Analysis of Various Oxide Materials with Thermo Scientific ARL OPTIM'X WDXRF Spectrometer

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Key Words
ARL OPTIM'X, spectrometer, oxides, X-ray fluorescence, XRF

Goal
To show that the Thermo Scientific™ ARL™ OPTIM'X WDXRF instrument permits the analysis of a large variety of oxide materials with good accuracy using the General Oxide calibration, at 200 W.

Introduction
Wavelength dispersive X-ray fluorescence (WDXRF) allows measurement of up to 84 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%).

Instrumentation


The ARL OPTIM'X is a WDXRF instrument designed for ease of use with minimal operation and maintenance costs. The instrument is fitted with a Thermo Scientific SmartGonio covering elements from fluorine (^{9}F) to uranium (^{92}U). A rhodium anode X-ray tube is used and the geometry of the instrument is optimized to provide the highest sensitivity. Two power versions exist, either 50 W or the new 200 W version which has been used for the tests shown in this report.

The instrument does not require external or internal water cooling, and has 10 times better spectral resolution than a conventional EDXRF instrument as well as superior precision and stability. It has a good performance for sodium (^{11}Na), magnesium (^{12}Mg) and even for fluorine (^{9}F). Ease of operation is obtained through the state-of-the-art OXSAS software running under Windows® 7 environment.

Calibration ranges and results
The Thermo Scientific ARL OPTIM'X Series WDXRF instrument, calibrated with the General Oxide program allows the analysis of a 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. The wide concentration ranges that can be addressed are shown in Table 1. The key for this capability is the sample preparation where the mineral samples diluted with a flux is fused at 1050°C in order to obtain a glassy fusion bead (Figures 1 and 2). A working curve is established for each element by correlating the XRF intensities with the concentration values of each standard sample. The Multi-Variable-Regression calculation incorporated in OXSAS analytical software is used with theoretical alpha factors in order to correct for all matrix effects. Loss on ignition values, which spread up to 47 % can be used for correction purposes in the multivariable regression. The Standard Error of Estimation (SEE) shown in Table 1 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 data of a given oxide.

Element/ Oxide	Crystal	Calibration ranges (%) for ignited samples	Typical SEE (%)
CaO	LiF200	0.03 - 94.4	0.29
SiO_2	InSb	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	AX06	0.16 - 89.2	0.2
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	InSb	0.06 - 40.0	0.10
SO_3	InSb	0.05 - 3.7	0.15
Na_2O	AX06	0.4 - 10.4	0.2

Table 1: Concentration ranges and Standard Error of Estimation for the various oxide types using the SmartGonio™

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Figure 1: One crucible and one mould are installed on this 2-station fusion machine

Figure 2: Typical fusion beads

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 20s per element with the SmartGonio. Depending on the precision required the counting time for any element can be increased or decreased.

When extraordinary performance is required for one or two specific elements fixed channels can be added. They will count during the full time when the SmartGonio is analyzing the other elements. Longer counting time will clearly improve the limit of detection and precision for the corresponding elements/oxides measured on fixed channels.

Table 2 gives some comparative data for limits of detection at 20s and 100s counting time.

Elements	Typical LoD SmartGonio *(3 SIGMA) 20s peak and background*	Typical LoD SmartGonio *(3 SIGMA) 100s peak and background*
CaO	45 ppm	20 ppm
SiO_2	160 ppm	72 ppm
Fe_2O_3	60 ppm	27 ppm
MgO	390 ppm	175 ppm
Al_2O_3	230 ppm	103 ppm
MnO	35 ppm	16 ppm
K_2O	30 ppm	13 ppm
Cr_2O_3	32 ppm	14 ppm
TiO_2	39 ppm	17 ppm
P_2O_5	150 ppm	67 ppm
SO_3	220 ppm	99 ppm
Na_2O	600 ppm	269 ppm

Table 2: Typical limits of detection obtained on various oxide types using samples fused 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. 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 when needed.

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 for 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 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 our company.

