AN APPLICATION REPORT FROM
SPECTRO ANALYTICAL INSTRUMENTS

XRF-104

## SPECTRO XEPOS (XEP05)

# High Precision Analysis Using Energy-Dispersive X-Ray Fluorescence Spectrometry

## Introduction

Users in science, industry, and business routinely use spectrometric analysis on materials of diverging composition. The applications vary widely and in many cases the precise determination of major and minor element concentrations is critical. Typically wavelength-dispersive X-ray fluorescence (WD-XRF) instruments are used for these applications as they are known to provide the required precision. Energy-dispersive X-ray fluorescence (ED-XRF) instruments historically have been used for screening analysis. However, modern instruments have reached a level of precision comparable to that achievable with WD-XRF. Therefore they are now suitable for analyzing major and minor elements as well as selected trace elements in various matrices, like geological material, mining samples, cement, ceramics, refractories or glass. The fusion preparation technology is mainly used to reduce matrix effects and to improve accuracy and precision of analysis. In contrast to pressed powder pellets, grain size effects or mineralogical effects are eliminated. Analyzing samples prepared as fused beads provides the basis for excellent accuracy when determining major and minor element’s concentrations in all samples with oxidic sample matrix.

This paper mainly covers as example the use of the SPECTRO XEPOS ED-XRF instrument to analyze major and minor elements in samples of geological and mineral materials, prepared as fused beads. Using polarization and direct excitation technologies, it proved a powerful analytical tool to satisfy the needs of high precision and accuracy.

## Sample Preparation

The fused beads were prepared using 1 gram of sample material and 8 grams of Lithium-tetraborate flux to prepare a bead with 40 mm diameter.

Note that the analyzer used can routinely process solid, powder, pressed powder, fused bead, or liquid samples.

### *ED-XRF*

The energy-dispersive X-ray fluorescence instrument treated in this paper identifies and quantifies the elements present in a substance using the following principle and methodologies:

A sample is subjected to X-rays emitted from a high-intensity X-ray tube. Some energy is absorbed by the atoms of elements in the sample. These excited atoms then emit X-ray fluorescent signals — along a spectrum of energies characteristic of the elements present. Element-specific signals are measured simultaneously, using a fixed, energy-dispersive semiconductor detector.

The radiation intensity of each elemental signal is proportional to the concentration of the element in the sample. This signal is processed in a multichannel analyzer, and the measured spectra are used to determine intensities. Concentrations are calculated using a calibration, as described in this paper.

## Analyzer

All measurements were made using a SPECTRO XEPOS (XEP05 P) simultaneous ED-XRF spectrometer from SPECTRO Analytical Instruments. This model was equipped with a forced-air-cooled, 50 W end-window X-ray tube — a bright laboratory-quality source optimized for maximum energy generation. The tube uses a unique thick binary-alloy cobalt-palladium anode to provide excellent excitation conditions for all major elements of interest in this application. It was combined with a newly developed adaptive excitation system to excite specific elements for further increased sensitivity.

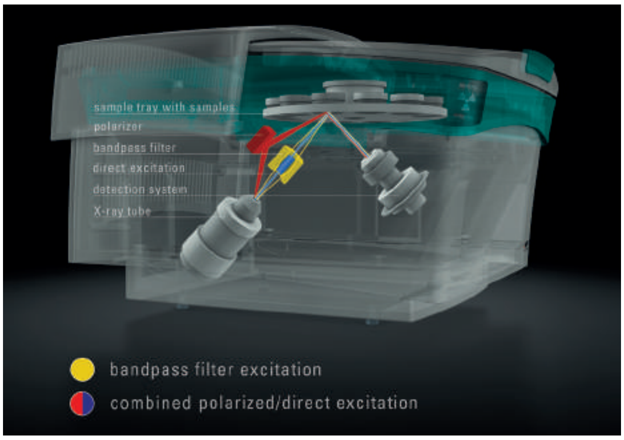

*Illustration 1: Instrument schematics showing the adaptive excitation*

The analyzer also featured a high-resolution silicon drift detector (SDD), plus the fixed excitation optics, including a filter changer in front of the X-ray tube. The highly stable spectral resolution of the SDD amounted to ≤130 eV (Mn Kα). The detection system can handle intensities up to an input rate of 1.5 million counts per second (cps). As already stated above, in many cases wavelength dispersive XRF (WD-XRF) instruments have been used for this application. Those instruments are operated under stable conditions to achieve best precision. This includes sample changing without switching off the tube and also keeping the excitation and detection area under controlled vacuum conditions.

