

Process and quality control by X-ray analysis

X-ray analysis, through X-ray diffraction (XRD) and X-ray fluorescence (XRF), is a well-established method for process and quality control of minerals and ores. However, as **Stefan Uhlig** and **Lutz Brügemann** of Bruker AXS* explain, there are new challenges for X-ray analytical systems in the area of on-stream process control. This feature reviews current XRF/XRD methods and highlights breakthroughs in improving X-ray analysis of industrial minerals.



Figure 1. New generation of compact D4 ENDEAVOR X-ray diffractometer support a wide range of industrial applications

In general, for X-ray analysis, all kinds of massive materials, such as rocks, minerals, ores, slags and similar samples have to be crushed. The crushed material is then finely pulverised in a vibrating disk mill or planetary ball mill to grain sizes of less than 50 μ .

The smaller and more equally grain-sized the sample, the more homogeneous the pressed powder sample will be. Through pressing under 10-20 tonnes for up to 10 seconds, the sample powder is pressed into aluminium cups, steel rings or freely, with or without a binding agent.

To avoid inhomogeneity and grain size effects, fused beads are used for highly accurate element analysis by X-ray fluorescence (XRF), mainly for quality control of finished products. Liquid samples or slurries can be directly analysed after pouring the sample into a disposable liquid cup (see Figure 4). This very simple preparation method is also suitable for very fast XRF analysis of loose mineral powders and ores.

Optimisation of XRF equipment

For near or at-line process control, smaller X-ray instruments are characterised by minimal floor space, simple installation, low maintenance and easy operation. These instruments, based primarily on the energy-dispersive (ED) XRF method, cannot compete with the analytical performance of their big brothers - the wavelength-dispersive (WD) laboratory instruments - which demand a more extensive laboratory environment and infrastructure.

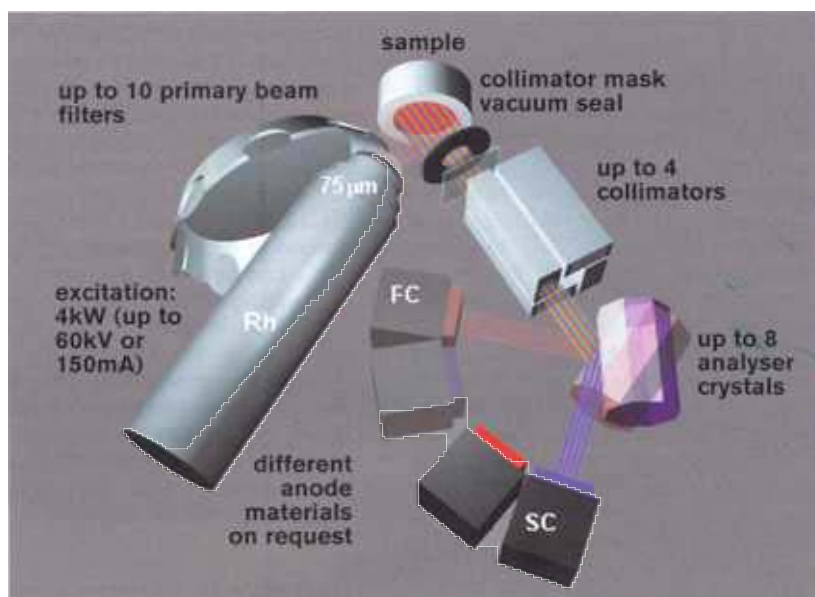
WD-XRF is characterised and differentiated from ED-XRF by the method of resolving the

element characteristic fluorescence radiation. In ED-XRF this is done directly in the detector supported by state-of-the-art electronics and deconvolution algorithms.

The high resolution of WD-XRF is achieved by applying the optical properties of the element's characteristic fluorescence radiation or wavelength. The element's characteristic wavelengths are first collimated and then dispersed at an analyser crystal under well-defined angles by a highly precise goniometer positioning (see Figure 2).

