Applications of High Performance XRF in Metals and Mining laboratories

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Overview

Metals and mining laboratories offer interesting analytical challenges in the sense that their materials and products can be very varied: wide elemental coverage, wide concentration ranges and varied samples matrices, varied sizes, coatings and layers, heterogeneities and inclusions. Wavelength dispersive XRF has always been put to the test in these areas alongside other trace analysis techniques. Analytical performance of XRF instruments is being constantly advanced in order to cope with such challenges. In this presentation, several applications will be presented in which the power and flexibility of latest WDXRF spectrometers are fully exploited.

Introduction

Wavelength dispersive XRF spectrometers are typically used for quantitative elemental analysis of many material types ranging from petrochemical, geochemical, metals, glass and ceramics, mining and cement. These samples are normally presented to the XRF instrument as uniform and homogenously prepared samples.

With the introduction of latest WDXRF spectrometer, a new dimension of sample analysis is now possible with sample surface mapping and small spot analysis. The small spot size allows analysis of embedded particles or inhomogeneous specimens and product failure investigations. Either qualitative or quantitative analyses can be obtained by simply measuring a chosen spot on the sample surface.

The mapping capability enables heterogeneity, contamination, gradient, segregation and inclusion determination and analysis. The mapping option can construct detailed composite maps of elemental distribution within a sample. The cartography control and overlay has a fine resolution of 0.1mm steps providing superior analysis for process improvement and problem solving applications.

This ability bridges the gap between traditional bulk analysis and standard micro-analysis using microscopic techniques such as SEM. A camera is included for selecting the spots or areas of interest.

Instrumentation

The ARL PERFORM'X spectrometer (figure 1) used in these tests was a 4200 watt system. This system is configured with 6 primary beam filters, 4 collimators, up to 9 crystals, 2 detectors, and a Rh anode X-ray tube with a 50 micron Be window for best performance from ultra light to heaviest elements.

The ARL PERFORM'X analyzer features small spot and mapping analysis allowing for 1.5 mm and 0.5 mm areas. All of the results presented used the 0.5 mm spot analysis configuration.

Iron base calibration at 0.5 mm

In order to assess the performance that can be reached when analyzing a spot of only 0.5 mm a calibration has been performed using ferrous base standard samples. The standards used in this small spot calibration can have diameters ranging from 11 mm to 30 mm; however they must be homogeneous in composition. Typical examples of these calibration curves are shown in figure 3.

Table 1 gives a summary of limits of detection obtained using a set of international steel standards with the 0.5 mm spot. Results were obtained by using 100 seconds per element counting times and the best conditions and parameters in regards to crystal, detector, collimator and power.

FIGURE 1. Sequential XRF Spectrometer with mapping and spotting capability (ARL PERFORM'X)

FIGURE 2. Cups for small spot analysis with 30 mm and 10 mm apertures

TABLE 1. Typical limits of detection in ferrous base with 0.5 mm spot size

Element	Line	LoD (ppm) 100s
Al	Kα	840
Si	Kα	725
P	Kα	208
S	Kα	160
Ti	Kα	317
V	Kα	205
Cr	Kα	160
Mn	Kα	250
Co	Kα	390
Ni	Kα	340
Cu	Kα	220
Ta	Lβ	330
Zr	Kα	57
Nb	Kα	55
Mo	Kα	60
Sn	Kα	265

Typical stability and precision tests

A stability test consisting of running a typical sample over 10 days was performed. Each element was analyzed using 100 seconds per element.

The stability of an instrument reflects the precision that can be obtained. It should be noted that the accuracy of the instrument is dependent upon the accuracy of the standards used to calibrate the instrument. The stability for each element is given in table 2 along with the certified and calculated concentrations

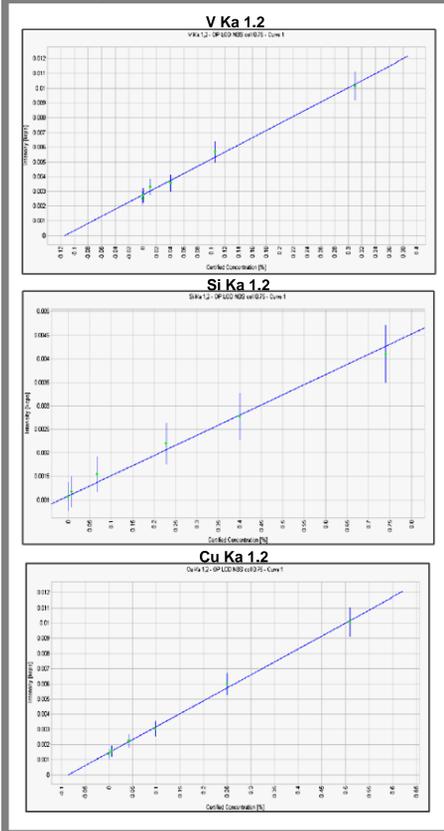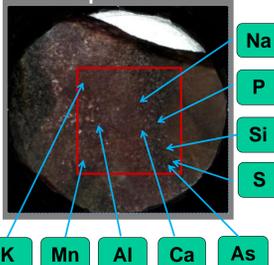**FIGURE 3. Calibration for V, Si and Cu with 0.5 mm spot**

FIGURE 5. Heterogeneous Manganese Rock Sample seen in the 30mm aperture

Standard-less analysis for small spot

One of the most useful recent development in XRF analytical programs has been the availability of "standard-less" packages. These packages allow for quantitative data to be obtained for completely unknown samples.