Due to the comparable lower sensitivities of ED-XRF in the past these settings were not commonly used in these instruments. The errors from instabilities in the excitation were overlayed with a larger statistical error of the analysis and therefore barely visible but generally leading to worse precision compared to WD-XRF.

*Illustration 2: Instrument measurement chamber with vacuum shutter*

SPECTRO XEPOS analyzers package high-quality components into a compact benchtop housing with a small footprint. As in the predecessor instruments the sample changing is possible without switching off the X-ray tube providing a basis for high precision. As in WD-XRF the excitation and detection area for this application is closed and kept under controlled vacuum conditions, when no measurement is performed. This is realized with a shutter between the excitation/detection area and the measurement compartment as shown in illustration 2. As the measurements are done under vacuum, the area underneath the shutter stays in vacuum and before starting an analysis the measurement compartment will be evacuated as well. Then the shutter opens and the analysis starts.

For highest precision the temperature in the lab should be kept constant, the same as for WD-XRF. It is recommended to keep the temperature stable within ± 3 °C.

All measurements are done under vacuum. The measurement parameters are given in Table 1.

| Element | kV | Measurement Time/s |
|---|---|---|
| Na – S | 22.5 | 300 |
| K – Mn<br>Ba – Nd | 22.5 | 120 |
| Fe – Zr<br>W – Th | 45.0 | 180 |

*Table 1: typical measurement conditions for fused beads*

To prove that this setup meets expectations, a glass reference sample from BAM was analyzed 35 times over the course of seven days. The results are displayed in Table 2.

| Element or Oxide | | Certified | Average | Std. dev. | RSD % |
|---|---|---|---|---|---|
| $Na_2O$ | % | | 13.73 | 0.02 | 0.15 |
| MgO | % | | 2.301 | 0.005 | 0.22 |
| $Al_2O_3$ | % | | 1.097 | 0.002 | 0.18 |
| $SiO_2$ | % | | 71.1 | 0.04 | 0.06 |
| S | mg/kg | 778 ± 34 | 772 | 2.1 | 0.27 |
| Cl | mg/kg | 247 ± 33 | 251 | 1 | 0.40 |
| $K_2O$ | % | | 0.71 | 0.0032 | 0.45 |
| CaO | % | | 10.57 | 0.02 | 0.19 |
| Ti | mg/kg | 98 ± 5 | 98.8 | 0.5 | 0.51 |
| V | mg/kg | 196 ± 12 | 197 | 0.4 | 0.20 |
| Cr | mg/kg | 10.7 ± 1.6 | 10.7 | 0.1 | 0.93 |
| MnO | mg/kg | 124 ± 5 | 124.5 | 0.2 | 0.16 |
| $Fe_2O_3$ | mg/kg | 422 ± 11 | 418 | 1.9 | 0.45 |
| Co | mg/kg | 39 ± 2 | 36 | 0.3 | 0.83 |
| Ni | mg/kg | 46.4 ± 1.8 | 46.5 | 0.2 | 0.43 |
| Cu | mg/kg | 89.5 ± 4.0 | 89.7 | 0.3 | 0.33 |
| Zn | mg/kg | 163 ± 8 | 162.5 | 0.4 | 0.25 |
| As | mg/kg | 100 ± 6 | 100.2 | 0.4 | 0.40 |
| Se | mg/kg | 19.6 ± 1.7 | 19.6 | 0.1 | 0.51 |
| Sr | mg/kg | 128 ± 6 | 127.4 | 0.2 | 0.16 |
| Zr | mg/kg | 623 ± 93 | 622.6 | 0.7 | 0.11 |
| Mo | mg/kg | 257 ± 9 | 227.9 | 0.4 | 0.18 |
| Cd | mg/kg | 54.3 ± 3.5 | 54.3 | 0.1 | 0.18 |
| Sn | mg/kg | 78.8 ± 5.5 | 78.6 | 0.3 | 0.38 |
| Sb | mg/kg | 110 ± 6 | 100.7 | 0.4 | 0.36 |
| Pb | mg/kg | 188 ± 7 | 187.3 | 0.3 | 0.16 |

*Table 2: Analysis results of 7-days repeatability test*

The results of the repeatability tests show the outstanding precision of the analyzer even for "light" elements like Na, Mg, Al, and Si.

