Complete soil and sediment analysis
Thermo Scientific ARL PERFORM’X Series Advanced X-Ray Fluorescence Spectrometers

INTRODUCTION

Geological samples are formed by constant deposits of inorganic and organic materials over millions of years. As layer of deposit accumulate upon layer, the weight creates pressure and increased temperature creating rocks or other formations. 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 importance as it gives not only indications of the mineral bodies present, but also environmental contaminates.

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 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 widely used technique for the analysis of geological base materials due to its (a) accuracy (b) precision (c) wide dynamic range of concentrations (ppm – 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, Thermo Fisher have developed factory calibrations specifically for geochemical sample analysis. This analysis involves two groups of elements or oxides: majors and minors and the trace elements.

The analysis of majors and minors should be as accurate as possible. In many processes, these elements are either material of interest or the largest influential factor in the analysis of other elements in the sample. If pressed pellets are used, there are multiple 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 (1000ºC – 1100ºC) so that the flux melts and dissolves the sample. The overall composition and heating conditions must be set in order to produce a one phase glass after cooling. The ratio sample:flux is usually 1:11.

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 – 50 ppm for example) difficult.

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

INSTRUMENT

The Thermo Scientific™ ARL™ PERFORM’X Series Spectrometer used for this analysis was a 4200-watt system. This system is configured with a gearless goniometer fitted with 4 collimators, up to nine crystals and two detectors. Six primary beam filters are available to improve peak to background ratio for selected elements. The 5GN+ X-ray tube provides best performance from ultra-light to heaviest elements thanks to the rhodium anode and its 50 micron Be window. This new 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 is capable of a high throughput thanks to its fast goniometer and dual sample loading and can cover up to 84 elements of the Mendeleev periodic table.

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.

The Secutainer system protects the primary chamber by vacuum collecting any loose powders in a specially designed container, easily removed and cleaned by any operator.

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.

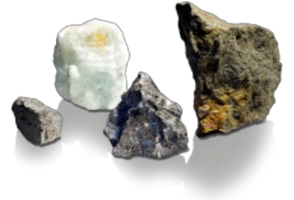


Table 1: Concentration ranges of the various oxide types with the standard errors of estimate achieved

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 – 3.7	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 precision and limits of detection in 40s obtained on various oxides (fusions with 1:12 dilution)

Elements	Average Conc (%)	Precision St. Dev. at the Avg Conc (%)	LoD ppm
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

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 Multivariable-Regression incorporated in the “state-of- the-art” Thermo Scientific™ OXSAS software. Theoretical alpha factors are used for all matrix corrections.

The trace element analysis consists of the measurement of 30 additional elements for quantification. Table 3 lists the elements, analytical ranges, standard errors of estimate (SEE), typical limits of detection (LoD) in 100s counting time, precision and analysis times used to achieve these results using the Thermo Fisher Scientific Geo-Chemical calibration.

Table 3: LoD – limit of detection and precision

Elements	Line	Analytical Range [ppm]	Number of Samples	SEE [ppm]	LoD [ppm] 100s	Precision [ppm]	At a Concentration of.. [ppm]	Analysis [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	-	-	-	-	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

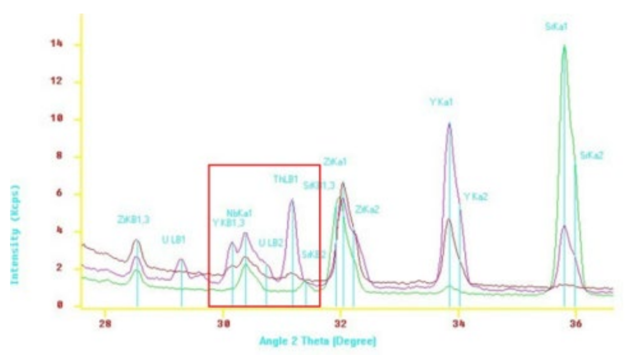
The ability to accurately analyze trace elements in geological samples depends upon the XRF instruments sensitivity, resolution and background/overlap correction functions. The ARL PERFORM’X Spectrometer offers the most sophisticated spectrometer on the market to tackle this. Graphs 1 and 2 illustrate the analysis strategy for background correction used with its fully digital goniometer. Its unique optical design allows for reduced background signal due to its polarization effect.

