ABSTRACT

There have been significant developments in the area of Wavelength Dispersive X-Ray Fluorescence (WDXRF) and X-Ray Diffraction (XRD) which can help the mining and minerals industry in addressing specific analytical tasks in a fully autonomous manner. For example, analysis of sediments, unknown elements in soils, and inclusions in rocks and clays can be handled using cost effective WDXRF systems only. Depending on the throughput requirements and detection of various elements, low power to high power sequential XRF systems have been designed for quantitative analysis. All the “known” materials are analyzed using dedicated calibration programs while the “unknown” or “non-routine” materials are handled using “standard-less” XRF analysis programs.

1. ANALYSIS OF SEDIMENTS

New ways of sample preparation are being experimented for sediments in order to avoid having only to mill and press them. Fusion bead preparation is a widely used sample prep technique for XRF. It also results in more complete analysis.

This prepared sediment powder can be analysed in the XRF instrument (Figure 1).

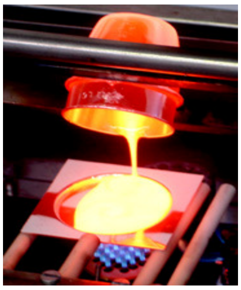

Figure 1: Fusion bead preparation

1.1 Calibration and results example

Ten standards were used for calibration of an ARL OPTIM’X. It is an entry level Wavelength Dispersive XRF (WDXRF) instrument with a nominal power of 50W but surprising high sensitivity thanks to close coupling geometry permitted by the small size of the X-ray tube and a compact goniometer. This SmartGonio™ can cover elements from F (Z=9) to U (Z=92). One of the advantages

One of the advantages of this instrument is its excellent spectral resolution which is up to ten times better than conventional EDXRF instruments notably for light elements from Na to Cl. The ARL OPTIM’X exhibits also superior precision, as well as excellent short and long term stability. Elements F, Na and Mg can be determined without doubt.

These standards allow covering the concentration ranges shown in Table 1. A working curve is established for each element by correlating XRF intensities and the concentrations for each oxide. The limitation in term of accuracy is due to the sample preparation and the variety of samples used in this test.

Elements/ Oxides	Analytical device	Calibration ranges	SEE (%)
Al2O3	**SmartGonio™**	***5% - 12%***	***0.07%***
MgO	**SmartGonio™**	***2.4% - 9%***	***0.14%***
SiO2	**SmartGonio™**	***34% - 38%***	***0.23%***
CaO	**SmartGonio™**	***32% - 47%***	***0.24%***
Cr2O3	**SmartGonio™**	***1.6% - 7.8%***	***0.16%***

Table 1: Summary of performance
SEE = Standard error of estimate: it is a measure of the accuracy

1.2 Stability tests

Tests were performed in order to determine the stability of analysis. For short term repeatability 10 consecutive measurements were performed on one of the samples. The repeatability test was done twice using counting times of 20s and 40s per element. Average concentration and standard deviations are shown in Table 2.

Element/ Oxide	Analytical device	*Average concentration %*	Counting time	*Std.Dev. %*	Counting time	*Std.Dev. %*
Al2O3	**SmartGonio™**	***9.74***	**20 s**	***0.034***	**40 s**	***0.027***
CaO	**SmartGonio™**	***44.1***	**20 s**	***0.034***	**40 s**	***0.033***
Cr2O3	**SmartGonio™**	***4.59***	**20 s**	***0.018***	**40 s**	***0.017***
MgO	**SmartGonio™**	***3.17***	**20 s**	***0.018***	**40 s**	***0.013***
SiO2	**SmartGonio™**	***36.2***	**20 s**	***0.041***	**40 s**	***0.026***
Total counting time			**100s**		**200s**	

Table 2: Results of a repeatability tests (10 runs) using counting times of 20s and 40s per element

Figure 2: Full automation of an ARL Optim'X

2. ANALYSIS OF PHASES BY INTEGRATED X-RAY DIFFRACTION

Since XRF is essentially capable of measuring total elemental composition only, wet chemical methods are generally used for the analysis of a given compound, for example analysis of Fe^{2+} (FeO) in sinters. These methods are not only time consuming but require the use of acids and chemicals and cannot be automated easily. X-ray diffraction can, in suitable cases, quantify the different forms of iron oxides in ores or the Fe^{2+} in sinters or distinguish alpha-Al_2O_3 in alumina etc. However, an independent and conventional X-ray diffractometer is neither justifiable in such process control environments, nor for reliable quantitative analysis of specific phases in particular.

