Total oxide X-ray analysis

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

Keywords

ARL PERFORM'X 4200 W, oxide, XRF, X-ray fluorescence

Introduction

There are many techniques for elemental analysis. However, none are as flexible in analytical range and material type as X-ray fluorescence. Wavelength dispersive X-ray fluorescence (WDXRF) allows measurement of up to 83 elements of the periodic table in samples of various forms and nature: solids or liquids, conductive or non- conductive. Other advantages of XRF over other techniques are speed of analysis, generally easy sample preparation, very good stability, precision and wide dynamic range (from ppm levels to 100 %).

The two largest factors in analysis accuracy and precision in WDXRF are accuracy of standards and sample preparation. Standard accuracies are typically derived by performing multiple analyses on a material by several different laboratories. The most common form of this type of analysis is done using round robin testing. A statistical computation of all results is performed to achieve a certified reference value for the measured elements. These materials are commercially available via many government agencies and private companies.

As for the second issue of sample preparation regarding powder and non-homogenous solids, fusion is the most accurate method of preparation for XRF. Fusing oxide materials is the best way to completely remove both grain size and mineralogical effects.

Essentially, the procedure consists of heating a mixture of sample and a borate flux, namely lithium tetraborate and/ or lithium metaborate at high temperature (1050 to 1100°C) so that the flux melts and dissolves the sample. The overall composition and cooling conditions must be such that the end product after cooling is a one phase glass.

The Thermo Scientific General Oxide calibration is a complete analytical package that provides the possibility to analyze a very large variety of minerals based on a sample preparation by fusion.

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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 innovative X-ray tube fitted with a low current filament ensures an unequalled analytical stability month after month.

The ARL PERFORM'X 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.

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

The ARL PERFORM'X analyzer also features small spot and elemental mapping analysis allowing analysis of 0.5 mm areas (or 1.5 mm on option). These features enhance the capabilities of this XRF spectrometer by providing additional screening, contamination identification, inclusion analysis and segregation/ nonhomogeneity mapping.

Calibration ranges and results

The types of oxides that can be addressed with the General Oxide calibration and their concentration ranges are shown in Table 1. A working curve is established for each element using the multivariable- regression incorporated in the state-of-the-art Thermo Scientific OXSAS software package.

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 - 15.7	0.11
SO_3	0.05 - 3.7 - 45	0.05
K_2O	0.03 - 14.3	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 1. Concentration ranges of the various oxide types with the standard errors of estimate achieved.

Theoretical alpha factors are used for all matrix corrections. Loss on ignition values, which spread up to 47 % can be used for correction purposes in the multivariable regression. The Standard Error of Estimate (SEE) is a measure of the accuracy of analysis. It is the average error between the certified concentrations of the standard samples and the calibration curve for a given oxide. Gypsum has been added recently hence the additional high level sulfur oxide value.

Elements	Average Conc %	St. Dev. (%)	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

Table 2. Precision at low levels and typical limits of detection in 40s obtained on various oxides (fusions with 1:12 dilution).

Elements	Analytical Line	Concentrations %	St. Dev.
Na_2O	Kα	0.48	0.007
MgO	Kα	13.40	0.01
Al_2O_3	Kα	8.10	0.01
SiO_2	Kα	39.60	0.03
P_2O_5	Kα	0.04	0.0009
SO_3	Kα	0.15	0.0015
K_2O	Kα	0.17	0.0011
CaO	Kα	14.63	0.0093
TiO_2	Kα	3.71	0.0067
Cr_2O_3	Kα	0.07	0.0007
MnO	Kα	0.17	0.0009
Fe_2O_3	Kα	18.37	0.0107

Table 3. 12-day stability test without any drift correction.

Conclusion

It is seen that analysis of fused beads can be performed with ease on the ARL PERFORM'X sequential XRF spectrometer. The precision and accuracy are shown to be excellent in short term and long term analyses. On special request all calibration ranges can be extended with the simple addition of more certified reference standards.

Furthermore, operation is made easy through the state-of-the-art Thermo Scientific OXSAS software which operates with the latest Microsoft Windows® 10 packages..