

Total oxide X-ray analysis with ARL 9900 IntelliPower Series Simultaneous/Sequential X-ray Fluorescence Spectrometers

Author: Didier Bonvin
Product Manager, XRF

Introduction

Wavelength-dispersive X-ray fluorescence (WD-XRF) 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 %).

Accuracy of analysis of powders can be impaired by particle size effects and mineralogical effects. Although inhomogeneities and particle size effects can often be minimized by grinding below 50 microns and pelletizing at high pressure, often mineralogical effects cannot be completely removed or harder particles cannot be broken down below the required size.

Figure 1: Many different materials can be analyzed with an ARL 9900 spectrometer calibrated with our General Oxide calibration.

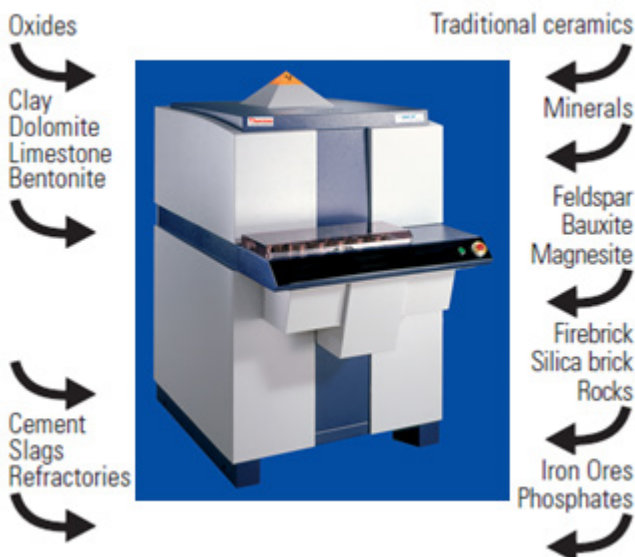


Figure 2: Transformation of the powder material into a glassy sample by fusion at high temperature.



Fusing these oxidic materials is the best way of completely removing 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 (1000°-1200°) 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™ ARL™ 9900 Series X-ray Fluorescence Spectrometer can be calibrated from the factory as a complete analytical package which provides the possibility to analyze a large variety of minerals (Figure 1), using the general oxide calibration based on a sample preparation by fusion (Figure 2).

Calibration ranges and results

The types of oxides that are 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 “state-of-the-art” Thermo Scientific™ 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 concentrations of the standard samples and the calibration curve for a given oxide.

The limits of detection (LOD) determined with precision tests at low concentrations are listed in Table 2 for the various oxides when the universal goniometer is used. The analysis time per element can range from 4 to 40 seconds depending on the element and the precision required. Obviously the total counting time can be decreased substantially when fixed channels monochromators are used for several elements/oxides.

Sample preparation

Standard samples are dried prior to being fused as shown in Figure 2. Standards are prepared from ignited or non-ignited powder as 35 mm diameter fused beads. Ignition is carried out for one hour at 1050°C when required. The fusion is made from 0.7 grams of sample, 7.7 grams of Fluorex 65 and 0.02 grams of LiBr (dilution 1:11) on a Katanax electrical fusion machine or a gas fusion machine (Vulcan or Fluxana).

Two types of sample preparation can be used:

a. 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 to the Pt-Au crucible in case small metallic particles are present in the sample.

b. 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 case small metallic particles are present. Samples prepared by both methods can be analyzed using the same calibration curves.

Table 1: Concentration ranges of the various oxide types with the Standard Errors of Estimate (SEE) achieved.

Elements	Range [%] ignited samples	SEE [%]
Al ₂ O ₃	0.04 - 89.2	0.16
CaO	0.006 - 94.4	0.32
Cr ₂ O ₃	0.05 - 17.2	0.03
Fe ₂ O ₃	0.05 - 93.9	0.15
K ₂ O	0.06 - 15.4	0.03
MgO	0.03 - 96.7	0.22
MnO	0.01 - 5.2	0.03
Na ₂ O	0.03 - 10.06	0.05
P ₂ O ₅	0.01 - 37.83	0.15
SO ₃	0.015 - 2.95	0.05
SiO ₂	0.26 - 99.9	0.23
TiO ₂	0.01 - 3.8	0.03

Table 2: Typical limits of detection on ARL 9900 Intellipower Series in 100s obtained on various oxides (fusions with 1:12 dilution).

	3600 W (3σ) [ppm]	2500 W (3σ) [ppm]	1200 W (3σ) [ppm]
CaO	12	14	20
SiO ₂	13	15	22
Al ₂ O ₃	32	38	55
Fe ₂ O ₃	12	14	20
MgO	74	89	128
Na ₂ O	143	172	248
SO ₃	17	20	29
K ₂ O	10	12	17
P ₂ O ₅	17	20	29
MnO	8	9	13
Cr ₂ O ₃	7	8	12
TiO ₂	7	8	12

Factory pre-calibration

The pre-calibration of the ARL 9900 WDXRF Spectrometer can be carried out directly in the factory prior to delivering the spectrometer to the client. We use certified standard samples prepared on a Katanax electrical fusion machine or a gas fusion machine (Vulcan VAA2 or Fluxana depending on customer choice). No standard samples are delivered with this pre-calibration, but a set of six stable and polished setting-up samples for maintenance of the calibration curves over time.

Alternatively a kit of 24 international certified standards of oxide materials is available to allow the customer to calibrate the instrument on-site using his own sample preparation equipment.

Conclusion

These results show that various types of minerals, raw materials as well as oxidic products can be analyzed with good accuracy and precision by coupling wavelength dispersive X-ray fluorescence and a sample preparation as fusion beads.

Thanks to a clever management of power, the ARL 9900 Intellipower Spectrometers can operate up to 2500 W without requiring external water cooling. Therefore neither tap water, nor a water cooler is required in these cases. At higher power levels (3.6 kW or 4.2 kW), energy savings and reduced stress on the X-ray tube are obtained thanks to intelligent management of the X-ray tube power. The configuration of the ARL 9900 Intellipower Spectrometers can be chosen either with just one sequential goniometer or with the addition of fixed channels to speed up the response time.

Furthermore the state-of-the-art OXSAS Analytical Software under Windows® 10 provides comprehensive analytical functions and ease of use.

Find out more at thermofisher.com/9900