2.1. Instrumentation

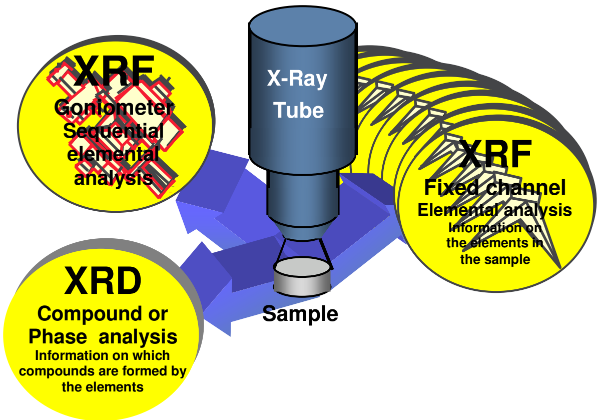

Figure 3: Integration of XRF and XRD in the same instrument: one sample, one instrument, one analysis

There are nowadays spectrometers like the ARL 9900 Series that integrate both X-ray fluorescence and X-ray diffraction in one single instrument. Two versions of this unique instrument exist: either an instrument that integrates a Compact XRD system allowing getting both XRF and XRD results using a single X-ray tube (Figure 1) or an X-ray Workstation that integrates a full XRD system along the XRF devices.

The salient features of such instruments are:

- Modular construction enabling to select analysis devices such as XRF goniometer, XRF monochromators and integrated XRD system.
- Configurations can be defined to achieve speed of analysis, sample throughput or limits of detection, specific or full X-ray diffraction as required.
- High sensitivity thanks to optimized X-ray optical design for monochromators and goniometers.
- Latest generation end-window tube with Rh anode providing broad spectrum excitation. Extra-thin window (50 microns) increases sensitivity for light elements.
- Geometry with X-Ray tube above sample preventing damage to instrument in case of defective samples (pressed pellets) and ensuring high uptime in routine use.
- Fast gearless XRF goniometer with such positioning accuracy that precision is equivalent to fixed channels. Allows also semi-quantitative and standardless analysis through state-of-the-art QuantAS™ and UniQuant™ software options.
- High stability of analysis thanks to global and local thermal control systems.

2.2 Analysis of free lime in slags

Another useful application of phase analysis exists for slags. It is the determination of free lime in slags. This becomes important as slags are nowadays being sold in order to serve as base materials in road construction or as alternative raw materials in the cement industry. In these cases low free lime levels are necessary in order to be sure that the volume of the material will not increase when hydrated as free lime transforms into calcium hydroxide.

3. CONCLUSION

The analytical needs of the modern earth science research demand more comprehensive and process-integrated instrumentation. Two trends seem to emerge in the way the analytical instruments are positioned in this industry.

Firstly there is a move towards decentralization of the measurements to get the analytical instruments closer to the process itself. Indeed, most mineral and mining exploitation would like to see that the analytical capability moves closer to the process where the answer is truly needed. New low power WDXRF instruments like the ARL Optim'X can answer to this requirement notably in the case of analysis of directly soils, sediments and rocks.

Secondly there is a need for higher level of information content from each analytical instrument. An integrated XRF-XRD instrument like the ARL 9900 X-ray spectrometer offer state-of-the-art instrumentation to perform XRF as well as phase determination for specific analytical requirements in the minerals industry.

Short Biography Renaat Van Geel

Born in 1961 in Belgium.
Engineering Masters degree in electronics / '83 from PTS Antwerpen - Belgium
Working since '84 in the field of analytical instruments and spectrometry in several roles for Thermo Fisher Scientific;
Starting with service and application support on AAS and ICP
Application specialist for ICP and ICP-MS.
Sales engineer for AAS, ICP, ICP-MS, FT-IR, UV-Vis, X-Ray and OES during several years
Starting and establishing commercial operations in BeNeLux for ThermoFisher Scientific as BNL Sales Manager in the spectroscopy division.
Acting now as European Commercial Marketing Manager for Bulk Elemental Products (XRF, XRD and OES) out of Ecublens (CH)