To test the analyzer's performance for the application of geological samples as fused beads a set of geological reference samples was analyzed for calibration.

## Calibration

Calibration for major and minor elements was performed by measuring a series of international geological and mineral reference materials. The correlation graph between given and analyzed concentrations are shown for $Na_2O$ and $Fe_2O_3$ as examples in Figures 1 and 2.

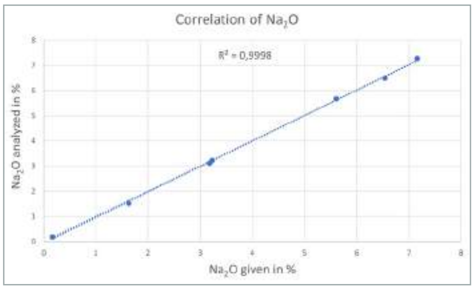

*Figure 1: Correlation for $Na_2O$ in geological samples prepared as fused beads*

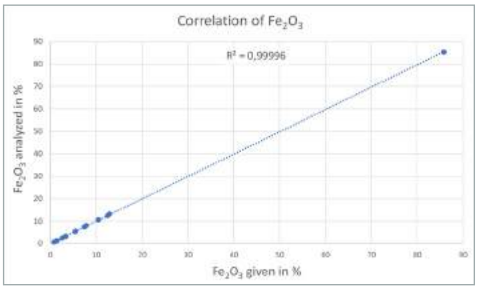

*Figure 2: Correlation for $Fe_2O_3$ in geological samples prepared as fused beads*

## Analytical Performance

The exceptional performance of the SPECTRO XEPOS is demonstrated below. Analytical results for geological reference materials are shown in Tables 3 and 4.

| Geological reference sample GSR-7 | | |
|---|---|---|
| **Oxide** | **Certified [Wt %]** | **Analyzed [Wt %]** |
| $Na_2O$ | 7.16 ± 0.06 | 7.27 ± 0.09 |
| MgO | 0.65 ± 0.05 | 0.723 ± 0.013 |
| $Al_2O_3$ | 17.72 ± 0.07 | 17.68 ± 0.03 |
| $SiO_2$ | 54.48 ± 0.06 | 54.65 ± 0.03 |
| $K_2O$ | 7.48 ± 0.07 | 7.45 ± 0.07 |
| CaO | 1.39 ± 0.03 | 1.381 ± 0.003 |
| $Fe_2O_3$ | 7.41 ± 0.06 | 7.438 ± 0.010 |
| $TiO_2$ | 1.4 ± 0.04 | 1.439 ± 0.002 |
| MnO | 0.008 ± 0.002 | 0.001 ± 0.001 |
| $Fe_2O_3$ | 0.66 ± 0.06 | 0.607 ± 0.004 |

*Table 3: Analytical results including counting statistical error (2 sigma) for the geological reference material GSR-7 (NCS DC71301).*

| Gypsum reference sample GYP-D | | |
|---|---|---|
| **Oxide** | **Certified [Wt %]** | **Analyzed [Wt %]** |
| MgO | 1.73 ± 0.1 | 1.72 ± 0.02 |
| $Al_2O_3$ | 2.03± 0.1 | 2.09 ± 0.01 |
| $SiO_2$ | 8.7 ± 0.3 | 8.69 ± 0.01 |
| $SO_3$ | 36.7 ± 0.4 | 36.92 ± 0.01 |
| $K_2O$ | 0.54 ± 0.07 | 0.55 ± 0.002 |
| CaO | 28.2 ± 0.6 | 28.0 ± 0.01 |
| $Fe_2O_3$ | 1.08 ± 0.06 | 1.02 ± 0.003 |
| SrO | 0.18 ± 0.02 | 0.18 ± 0.0002 |

*Table 4: Analytical results including counting statistical error (2 sigma) for the geological reference material Gypsum GYP-D.*

