

## Total oxide X-ray analysis

### ARL X900 Simultaneous/Sequential X-Ray Fluorescence Spectrometer

#### Authors

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Figure 1. Many different materials can be analyzed with an ARL X900 Spectrometer calibrated with our General Oxide calibration.



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

#### Introduction

Wavelength dispersive X-ray fluorescence (WDXRF) allows measurement of up to 84 periodic table elements in samples of various forms and nature:

solids or liquids, conductive or non-conductive. Advantages of XRF over other techniques are speed of analysis, easy sample preparation, reliable 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. Inhomogeneities and particle size effects can often be minimized by grinding below 50 microns and pelletizing at high pressure, but mineralogical effects cannot be completely removed, and some hard particles cannot be broken down below the required size.

Fusing these oxidic materials is the best way of completely removing grain size and mineralogical effects. Essentially, the procedure consists of heating a portion of sample with a borate flux, usually lithium tetraborate and/or lithium metaborate. At high temperature (1000 ° - 1100 °C), 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 (Figure 2).

The ARL X900 Series XRF spectrometer can be calibrated from the factory as a complete analytical package that provides the possibility to analyze a large variety of minerals, using the general oxide calibration based on a sample preparation by fusion (Figure 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 multivariable regression incorporated in the Thermo Scientific™ OXSAS™ Analysis 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 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.

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 1 hour at 1050 °C when required. The fusion is made from 0.7 grams of sample, 7.7 grams of flux mix (66%  $\text{Li}_2\text{B}_4\text{O}_7$  - 34%  $\text{LiBO}_2$ ) and 0.02 grams of LiBr (dilution 1:11) on a Katanax® Inc. 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 to improve analysis accuracy. Note that fusion from non-ignited samples can be fatal to the Pt-Au crucible when 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 when small metallic particles are present.

			0.02 g LiBr non-wetting agent
Elements/ oxides	Range (%) ignited samples	Crystal	Typical SEE (%) universal gonio
$\text{Al}_2\text{O}_3$	0.2 – 90.8	PET	0.16
CaO	0.02 – 98.6	LiF200	0.35
$\text{Cr}_2\text{O}_3$	0.1 – 17.2	LiF200	0.02
$\text{Fe}_2\text{O}_3$	0.1 – 93.8	LiF200	0.2
$\text{K}_2\text{O}$	0.02 – 15.4	LiF200	0.03
MgO	0.05 – 95.4	AX06	0.4
MnO	0.02 – 5.5	LiF200	0.04
$\text{Na}_2\text{O}$	0.2 – 10.06	AX06	0.07
$\text{P}_2\text{O}_5$	0.2 – 37.7	PET	0.075
$\text{SO}_3$	0.07 – 57	PET	0.05
$\text{SiO}_2$	0.4 – 99.9	PET	0.19
$\text{TiO}_2$	0.03 – 7.7	LiF200	0.03

**Table 1. Concentration ranges of the various oxide types with the SEE achieved.**

## Typical LODs on ARL X900 Series

	4200 W	2500 W	1500 W
	(3 sigma) (ppm)	(3 sigma) (ppm)	(3 sigma) (ppm)
CaO	12	14	18
$\text{SiO}_2$	13	15	20
$\text{Al}_2\text{O}_3$	32	38	50
$\text{Fe}_2\text{O}_3$	12	14	18
MgO	74	89	115
$\text{Na}_2\text{O}$	143	172	223
$\text{SO}_3$	17	20	26
$\text{K}_2\text{O}$	10	12	15
$\text{P}_2\text{O}_5$	17	20	26
MnO	8	9	12
$\text{Cr}_2\text{O}_3$	7	8	11
$\text{TiO}_2$	7	8	11

**Table 2. Typical limits of detection in 100s obtained on various oxides using the goniometer at various power levels (fusions with 1 part sample / 11 parts flux).**

## Typical repeatability data

The following tables show typical results obtained with the universal goniometer on fusion beads of various oxidic materials. Analysis with the goniometer is sequential, hence elements/oxides will be measured one after the other. The total analysis time for the first example is 220 seconds for the nine oxides (Cr<sub>2</sub>O<sub>3</sub> is not shown as its % level was below the limit of detection).

Time	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s
Run	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MnO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	TiO <sub>2</sub>
1>	8.24	59.78	11.62	2.74	6.49	4.23	0.316	4.129	0.569	0.061	0.153
2>	8.28	59.76	11.64	2.74	6.49	4.25	0.318	4.154	0.573	0.052	0.151
3>	8.27	59.87	11.59	2.74	6.50	4.26	0.316	4.171	0.577	0.049	0.153
4>	8.28	59.71	11.59	2.73	6.50	4.25	0.316	4.164	0.574	0.052	0.148
5>	8.25	59.91	11.61	2.76	6.49	4.23	0.315	4.158	0.568	0.048	0.151
6>	8.28	59.72	11.70	2.76	6.49	4.23	0.316	4.143	0.572	0.055	0.152
<b>Avg</b>	<b>8.26</b>	<b>59.79</b>	<b>11.63</b>	<b>2.75</b>	<b>6.49</b>	<b>4.24</b>	<b>0.316</b>	<b>4.153</b>	<b>0.572</b>	<b>0.053</b>	<b>0.151</b>
<b>Std dev</b>	<b>0.018</b>	<b>0.079</b>	<b>0.04</b>	<b>0.011</b>	<b>0.005</b>	<b>0.014</b>	<b>0.001</b>	<b>0.015</b>	<b>0.003</b>	<b>0.005</b>	<b>0.002</b>

Table 3 a. Short term repeatability on a rock fused bead - goniometer at 20 seconds per line - 40kV/70mA.