Stability tests

In order to show the excellent repeatability of the ARL OPTIM'X for the analysis of various types of oxide materials at 200W, both in short and long term, stability tests were performed. 20s counting time for peaks and backgrounds were used for each element measured on the SmartGonio. For short term repeatability 11 consecutive measurements were performed on several samples. Average concentration and standard deviations are shown in Tables 3 to 6.

Limestone	Ca	Fe	K	Mg	Mn	P	S	Si	Ti
Run #1	35.91	0.212	0.029	21.60	0.013	0.027	0.124	0.573	0.010
Run #2	35.76	0.211	0.027	21.54	0.013	0.016	0.116	0.596	0.009
Run #3	35.81	0.213	0.026	21.72	0.009	0.020	0.100	0.584	0.013
Run #4	35.80	0.212	0.028	21.78	0.014	0.010	0.119	0.593	0.009
Run #5	35.73	0.210	0.027	21.61	0.012	0.017	0.124	0.615	0.007
Run #6	35.78	0.210	0.032	21.69	0.012	0.018	0.118	0.605	0.012
Run #7	35.92	0.209	0.028	21.59	0.012	0.027	0.108	0.586	0.007
Run #8	35.84	0.213	0.028	21.69	0.011	0.021	0.123	0.593	0.010
Run #9	35.85	0.208	0.027	21.66	0.014	0.021	0.123	0.603	0.007
Run #10	35.87	0.212	0.029	21.58	0.014	0.021	0.108	0.607	0.008
Run #11	35.81	0.206	0.029	21.71	0.011	0.023	0.114	0.583	0.015
Average	35.83	0.211	0.028	21.65	0.012	0.020	0.116	0.594	0.010
Std Dev	0.06	0.0022	0.0017	0.07	0.0016	0.0046	0.0077	0.0118	0.0025

Table 3: Results of a precision test (11 runs) for a limestone sample: counting time 20s on peak and background

Iron ore	Al	Ca	Fe	K	Mg	Mn	P	S	Si	Ti
Run #1	0.793	0.471	95.27	0.082	0.815	0.015	0.032	0.202	4.19	0.057
Run #2	0.797	0.468	95.14	0.086	0.891	0.018	0.023	0.192	4.12	0.052
Run #3	0.820	0.464	95.14	0.088	0.816	0.018	0.032	0.176	4.12	0.058
Run #4	0.794	0.470	95.18	0.088	0.824	0.017	0.020	0.202	4.14	0.055
Run #5	0.791	0.467	95.29	0.090	0.830	0.019	0.013	0.212	4.16	0.056
Run #6	0.774	0.480	95.07	0.087	0.820	0.020	0.024	0.193	4.14	0.051
Run #7	0.826	0.477	95.10	0.087	0.822	0.015	0.036	0.198	4.13	0.056
Run #8	0.802	0.467	95.06	0.085	0.837	0.017	0.031	0.203	4.12	0.054
Run #9	0.826	0.467	95.03	0.086	0.791	0.018	0.040	0.202	4.13	0.055
Run #10	0.814	0.463	95.12	0.083	0.780	0.019	0.022	0.200	4.14	0.057
Run #11	0.808	0.462	95.14	0.089	0.817	0.017	0.052	0.206	4.10	0.050
Average	0.804	0.468	95.14	0.086	0.822	0.017	0.030	0.199	4.13	0.055
Std Dev	0.016	0.005	0.08	0.002	0.027	0.001	0.010	0.009	0.022	0.002

Table 4: Results of a precision test (11 runs) for an iron ore: counting time 20s on peak and background

