APPLICATION NOTE

No. AN41702

General oxide calibration

ARL OPTIM'X Low Power WDXRF Sequential-Simultaneous Spectrometer

Key words
ARL OPTIM'X, oxide, minerals, X-ray fluorescence, XRF

Introduction

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. 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 Thermo Scientific ARL OPTIM'X low power WDXRF instrument, calibrated with the General Oxide program allows the analysis of a very large variety of minerals, e.g. dolomite, limestone, bentonite, marl, sand, laterite, feldspar, bauxite, magnesite, firebrick, silica brick, sillimanite, rocks, slags, cement, iron ores, ceramics, etc.

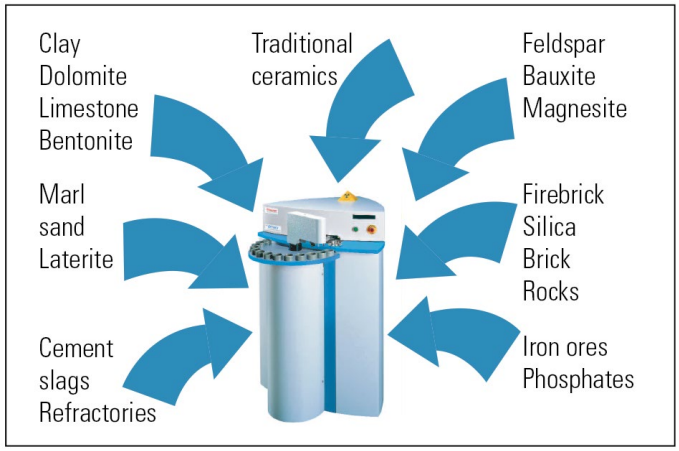

Figure 1: Various materials analyzed by the ARL OPTIM'X with a General Oxide calibration

Calibration ranges and results

The types of oxides which can be addressed and their concentration ranges are shown in table 1. A working curve is established for each element using the Multi-Variable-Regression incorporated in the OXSAS software package. 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 multi-variable regression. The Standard Error of Estimate (SEE) is a measure of the accuracy of analysis. It is the average error between the certified concentration of the standard samples and the calibration curve of a given oxide.

The limits of detection (LOD) determined with precision tests at low concentrations are listed in Table 2 for the various oxides.

The analysis times were 60s per element with the SmartGonio™. Two fixed channels can also be added for specific elements. Depending on the element and the precision required its counting time can be modified. The fixed channels can count during the full time when the SmartGonio is analyzing, thus improving the limit of detection and precision for the corresponding elements/ oxides, e.g. 10 minutes in this example. Table 2 gives some comparative data for limits of detection.

Element	Crystal	Range [%]	Typical SEE [%] ignited samples
CaO	LiF200	0.03 - 94.4	0.29
SiO_2	PET	0.35 - 99.7	0.21
Fe_2O_3	LiF200	0.025 - 94	0.15
MgO	AX06	0.2 - 97.3	0.2
Al_2O_3	PET	0.16 - 89.2	0.16
K_2O	LiF200	0.03 - 15.4	0.05
MnO	LiF200	0.02 - 8 0.	03
Cr_2O_3	LiF200	0.02 - 17.4	0.03
TiO_2	LiF200	0.02 - 3.8	0.03
P_2O_5	PET	0.06 - 40.0	0.10
SO_3	PET	0.05 - 3.7	0.05
Na_2O	AX06	0.4 - 10.4	0.2

Table 1: Concentration ranges and Standard Error of Estimate and limits of detection for the various oxide types using the SmartGonio

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Element	Typical LOD SmartGonio (3 Sigma) 60S	Typical LOD fixed channel (3 Sigma) 120S	Typical LOD fixed channel (3 Sigma) 10’
CaO	75 ppm	60 ppm	27 ppm
SiO_2	160 ppm	150 ppm	67 ppm
Fe_2O_3	60 ppm	25 ppm	11 ppm
MgO	850 ppm	650 ppm	297 ppm
Al_2O_3	240 ppm	90 ppm	40 ppm
K_2O	68 ppm	30 ppm	13 ppm
MnO	53 ppm	n.m.	n.m.
Cr_2O_3	55 ppm	n.m.	n.m.
TiO_2	75 ppm	n.m.	n.m.
P_2O_5	200 ppm	50 ppm	22 ppm
SO_3	180 ppm	80 ppm	36 ppm
Na_2O	1000 ppm	1000 ppm	447 ppm

Table 2: Typical limits of detection obtained on various oxide types using samples fused with 1:12 dilution. (n.m. = not measured)

Sample preparation

Standard samples are dried prior to being fused. Standards are prepared from ignited or non-ignited powder as 35 mm diameter fused beads. In case of ignition it is carried out for 1 hour at 1050°C. The fusion is made from a mixture of sample and Fluorex 65 flux (dilution 1:12). A small amount of LiBr is used as non-wetting agent.

Two types of sample preparation can be used:

- No calcination of samples (→ quicker preparation for clean oxides)

  Loss on ignition is estimated by the software, therefore all elements must be measured for this automatic correction to work. If other elements/oxides than the 12 measured are present, the loss on ignition should be introduced through manual input in order to improve accuracy of analysis. Note that fusion from non ignited samples can be fatal for the Pt-Au crucible in case small metallic particles are present in the sample.

- Fusion from ignited samples (→ better accuracy and safer fusion)

  Samples are ignited at 1050°C for 1 hour and their loss on ignition (LOI) is determined. Samples are prepared from ignited powder as 35 mm diameter fused beads. Ignited samples are easier and safer to fuse especially in the case where small metallic particles are present.

  Samples prepared by both methods can be analyzed using the same calibration curves.

Calibration

The General Oxide pre-calibration can be carried out in the factory at Ecublens, Switzerland using international certified standards fused as mentioned. No standard samples are delivered with this pre-calibration, but a series of stable and polished setting-up samples for maintenance of the calibration over time are included.

Alternatively the instrument can be calibrated at the customer site using a kit of 24 international certified standards of oxide materials available from us.

Configurations for the analysis of oxides

The configurations that are recommended for the analysis of oxides are the following:

- ARL OPTIM’X WDXRF spectrometer in sequential configuration: SmartGonio for elements F to Fe (crystals AX06 and PET; detector FPC)

- ARL OPTIM’X WDXRF spectrometer in sim-seq configuration: Fixed channels for Na and Mg and SmartGonio for elements Al to Zn (crystals PET and LiF200; detector FPC)

The latter configuration will allow faster analysis due to parallel analysis of the fixed channels and the SmartGonio.

Together with the above mentioned instruments an analytical package can be proposed consisting of the following items:

- “General Oxide” calibration including a set of six stable and polished setting-up samples for maintenance of the calibration over time

- Fusion machine to transform oxidic materials into glass beads (e.g. Claisse Fluxy or Vulcan VAA)

- Pt/Au crucible and Pt/Au mould

- Fusion flux Fluorex-65 (66 % $Li_2B_4O_7$ - 34 % $LiBO_2$)

- Fusion additive LiBr

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Final remarks

A large variety of oxide materials can be analysed with good accuracy using the General Oxide calibration.

The high dilution makes it possible to fuse all these various materials, even the ones with high levels of manganese, chrome or iron oxides. The drawback is that the limits of detection are higher due to the dilution effect.

Therefore in case some of the calibration ranges should be extended towards lower levels the use of a lower dilution should be considered, e.g. 1:5 for example.

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