Time	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s
Run	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MnO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	TiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>
1>	63.65	20.20	3.701	2.434	4.850	0.410	0.190	0.138	0.075	2.326	0.153	0.0010
2>	63.61	20.14	3.651	2.428	4.866	0.415	0.185	0.166	0.072	2.332	0.156	0.0011
3>	63.65	20.23	3.715	2.399	4.846	0.410	0.188	0.154	0.073	2.314	0.154	0.0008
4>	63.62	20.17	3.651	2.435	4.862	0.416	0.186	0.172	0.073	2.325	0.158	0.0011
5>	63.71	20.17	3.707	2.433	4.856	0.410	0.189	0.125	0.072	2.317	0.152	0.0010
6>	63.62	20.22	3.665	2.455	4.866	0.413	0.189	0.185	0.075	2.321	0.156	0.0009
<b>Avg</b>	<b>63.64</b>	<b>20.19</b>	<b>3.682</b>	<b>2.431</b>	<b>4.858</b>	<b>0.412</b>	<b>0.188</b>	<b>0.157</b>	<b>0.073</b>	<b>2.323</b>	<b>0.155</b>	<b>0.0010</b>
<b>Std dev</b>	<b>0.036</b>	<b>0.035</b>	<b>0.029</b>	<b>0.018</b>	<b>0.008</b>	<b>0.003</b>	<b>0.002</b>	<b>0.022</b>	<b>0.002</b>	<b>0.006</b>	<b>0.002</b>	<b>0.0001</b>

Table 3 b. Short term repeatability on a cement fused bead - goniometer at 20 seconds per line - 40kV/70mA.

Time	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s	20 s
Run	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MnO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	TiO <sub>2</sub>
1>	30.86	0.292	0.065	21.44	0.448	0.004	0.073	0.005	0.0085	0.040	0.0011
2>	30.90	0.294	0.075	21.51	0.444	0.004	0.074	0.007	0.0081	0.038	0.0014
3>	30.86	0.291	0.068	21.54	0.445	0.004	0.074	0.009	0.0084	0.039	0.0010
4>	30.88	0.294	0.066	21.49	0.446	0.004	0.074	0.001	0.0096	0.044	0.0015
5>	30.90	0.300	0.069	21.56	0.446	0.004	0.075	0.012	0.0091	0.046	0.0012
6>	30.88	0.293	0.067	21.53	0.447	0.004	0.073	0.001	0.0085	0.035	0.0021
<b>Avg</b>	<b>30.88</b>	<b>0.294</b>	<b>0.068</b>	<b>21.51</b>	<b>0.446</b>	<b>0.004</b>	<b>0.074</b>	<b>0.006</b>	<b>0.0087</b>	<b>0.040</b>	<b>0.0011</b>
<b>Std dev</b>	<b>0.019</b>	<b>0.003</b>	<b>0.003</b>	<b>0.043</b>	<b>0.001</b>	<b>0.0005</b>	<b>0.0010</b>	<b>0.005</b>	<b>0.0054</b>	<b>0.004</b>	<b>0.0004</b>

Table 3 c. Short term repeatability on a dolomite fused bead - goniometer at 20 seconds per line - 40kV/70mA. Note that due to the dilution Na<sub>2</sub>O is at the Limit of detection, hence the poor standard deviation.

Analysis with fixed monochromator channels permits faster analysis and equal or better precision.

### Factory pre-calibration

The pre-calibration of the ARL X900 WDXRF Spectrometer can be carried out in the factory prior to delivering the spectrometer to the client. We use a series of certified standard samples prepared on a Katanax electrical fusion machine or a gas fusion machine (Vulcan VAA2 or FLUXANA VITRIOX® Gas depending on customer choice). No standard samples are delivered with this pre-calibration, but a set of six stable and polished setting-up samples is included for maintenance of the calibration curves over time.

Alternatively, a kit of 24 international certified standards of oxide materials can be ordered to permit 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 clever management of power, the ARL X900 Spectrometer can operate at 1500 W and 2500 W without requiring external water cooling. Neither tap water nor a water cooler is required in these cases. At higher power levels (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 X900 Spectrometers can be chosen either with just one sequential goniometer or with the addition of fixed channels to speed up the response time. The ARL X900 series spectrometers do not require compressed air and use a very small flow of P10 detector gas.

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