Due to this wavelength-dispersive resolution the complete detector capacity can be applied to just one element line. In ED-XRF the energy-dispersive detector has to record

Figure 2. WD-XRF analysis is based on the optical dispersion of the element characteristic fluorescence radiation applying a highly precise goniometer and optics



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Figure 3. Bench-top size S2 RANGER spectrometer for at-line process and quality control

the sum of intensities coming from all the different elements in a specimen. Therefore WD-XRF, in general, offers the highest resolution, above all for the light elements (atomic number below 13), and a higher precision due to the higher count yield performance.

Many attempts had been made over the last decade to develop more compact wavelength-dispersive spectrometers and to improve the analytical capability of bench-top size energy-dispersive XRF instruments. One successful development was to combine the high analytical performance and flexibility of a stand-alone wavelength-dispersive X-ray spectrometer and the space saving advantages and cost efficiency of an energy-dispersive X-ray spectrometer.

This resulted in a small WD X-ray spectrometer with a volume of much less than 1m³ yet offering the full analytical performance of a typical laboratory WD-XRF system (elemental range from boron to uranium in solids and powders, sodium to uranium in liquid samples, precision up to 0.1% relative). The installation and running costs of such a "plug 'n' analyse" spectrometer have been minimised since its operation requires neither compressed air, cooling water or detector gas (e.g. the new S4 EXPLORER WD-XRF spectrometer).

A further step was to improve the analytical capability and performance of ED-XRF. The goal was to make operation and sample handling easier through an intuitive touch screen interface, and more convenient, based on an all-in-one instrument combined with revolutionary new evaluation methods for routine samples and totally unknown materials.

The self-explaining touch screen operation provides full analytical functionality without keyboard and mouse, even for users without any experience in PC operation, to get results from the very first day. The compact all-in-one design of modern bench-top spectrometers with integrated computer, touch screen, printer and vacuum pump ensure minimum space requirements, single port connection, and fast installation and relocation (see Figure 3).

Instrumentation for phase analysis

In X-ray diffraction (XRD), X-rays of a known wavelength are used for the examination of the samples. Using Bragg's Law the determination of the lattice spacing d_{hkl} , which are characteristic for any crystallographic or mineralogical phase, can be obtained by measuring the reflection angles $2\theta_{hkl}$ with the help of a diffractometer.

Modern X-ray diffractometers combine state-of-the-art X-ray diffraction technology and sample handling versatility to provide fast qualitative and quantitative determination of minerals and simple operation.

New sample handling concepts allow the loading of samples of varying shape, morphology, composition, and quantity as well as being able to define a wide range of measuring tasks specific to each sample, all at the same time (see Figure 1). Modern process diffractometers show a compact robust design, incorporate highly precise goniometers, innovative X-ray optics and detectors to ensure excellent analytical results.

Recently, new promising developments have been achieved in applying powder diffraction technology to on-stream determination of mineralogical composition of flotation slurries. Based on conventional X-ray diffractometer innovative sample stages and measurement, attachments have been developed to measure solid copper minerals from flotation.

Flexible sample handling

Modern analytical X-ray systems fit the user's requirements of sample handling today and for the future by modular sample changer concepts with full access to process automation. This achieves an advantage in all industrial applications where a user-specific input of process samples is requested.

Fully integrated large sample magazines (50 and more positions) and automatic, safe measurement routines of large sample measuring sets ensure a maximum of unattended measuring capacity.

At any time longer, routine measurements can easily be interrupted for priority samples for immediate process control. For laboratory automation the spectrometers can be equipped with a process automation sample magazine to handle powder samples pressed in steel rings without sample holders to take process samples from a conveyor belt or a robot (see Figure 5).

Modern compact X-ray instruments with small foot print and low requirements for installation make containerised at-line, or even mobile, laboratories a reality.

Analytical software – almost an expert system

In XRF analysis, modern fundamental parameter programs provide fast, easy calculation of appropriate correction coefficients ('variable alphas') to compensate inter-element influences (matrix effects). This allows definition of universal calibrations over a wide concentration range.

