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X-ray fluorescencee

# Analysis of various oxide materials

## ARL OPTIM'X WDXRF Spectrometer

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ARL OPTIM'X XRF spectrometer

### Introduction

Almost all modern industrial materials and products depend on the mining, extraction and quality of their corresponding raw materials. With the ever increasing demand for high grade mineral sources, there is a need for improved productivity while meeting environmental and quality standards.

This demand calls for efficient techniques to help mining operations and laboratories. X-ray fluorescence is a well-established elemental analysis technique suitable for a wide range of raw materials, minerals, and industrial products. The 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 General Oxide calibration on the Thermo Scientific ARL OPTIM'X WDXRF 200W spectrometer permits the analysis of a large variety of oxide materials with good accuracy.

### 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 from oxygen to americium. 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 200 W, version which has been used for the tests shown in this report.

The ARL OPTIM'X does not require external or internal water cooling, and has 5 to 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.

### Calibration 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. Notably, the calibration includes a high level of sulfur oxide ($SO_3$, 46.5%), which enables the analysis of gypsum, $CaSO_4$. 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 (Figure 2) thus removing both grain size and mineralogical effects.

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 the 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 | Calibration ranges (%) for ignited samples | Typical SEE (%) |
|---|---|---|
| CaO | 0.03 – 94.4 | 0.29 |
| $SiO_2$ | 0.35 – 99.7 | 0.21 |
| $Fe_2O_3$ | 0.025 – 94 | 0.15 |
| MgO | 0.2 – 97.3 | 0.2 |
| $Al_2O_3$ | 0.16 – 89.2 | 0.2 |
| $K_2O$ | 0.03 – 15.4 | 0.05 |
| MnO | 0.02 – 8 | 0.03 |
| $Cr_2O_3$ | 0.02 – 17.4 | 0.03 |
| $TiO_2$ | 0.02 – 3.8 | 0.03 |
| $P_2O_5$ | 0.06 – 40.0 | 0.10 |
| $SO_3$ | 0.05 - 3.7 - 46.5 | 0.15 |
| $Na_2O$ | 0.4 – 10.4 | 0.2 |

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

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 20 s per element with the SmartGonio. Depending on the precision required the counting time for any element can be increased or decreased. Table 2 gives comparative data for limits of detection at 20 s and 100 s counting time at 200 W power.

When extraordinary performance is required for one or two specific elements , the ARL OPTIM'X can be fitted with additional fixed channel monochromators. The fixed channels will measure in parallel to the SmartGonio, and for the full time of the analysis. This enables longer counting times for the elements on the fixed channels, which improves the limit of detection and precision for the corresponding oxides.

| 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 1:11 dilution.**

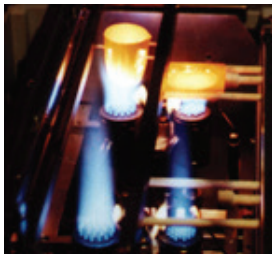

**Figure 1. One crucible and one mould are installed on this 2-station gas fusion machine.**

**Figure 2. Typica fusion beads.**

## 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 950°C. The fusion bead is then made from a mixture of sample and lithium tetraborate - lithium metaborate flux (65% - 35%) at a dilution of 1:11. A small amount of non-wetting agent is used 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 destroy 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 950°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.

## Maintenance

General oxide calibration can be maintained over years by running stable and polished setting-up samples that correct for any noticeable drift at regular intervals.

## Stability tests

Stability tests were performed to show the excellent repeatability of the ARL OPTIM'X 200 W for the analysis of various types of oxide materials. For each element measured on the SmartGonio, 20 s counting time for peaks and backgrounds were used. 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 | CaO | $Fe_2O_3$ | $K_2O$ | MgO | MnO | $P_2O_5$ | $SO_3$ | $SiO_2$ | $TiO_2$ |
|---|---|---|---|---|---|---|---|---|---|
| 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 dolomite sample: counting time 20s on peak and background.**

| Iron ore | $Al_2O_3$ | CaO | $Fe_{Tot}$ | $K_2O$ | MgO | MnO | P | S | $SiO_2$ | $TiO_2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Run #1 | 0.793 | 0.471 | 65.24 | 0.082 | 0.815 | 0.015 | 0.032 | 0.202 | 4.19 | 0.057 |
| Run #2 | 0.797 | 0.468 | 65.14 | 0.086 | 0.891 | 0.018 | 0.023 | 0.192 | 4.12 | 0.052 |
| Run #3 | 0.820 | 0.464 | 65.14 | 0.088 | 0.816 | 0.018 | 0.032 | 0.176 | 4.12 | 0.058 |
| Run #4 | 0.794 | 0.470 | 65.17 | 0.088 | 0.824 | 0.017 | 0.020 | 0.202 | 4.14 | 0.055 |
| Run #5 | 0.791 | 0.467 | 65.25 | 0.090 | 0.830 | 0.019 | 0.013 | 0.212 | 4.16 | 0.056 |
| Run #6 | 0.774 | 0.480 | 65.10 | 0.087 | 0.820 | 0.020 | 0.024 | 0.193 | 4.14 | 0.051 |
| Run #7 | 0.826 | 0.477 | 65.12 | 0.087 | 0.822 | 0.015 | 0.036 | 0.198 | 4.13 | 0.056 |
| Run #8 | 0.802 | 0.467 | 65.09 | 0.085 | 0.837 | 0.017 | 0.031 | 0.203 | 4.12 | 0.054 |
| Run #9 | 0.826 | 0.467 | 65.07 | 0.086 | 0.791 | 0.018 | 0.040 | 0.202 | 4.13 | 0.055 |
| Run #10 | 0.814 | 0.463 | 65.13 | 0.083 | 0.780 | 0.019 | 0.022 | 0.200 | 4.14 | 0.057 |
| Run #11 | 0.808 | 0.462 | 65.14 | 0.089 | 0.817 | 0.017 | 0.052 | 0.206 | 4.10 | 0.050 |
| Average | 0.804 | 0.468 | 65.14 | 0.086 | 0.822 | 0.017 | 0.030 | 0.199 | 4.13 | 0.055 |
| Std Dev | 0.016 | 0.005 | 0.05 | 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 | $Al_2O_3$ | CaO | $Cr_2O_3$ | $Fe_2O_3$ | $K_2O$ | MgO | MnO | $Na_2O$ | $P_2O_5$ | S | $SiO_2$ | $TiO_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 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 | $Al_2O_3$ | CaO | $Cr_2O_3$ | $Fe_2O_3$ | $K_2O$ | MgO | MnO | $P_2O_5$ | $SO_3$ | $SiO_2$ | $TiO_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 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 20 s 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 compared to pressed pellet calibrations due to the dilution effect. If required, the calibration ranges can be extended towards lower levels by using longer counting times. Alternatively, a lower dilution of for example 1:5 should be considered for the fused bead preparation.

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 are obtained with the SmartGonio for all elements. In many cases, the counting times could be further decreased from 20 s to 10 s to reduce the analysis time. Likewise, if better results are required for any element, the counting time for that particular element can be increased.