APPLICATION NOTE

# Analysis of metallurgical slags with ARL QUANT'X EDXRF Spectrometer

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## Introduction
Slags originate from various stages in the iron and steel process, e.g. blast furnace, converter, basic oxygen furnace, electric arc furnace or ladle. In the blast furnace, slag is formed from impurities in the iron ores (known as the gangue), the flux and coke ash; it is a complex mixture of silica, alumina, sulfides and oxides of calcium and magnesium, as well as smaller amounts of manganese and iron oxides.

In an electric arc furnace, the slag formation process can be controlled by addition of oxygen, carbon and slag formers such as lime (CaO) and magnesia (MgO) to the melt. Oxygen and carbon promote formation of CO instead of MnO and FeO and keep these elements in their (valuable) elemental metallic form, while the basic slag formers help neutralize the acidity of the slag and prolong the life of refractory (heat-resistant) bricks in the furnace. Proper and timely monitoring of slag composition is an essential factor in controlling the modern smelting process.



X-ray Fluorescence spectrometry (XRF) has been proved a uniquely fast and reliable method for measuring slags in solid-state with low sample preparation, minimal operator skill, and excellent repeatability. Depending on the equipment type and configuration, measurement times range from minutes down to seconds. This publication presents the procedure and typical results obtained with the Thermo Scientific™ ARL™ QUANT'X XRF Spectrometer, which has been used to measure Mg (Magnesium) and heavier elements in slags at many sites throughout the world.

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## Instrumentation

The ARL QUANT'X Spectrometer is based on the Energy-Dispersive (EDXRF) principle that allows a single highly-sensitive detector to measure the emission lines of all elements from Sodium (Na, Z=11) to Uranium (U, Z=92). While EDXRF has increasingly limited sensitivity to lighter elements and is rarely used to measure Sodium (Na) or Magnesium (Mg) at concentrations below 1%, advances in technology now extend its range into applications traditionally served by the more sensitive and larger Wavelength-Dispersive (WDXRF) spectrometers.

The full vacuum chamber, large active area and the low operating temperature and noise characteristics of the Silicon Drift Detector (SDD) allow the ARL QUANT'X Spectrometer to achieve remarkable sensitivity and repeatability. Unlike most laboratory-grade instruments, the durable mechanical design, compact footprint and minimal site requirements of the ARL QUANT'X Spectrometer permit placement in rough environments, e.g. next to the furnace. Routine analysis can be performed by unskilled personnel, and the hardware is controlled solely by software to assure data integrity and reduce operational complications due to mechanical buttons or controls.

## Excitation conditions

In EDXRF, sensitivity and precision are achieved by targeted excitation of the sample to fluoresce only the elements of interest. An instrument with more flexibility and control over the excitation efficiency and background typically shows better performance. The ARL QUANT'X Spectrometer offers a virtually unlimited combination of excitation voltages 4-50 kV and multiple primary beam filters for optimal background control. As shown in Table 1, two spectra were collected off each slag sample, for a total counting time of 180 seconds in a low vacuum atmosphere.

Table 1. Analytical settings.

| Spectrum | kV | Filter | Time (s) | Analytes |
|----------|-----|--------|----------|----------------|
| 1 | 4 | None | 120 | Mg, Al, Si, P |
| 2 | 12 | Al | 60 | Ca, Ti, Mn, Fe |

Figure 1 shows an example of three very different slag samples under the two excitation conditions. The concentrations of these slags are given in Table 3.
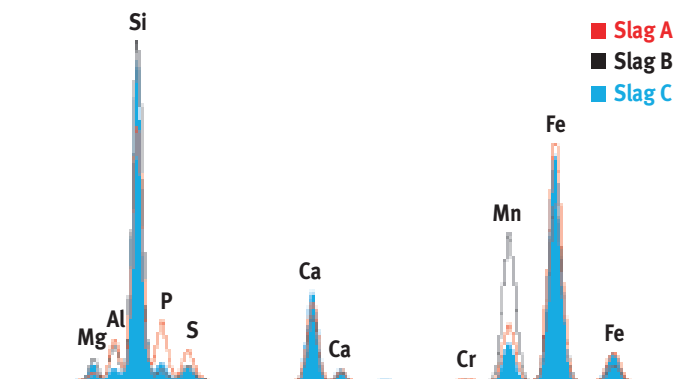


Figure 1. Spectra of three slags under two excitation conditions.