All calibrations are based on international certified reference materials.

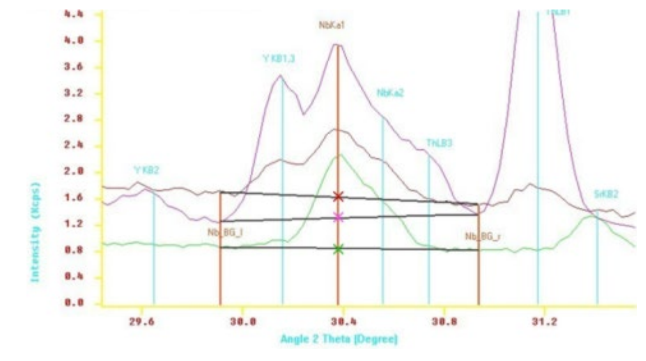
CONCLUSION

Analysis of geological samples can be performed with high performance with the ARL PERFORM’X Sequential XRF Spectrometer. The highest accuracy for the major and minor elements is obtained using the 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 matrices. It should be noted that all calibration ranges and elements analyzed can be extended with the simple addition of certified reference standards.

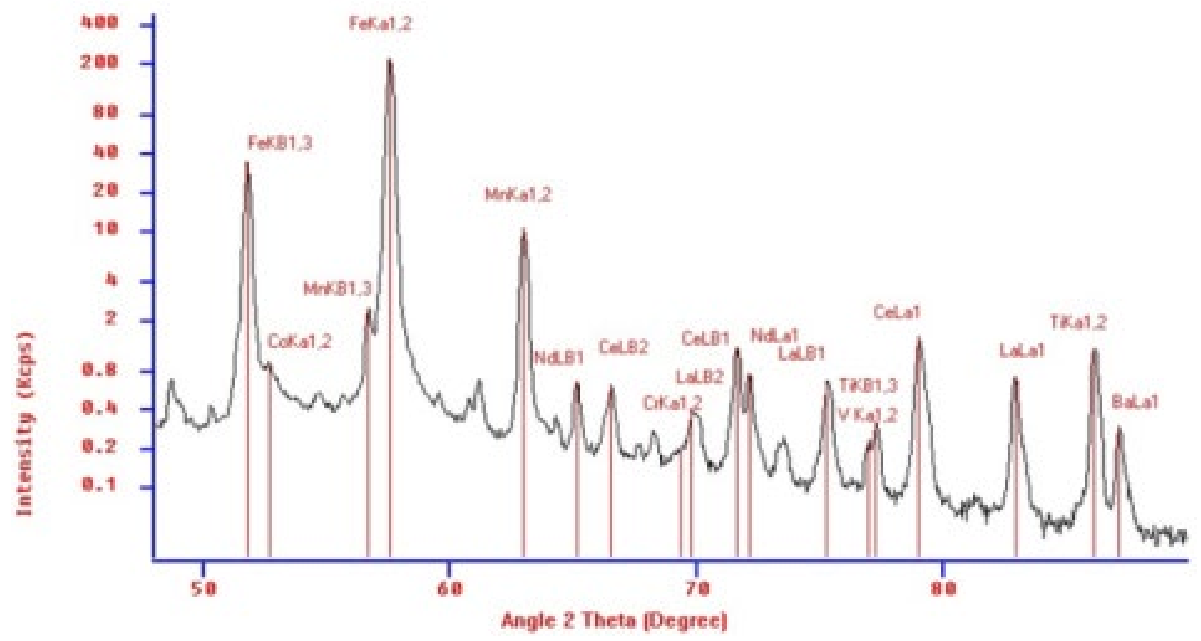
Operation is made easy through the state-of-the-art OXSAS software that runs with the latest Microsoft Windows® 10 package.



Graph 1: 2-Theta scans from 25 degrees to 38 degree using LiF220 crystal and scintillation detector



Graph 2: zoomed region of graph 1



Graph 3: 2-Theta scan from 55 degrees to 90 degree using LiF220 crystal and scintillation detector showing the excellent spectral resolution

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