	98	0.6	8.6	1457	6
Pb	Lβ	LoQ-5200	13	46	1.2	2	308	10
Zn	Kα	LoQ-1000	12	25	0.5	1.5	362	6
Sn	Kα	LoQ-400	7	1	3.5	3.9	40	20
Sb	Kα	LoQ-40	9	3	3.5	3	30	20
W	Lα	LoQ-120	7	2	1.2	2.2	36	6
Mo	Kα	LoQ-90	4	2	0.4	0.9	8	6
Mn	Kα	LoQ-10000	11	16	0.7	4.7	1383	6
Nb	Kα	LoQ-100	7	1	0.3	0.7	15	6
Ni	Kα	LoQ-180	12	3	0.7	0.7	16	6
V	Kα	LoQ-170	13	9	0.5	1.9	42	6
Y	Kα	LoQ-40	6	3	0.5	0.3	32	6
S	Kα	LoQ-4000	10	250	1.2	3.6	96	6
Sr	Kα	LoQ-340	10	6	0.5	1	23	6
Te	Kα	LoQ-500	2	NA	NA	NA	NA	20
Zr	Kβ	LoQ-230	8	6	0.4	2.4	188	20
Th	Lα	LoQ-70	9	1	0.6	1.1	20	20
U	Lα	LoQ-17	5	1	1	0.8	8	10
Rb	Kα	LoQ-500	14	6	0.3	1.3	265	6
Hg	Lα	LoQ-35	5	3	1.4	2.1	30	100



Graph 1: 2-Theta pack scan from 25



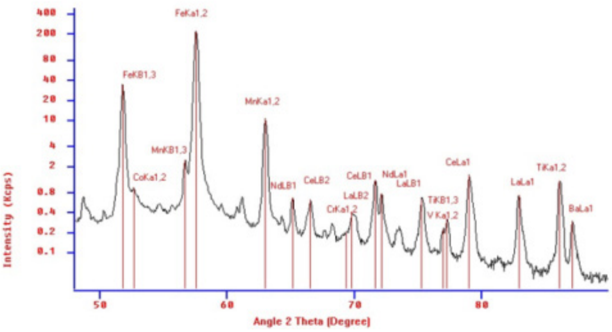
Graph 2: Zoomed in region of graph 1.

The ability to accurately analyze trace elements in geological samples depends upon the XRF instrument sensitivity, resolution and background/overlap correction functions. The ARL PERFORM'X spectrometer offers the most sophisticated spectrometer on the market to tackle these very issues. Graphs 1 and 2 illustrate the accuracy and precision achievable from background correction with its completely digital goniometer and unique optical design allowing for reduced background signal due to its polarization effect. Graph 3 shows the superior resolution provided by the enhanced optical configuration.

The Thermo Fisher Scientific X-ray tube is an exclusive filament design which reduces the current needed to produce the same excitation as a standard X-ray tube.

This feature reduces dramatically the tungsten buildup on the tube window, allowing for improved long-term stability.

All calibrations are based on international certified reference materials for which the certificates of analysis are provided.



Graph 3: 2-Theta pack scan from 55° to 90° using LiF220 crystal and scintillation detector showing the excellent spectral resolution and the low spectral background (log scale on the vertical axis).

Conclusion

It is seen that analysis of geological samples can be performed with ease on the ARL PERFORM'X Sequential XRF Spectrometer using a 2-step process. The precision and accuracy for the major and minor elements are best preformed using a standard fused bead method, while trace element analysis is best performed using a simple pressed pellet method.

This method allows for complete elemental analysis of many material types and matrixes. It should be noted that all calibration ranges and elements analyzed can be extended with the simple addition of more certified reference standards.

Furthermore, operation is made easy through the innovative OXSAS software operates with the latest Microsoft Windows® 10 packages.

To see our full X-ray product portfolio, please visit
thermofisher.com/XRF