## Sample preparation

For qualitative analysis, XRF can be used with no sample preparation at all, regardless of sample shape or size. However, for meaningful quantitative analysis, slag samples are typically crushed and ground in a mill to produce particle size of less than 50 microns, which helps minimize particle-size effects. Although the powder can be analyzed directly, accuracy and sample-to-sample repeatability are improved if the powder is pressed into what's called a "pellet" using a manual or automatic press at 15-20 tons.

## Calibration

Most applications of XRF in industrial process control are calibrated using empirical calibrations on the basis of primary or secondary standards. The results reported below were obtained using a multi-variable regression curve based on 20 secondary slag standards. All calibration functions, curve display and fit evaluations are included in the standard software package supplied with the ARL QUANT'X Spectrometer.

Table 2 shows the Standard Error of Estimate (SEE) for all the oxides of interest in arc-furnace slags. The SEE is the average difference between the certified and calculated concentrations of a given analyte.

Table 2. Summary of calibration accuracy.

| Analyte | Spectrum | Cal Range (%) | | SEE % |
|---------|----------|-----|-----|-------|
| | | Min | Max | |
| $Fe_2O_3$ | 2 | 1.6 | 34 | 0.23 |
| $Al_2O_3$ | 1 | 0.5 | 20 | 0.26 |
| MgO | 1 | 1 | 22 | 0.49 |
| $P_2O_5$ | 1 | 0.01 | 16.7 | 0.09 |
| $SiO_2$ | 1 | 4.9 | 34.4 | 0.55 |
| CaO | 2 | 2.2 | 59 | 0.65 |
| MnO | 2 | 1.2 | 18.6 | 0.18 |
| $TiO_2$ | 2 | 0.09 | 0.73 | 0.02 |

## Repeatability

Repeatability tests were performed to show the typical precision achieved by the ARL QUANT'X Spectrometer for the 3 minute total counting time. The statistical summary of ten measurements of three slag samples is presented in Table 3.

Table 3. Measurement precision.

| | Slag A | | | Slag B | | | Slag C | | |
|---|---|---|---|---|---|---|---|---|---|
| | Nominal | Average | 1-Sigma | Nominal | Average | 1-Sigma | Nominal | Average | 1-Sigma |
| $Al_2O_3$ | 0.57 | 0.79 ± 0.03 | | 3.10 | 3.32 ± 0.05 | | 3.79 | 3.68 ± 0.02 | |
| CaO | 46.0 | 45.5 ± 0.3 | | 32.6 | 32.8 ± 0.2 | | 40.1 | 38.4 ± 0.2 | |
| Fe | 19.2 | 19.1 ± 0.1 | | 14.3 | 14.3 ± 0.1 | | 19.9 | 19.5 ± 0.1 | |
| MnO | 5.70 | 5.75 ± 0.04 | | 18.6 | 19.0 ± 0.2 | | 7.96 | 7.41 ± 0.04 | |
| MgO | 5.50 | 5.12 ± 0.08 | | 18.6 | 19.0 ± 0.2 | | 3.73 | 3.50 ± 0.06 | |
| $P_2O_5$ | 0.71 | 0.82 ± 0.01 | | 0.47 | 0.26 ± 0.03 | | 3.06 | 3.00 ± 0.02 | |
| $SiO_2$ | 14.90 | 15.51 ± 0.06 | | 19.40 | 19.50 ± 0.07 | | 13.03 | 12.31 ± 0.04 | |
| $TiO_2$ | 1.10 | 1.12 ± 0.04 | | 0.53 | 0.48 ± 0.03 | | 0.38 | 0.42 ± 0.04 | |

In some cases, the difference between the nominal (given) composition and the average measured result was much larger than 3-sigma of variation due to the instrument itself. Here, the real variation is caused by the sample (pellet) preparation and the large variety of slags used in this test. For this reason, optimal accuracy for slag measurement would be achieved by fusing the samples with lithium tetraborate, which removes grain size and mineralogical effects.

## Conclusion

The ARL QUANT'X EDXRF Spectrometer has been used to successfully analyze various components in slags. While the performance of EDXRF in terms of speed, repeatability and sensitivity to light elements does not match that of WDXRF, the small size, robust architecture, mechanical simplicity, and excellent analytical value of the ARL QUANT'X Spectrometer make it a sensible choice for many industrial environments.

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