## Repeatability

The precision of the SPECTRO XEPOS was examined by analyzing the geological reference material BE-N 10-times consecutively. Table 5 shows the absolute standard deviation (ASD) of the repeats compared to the counting statistical error (CSE) as well as the comparison between the average value and the certified values. These values demonstrate that the statistical counting error is the limiting factor in view of precision in the case of fused beads analysis.

| CRPG reference sample Basalt BE-N | | | | | | |
|---|---|---|---|---|---|---|
| **Oxide** | **Unit** | **Certified** | **Avg.** | **CSE** | **ASD** | **RSD** |
| $Na_2O$ | % | 3.18 ± 0.04 | 3.16 | 0.08 | 0.04 | 1,30% |
| MgO | % | 13.15 ± 0.08 | 13.12 | 0.04 | 0.03 | 0.23% |
| $Al_2O_3$ | % | 10.07 ± 0.08 | 10.03 | 0.02 | 0.01 | 0.10% |
| $SiO_2$ | % | 38.20 ± 0.12 | 38.04 | 0.02 | 0.02 | 0.05% |
| $P_2O_5$ | % | 1.05 ± 0.03 | 1.01 | 0.003 | 0.002 | 0.20% |
| $K_2O$ | % | 1.39 ± 0.02 | 1.38 | 0.003 | 0.002 | 0.14% |
| CaO | % | 13.87 ± 0.22 | 13.83 | 0.01 | 0.02 | 0.14% |
| $TiO_2$ | % | 2.61 ± 0.03 | 2.60 | 0.002 | 0.006 | 0.23% |
| $Fe_2O_3$ | % | 12.84 ± 0.06 | 12.79 | 0.01 | 0.01 | 0.08% |

*Table 5: Comparison between absolute standard deviation (ASD) of 10-repeats and counting statistical error (CSE, 1 sigma) measured for the geological reference material CRPG-BE-N (Basalt), as well as a comparison between the average value and the certified value.*

## Conclusions

The improvements in sensitivity obtained by the combination of the thick binary-alloy cobalt-palladium anode in combination with the adaptive excitation on one side and the use of a detection system enabling high count rates at excellent resolution builds the basis for an ED-XRF analyzer to obtain high precision. But those benefits only can be harvested in analysis precision if the complete analyzer is built for stability. This can be achieved by setting up the instrument comparable to a WD-XRF system, meaning keeping the excitation and detection area under controlled constant conditions.

The SPECTRO XEPOS simultaneous XRF spectrometer is a fast, precise, accurate and economic alternative to WD-XRF for the analysis of major and minor elements in a wide range of applications. This report has demonstrated its precision capability, as well as accuracy, when analyzing samples prepared as fused beads.

SPECTRO XEPOS can also be used to analyze trace and minor elements from the same materials when prepared as pressed powder pellets.  A separate application brief for this application is available.

## Choosing an ED-XRF analyzer

ED-XRF technology keeps getting better and better. Today's most advanced instruments can provide a quantum leap in performance, even over earlier top-ranked models. Look for the following benefits:

**High sensitivity and precision.** In multi-element analysis of major, minor, and trace element concentrations, it's critical to maximize spectrometric sensitivity and precision. Example: the newest SPECTRO XEPOS analyzers combine exclusive new excitation technology with innovative detector and tube designs. These help deliver up to 10X greater sensitivity and 3X better precision than previous models. So users get fast, accurate analysis of a wide range of elements, from sodium to uranium.

**Long-term stability.** Most ED-XRF analyzers shut down their X-ray tube between measurements. Unfortunately, resulting temperature variations can negatively affect repeatability and accurate readings. To ensure stability, look for an instrument that maintains constant tube power.

**Low detection limits.** Lower limits of detection (LODs) improve performance with minor and trace element concentrations. The best new models combine high sensitivity with minimized backgrounds, achieving exceptionally low LODs for a wide range of elements.

**Applications.** Some XRF analyzers have strengths in the analysis of trace and minor elements, others are optimized for light elements. For this application, the complete range is important and the analyzer should be prepared to give accurate results for the full range of elements.

**Lower costs.** Today, an advanced ED-XRF analyzer such as SPECTRO XEPOS exhibits significantly lower costs — of initial investment and long-term ownership — than wavelength dispersive X-ray fluorescence (WD-XRF) spectrometers. Yet it generally provides comparable performance.

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