Rock	Al	Ca	Cr	Fe	K	Mg	Mn	Na	P	S	Si	Ti
Run #1	8.22	15.10	0.073	18.82	0.182	13.24	0.173	0.740	0.055	0.312	38.83	3.88
Run #2	8.19	15.05	0.072	18.76	0.180	13.23	0.170	0.844	0.063	0.319	38.76	3.91
Run #3	8.19	15.04	0.073	18.78	0.181	13.36	0.174	0.850	0.052	0.313	38.71	3.90
Run #4	8.15	15.05	0.071	18.79	0.184	13.41	0.175	0.826	0.043	0.323	38.79	3.89
Run #5	8.22	15.05	0.072	18.81	0.182	13.16	0.169	0.830	0.059	0.315	38.76	3.90
Run #6	8.21	15.09	0.074	18.78	0.182	13.19	0.174	0.730	0.063	0.321	38.86	3.89
Run #7	8.29	15.10	0.070	18.78	0.179	13.23	0.170	0.804	0.045	0.306	38.70	3.90
Run #8	8.19	15.13	0.071	18.80	0.185	13.17	0.171	0.741	0.052	0.325	38.72	3.90
Run #9	8.21	15.07	0.075	18.78	0.179	13.17	0.174	0.814	0.059	0.328	38.69	3.88
Run #10	8.19	15.08	0.074	18.78	0.177	13.25	0.174	0.786	0.062	0.324	38.91	3.89
Run #11	8.31	15.03	0.073	18.78	0.183	13.35	0.178	0.889	0.044	0.303	38.82	3.89
Average	8.21	15.07	0.0724	18.79	0.181	13.25	0.173	0.805	0.054	0.317	38.78	3.89
Std Dev	0.04	0.03	0.0015	0.01	0.0024	0.081	0.0026	0.048	0.0072	0.0077	0.07	0.01

Table 5: Results of a precision test (11 runs) for a rock sample: counting time 20s on peak and background

Slags	Al	Ca	Cr	Fe	K	Mg	Mn	P	S	Si	Ti
Run #1	1.15	44.16	0.498	26.95	0.046	2.07	4.35	8.33	0.424	8.82	0.543
Run #2	1.16	44.23	0.502	26.96	0.050	2.16	4.36	8.32	0.417	8.79	0.550
Run #3	1.13	44.30	0.494	27.00	0.048	2.12	4.34	8.23	0.414	8.78	0.559
Run #4	1.13	44.23	0.502	26.99	0.049	2.15	4.35	8.27	0.403	8.83	0.552
Run #5	1.16	44.32	0.499	26.98	0.050	2.13	4.35	8.33	0.405	8.81	0.534
Run #6	1.16	44.30	0.498	26.99	0.048	2.14	4.36	8.34	0.423	8.91	0.554
Run #7	1.13	44.25	0.498	27.02	0.048	2.12	4.35	8.35	0.416	8.82	0.541
Run #8	1.17	44.27	0.504	26.95	0.052	2.17	4.33	8.30	0.418	8.82	0.555
Run #9	1.17	44.18	0.498	26.91	0.047	2.09	4.36	8.30	0.428	8.73	0.543
Run #10	1.13	44.28	0.501	27.00	0.050	2.16	4.35	8.38	0.420	8.81	0.548
Run #11	1.15	44.26	0.499	26.98	0.048	2.12	4.33	8.24	0.434	8.79	0.550
Average	1.15	44.25	0.499	26.98	0.049	2.13	4.35	8.31	0.418	8.81	0.548
Std Dev	0.02	0.05	0.003	0.03	0.001	0.03	0.01	0.04	0.009	0.04	0.007

Table 6: Results of a precision test (11 runs) for a slag sample: counting time 20s on peak and background

Conclusion

A large variety of oxide materials can be analyzed 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 limit of detection and precision are higher due to the dilution effect. Therefore in case some of the calibration ranges should be extended towards lower levels longer counting times should be used or alternatively a lower dilution should be considered, e.g. 1:5 for example.

The ARL OPTIM'X WDXRF instrument permits successful analysis of various oxide materials using a single calibration based on a preparation as fused beads. Good repeatability and reproducibility is obtained with the SmartGonio for all elements. The counting times could be decreased from 20s to 10s in many cases. But if better results are required for any element, the counting time for that particular element can be increased.

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