User-friendly XRF software packages also include universal and specialised precalibrated analytical programs to easily extend the range of analytical routines. Of

primary interest are universal programs, which allow analysis of nearly all elements of the periodic table, in the different materials that can enter an XRF process and quality control laboratory in the minerals and mining industry.

Any sample – metal cuttings, minerals, rock pieces, slurries or even alternative liquid fuels – can be analysed with such a uniform precalibrated program for "standardless" XRF analysis.

The price to pay for such an absolute universality, however, is the limited accuracy of the results; these results may vary between 'almost' quantitative results of well-prepared homogeneous samples and more or less rough chemical characterisation of major and minor compounds for extremely small, bulky or untreated samples.

A frequent method is to apply XRD to qualitative phase analysis. For this purpose the angular position and the relative intensities of the measured reflections of the sample are compared with the line patterns stored in the ICCD database.

The database contains line patterns of more than 80,000 different phases. Since each line represents a characteristic 'fingerprint' of the corresponding phase, the comparison of the measurement with the database yields information about the phases that the sample contains.

XRD is the unique technique to obtain this crystallographic information. The width and shape of the reflections are characteristic for the size of the crystallites in the sample. This makes XRD very well suited for the determination of the crystallite size.

Traditionally, the Absorption-Diffraction Method ('regression method') is applied for quantitative XRD determination by means of conventional single line analysis.

In general, when using carefully prepared standards, the phase composition of unknown samples can be determined with high accuracy. More recently, X-ray powder diffraction in combination with quantitative Rietveld analysis has been shown to offer new insights into in the field of industrial minerals and ores.

The latest developments of dedicated Rietveld software for quantitative phase analysis, now make a decisive breakthrough possible with particular emphasis placed on improving speed, stability, and convergence thus eliminating the major deficiencies of traditional XRD evaluation routines.

This not only allows the analysis of extremely complex phase mixtures in the shortest time possible, but also a fully automated on-line phase analysis for production control and quality management, without any user input.

In addition, using the latest PSD (position sensitive detector) detector technology in a new process diffractometer, measurement and evaluation times can be reduced to minutes.

Another advantage of modern XRD routines

is that there is no more need for a parameter turn-on sequence. As a result, a fully automatic quantitative analysis from XRD data is possible without any user input and can be used for unattended process and quality control for the first time.

Modern X-ray analytical software is open for easy integration into LIM systems or customised software packages, e.g. user-specific programs for process and quality control, and computer networks.

Analytical results and graphics can be easily integrated within latest programs of the Windows™ world for reporting and documentation. Internal data communication of the X-ray system control software is based on the TCP/IP Client/Server protocol.

Therefore, the complete functionality is available on any computer within the lab or plant network. Modern analytical X-ray systems are open for communication via modem or the Internet to support remote diagnostics and on-line assistance.

A practical application for this can also be to have the Group's central lab responsible for calibration and recalibration of different process control labs scattered all over the country or continent – even overseas – via the Internet there are no borders anymore.

Conclusion

Minimal effort in sample preparation, short measuring times, extreme analytical flexibility, high accuracy and precision, as well as full integration in automation systems are important advantages of modern analytical X-ray instruments for elemental and phase analysis in process and quality control.

User-friendly XRF software packages also include universal and specialised precalibrated analytical programs to easily extend the range of analytical routines.

A breakthrough in the application of quantitative analysis by XRD is the latest development of the dedicated standardless Rietveld software allowing fully automated phase analysis of even extremely complex phase mixtures in the shortest time possible without any user interaction.


Modern compact X-ray instruments with small footprint and low requirements for installation perfectly fit the needs for elemental and phase analysis in process and quality control of industrial minerals and ores. 



Figure 4. Simple and fast sample preparation for element analysis by XRF



Figure 5. Easy integration of analytical X-ray instruments into process automation taking over, for example, process samples from a conveyor belt