As in many real life situations, obtaining any or enough standards to create a calibration is not always possible. This is certainly the case when analyzing defects or unknown contaminations. In such situations, standard-less software such as Thermo Scientific UniQuant package are a real help. UniQuant is a universal calibration based on 64 pure element standards that allows for concentration determination of unknown samples in any matrix by using complex mathematical algorithms for up to 79 elements. These algorithms correct for matrix effects as well as inter-elemental effects to provide precise quantitative results.

Inclusions in glasses

Glass samples have been submitted for analysis. One of the samples shows a shiny spot that we cannot determine in the traditional way (figure 4). This sample has been analyzed with UniQuant to obtain the global composition over a diameter of 29mm (table 3). The UniQuant pre-defined counting times and analytical conditions and parameters with regard to crystal, detector, collimator and power have been used. As the sample is a glass the results are expressed as oxides. Such analysis does not permit to assess if the shiny spot may affect the elemental determinations. In order to determine the nature of the inclusion three spot analyses were performed for various metal elements and Si, one on the shiny area and two on the glass surface (see table 4). This analysis quickly provides the information that the shiny inclusion is made principally of copper while there is no copper in the glass sample itself. This means that the result for CuO in table 3 can be removed as it does not belong to the glass matrix.

TABLE 2. : Accuracy and precision data in ferrous base for 0.5 mm spots

Element	Line	Cert. Conc. (%)	Analyzed Conc. (%)	Std Dev (%)
Al	Kα	0.24	0.21	0.047
Cr	Kα	1.31	1.32	0.015
Cu	Kα	0.1	0.10	0.010
Mn	Kα	1.5	1.47	0.026
Mo	Kα	0.03	0.03	0.002
Nb	Kα	0.05	0.06	0.003
Ni	Kα	0.32	0.32	0.017
P	Kα	0.03	0.02	0.008
Si	Kα	0.74	0.63	0.041
Sn	Kα	0.1	0.10	0.009
Ta	Lβ	N.A.	0.07	0.015
Ti	Kα	0.05	0.04	0.012
V	Kα	0.31	0.29	0.012
Zr	Kα	0.05	0.07	0.003

FIGURE 4. Glass sample with shiny inclusion

TABLE 3. UniQuant elemental determination of the full surface

Oxide/ Element	Conc. %	StdErr %
SiO_2	69.77	0.23
Na_2O	12.16	0.16
CaO	7.57	0.13
MgO	3.54	0.09
Al_2O_3	1.09	0.05
K_2O	0.330	0.016
SO_3	0.215	0.011
Fe_2O_3	0.200	0.010
TiO_2	0.0704	0.0035
BaO	0.0239	0.0052
Cl	0.0228	0.0011
CuO	0.0175	0.0009
MnO	0.0118	0.0007
ZrO_2	0.0091	0.0005
P	0.0073	0.0006
Cr_2O_3	0.0069	0.0006
SrO	0.0066	0.0003
SnO_2	0.0018	0.0009
ZnO	0.0016	0.0004

StdErr = error due to counting statistics

TABLE 4. UniQuant analysis of the shiny spot (all values in %)

Element	Spot	Glass Surface 1	Glass Surface 2
Al	0.74	0.26	0.50
Cu	24.34	0.01	0.02
Fe	1.57	0.38	0.16
Sn	1.19	0.67	0.50
Si	34.84	58.82	70.46

Mapping of a geological sample

Mapping of a geological sample illustrates the ability to define and locate grain boundaries and crystalline structures that are not visible to the naked eye. Figures 5 and 6 show a manganese rock sample having a clear inhomogeneous structure. XRF mapping identifies the constituents of the selected section of the sample. The interesting aspect of this analysis is the differences elemental segregations throughout the rock body. This provides basic information in order to understand how such rock formation have been formed and the chemical reaction which must have occurred during the formation..

FIGURE 6. Distribution for 9 elements on the chosen area

Conclusion

It is seen that analyses using small spots can easily be performed with the ARL PERFORM'X sequential XRF spectrometer. The precisions and accuracies are shown to be excellent for such a small analyzed area in these matrix types for routine or R&D analyses.

When only approximate analysis of an inclusion or a defect in a sample is needed, a standard-less program like UniQuant easily provides the required results. This analysis permits to quickly determine the nature of an inclusion or a defect in an heterogeneous sample.

The elemental mapping capability is a very interesting tool for all applications dealing with heterogeneity or concentration gradients in samples as well as when impurities or inclusions are found in given specimens. It is seen that analysis using mapping can easily be performed with latest WDXRF sequential XRF spectrometer. Operation is also made easy through the specific features of OXSAS analytical software.

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