

# Total Oxide X-Ray Analysis

## ARL ADVANT'X IntelliPower™ Series Sequential X-Ray Fluorescence Spectrometers

### Key Words

- ARL ADVANT'X
- Oxides
- Minerals
- XRF
- X-Ray Fluorescence

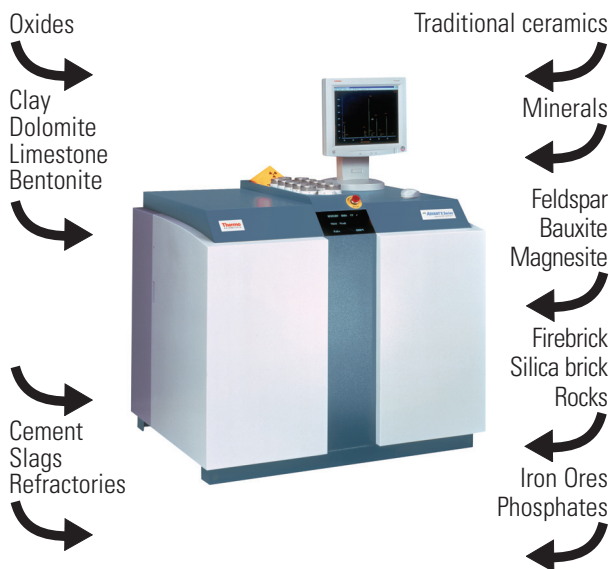


Fig. 1: Many different materials can be analyzed using the ARL TOXA package

### Introduction

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.

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 Total Oxide X-ray Analyzer (TOXA) is a complete analytical package which provides the possibility to analyze by Wavelength Dispersive X-Ray Fluorescence (WD-XRF) a very large variety of minerals, using the General Oxide calibration based on a sample preparation by fusion (Fig. 1).

### Calibration ranges and results

The types of oxides that 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 “state-of-the-art” 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. The analysis time per element can range from 4 to 40 seconds depending on the element and the precision required.

ELEMENT	RANGE [%] IGNITED SAMPLES	TYPICAL SEE [%] IGNITED SAMPLES
CaO	0.02 - 94.4	0.21
SiO <sub>2</sub>	0.35 - 99.7	0.17
Fe <sub>2</sub> O <sub>3</sub>	0.025 - 94	0.15
MgO	0.01 - 97.3	0.10
Al <sub>2</sub> O <sub>3</sub>	0.16 - 89.2	0.11
K <sub>2</sub> O	0.006 - 15.4	0.05
MnO	0.005 - 8	0.04
Cr <sub>2</sub> O <sub>3</sub>	0.002 - 17.4	0.03
TiO <sub>2</sub>	0.011 - 3.8	0.03
P <sub>2</sub> O <sub>5</sub>	0.014 - 40.0	0.04
SO <sub>3</sub>	0.015 - 3.7	0.05
Na <sub>2</sub> O	0.045 - 10.4	0.05

Table 1: Concentration ranges of the various oxide types with the Standard Errors of Estimate achieved

ELEMENT	TYPICAL LOD ON ARL ADVANT'X INTELLIPOWER SERIES		
	3600W (3 SIGMA) [PPM]	2500W (3 SIGMA) [PPM]	1200W (3 SIGMA) [PPM]
MnO	6	7	9
Cr <sub>2</sub> O <sub>3</sub>	5	6	8
TiO <sub>2</sub>	5	6	8
P <sub>2</sub> O <sub>5</sub>	13	16	20
SO <sub>3</sub>	13	16	20
Na <sub>2</sub> O	113	136	172
CaO	9	11	14
SiO <sub>2</sub>	10	12	15
Fe <sub>2</sub> O <sub>3</sub>	9	11	14
MgO	58	70	89
Al <sub>2</sub> O <sub>3</sub>	25	30	38
K <sub>2</sub> O	8	10	12

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

### 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. Ignition is carried out for 1 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 1:12) on a Claisse Fluxer machine or a Vulcan fusion machine.

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.

### Total Oxide X-ray Analyzer package

The package consists of the following items:

- ARL ADVANT'X SeriesWD-XRF spectrometer including the General Oxide calibration covering the ranges of Table 1
- Fusion machine to transform oxide materials into glass beads (Claisse Fluxy or Vulcan VAA2)
- 1 Pt/Au crucible and 1 Pt/Au mould
- Ultrasonic bath to clean mould and crucible after use
- 1 kg Fluorex-65 (66%Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-34% LiBO<sub>2</sub>): fusion flux
- 50 gr LiBr fusion additive
- A set of six stable and polished setting-up samples for maintenance of the calibration curves over time (A0 36057, A0 38173 and A0 35918)

The pre-calibration of the instrument is carried out in the factory at Ecublens, Switzerland using standards prepared on a Claisse Fluxy or Vulcan VAA2 machine (depending on customer choice). No standard samples are delivered with this pre-calibration .

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 X-ray fluorescence and a sample preparation as fusion beads.

Thanks to a clever management of power, the Thermo Scientific ARL ADVANT'X Intellipower spectrometers can operate at 1200W and even 2500W 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.

Furthermore the new state-of-the-art OXSAS analytical software under Windows® XP Professional provides comprehensive analytical functions and ease of use.

In addition to these offices, Thermo Fisher Scientific maintains a network of representative organizations throughout the world.

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