

Coal quality assured

Stefan Uhlig, Arnd Bühler and Lutz Brügemann, Bruker AXS GmbH, Germany, investigate the use of modern X-ray analysis for process and quality control.

X-ray analysis is a well-established method for process and quality control in the coal industry. One principally distinguishes structure and phase analysis by way of X-ray diffraction (XRD) from elemental analysis by way of X-ray fluorescence analysis (XRF). Minimal effort in sample preparation, short measuring times, analytical flexibility, high reproducibility and full integration in automation processes are the main advantages of modern X-ray analytical systems. Using modern X-ray spectrometers, almost all elements of the periodic table from Boron to Uranium can be determined in powders, solids and liquid samples. Depending on the specific application, concentrations from the sub ppm level up to 100% can be analysed. The measurement takes only a few seconds per element, and the analysis runs fully automated. X-ray diffraction covers all analytical tasks from qualitative and quantitative mineral analysis, crystallite size determination to crystal structure refinement. For laboratory automation concepts, the X-ray instruments can be equipped with a process automation sample changer to take process samples from a conveyor belt or robot.

In general, for X-ray analysis, all kinds of bulky samples such as coals, lignites, coke, minerals, rocks, slags and ashes have to be crushed (e.g., in a crushing unit). The crushed material as well as pieces thereof are subsequently pulverised very finely in a vibrating disk mill or planetary ball mill in order to be suitable for analysis. The grain size diameter should then be less than 50 μm . The smaller and more equally grain-sized the sample, the more homogeneous the pressed powder sample will be.

Through pressing under 10 - 20 t with pressing times of up to approximately 10 s, the sample powder is pressed into aluminium cups, steel rings or directly with or without a binding agent. To avoid inhomogeneity and grain size effects, fused beads are used for highly accurate element analysis by XRF, mainly for quality control of finished products. Liquid samples, slurries or loose powder samples can directly be analysed after pouring the sample into a disposable liquid cup.

XRF instrumentation smaller and easier to use

For near or at-line process control, smaller X-ray instruments are characterised by minimal floorspace, simple installation, low maintenance and easy operation. These instruments, based primarily on the energy-dispersive (ED) X-ray fluorescence (XRF) method, could not compete with the analytical performance of their big brothers - the wavelength-dispersive (WD) laboratory instruments - demanding a more extensive laboratory environment and infrastructure. WD-XRF is characterised and differentiated from ED-XRF in the way that it

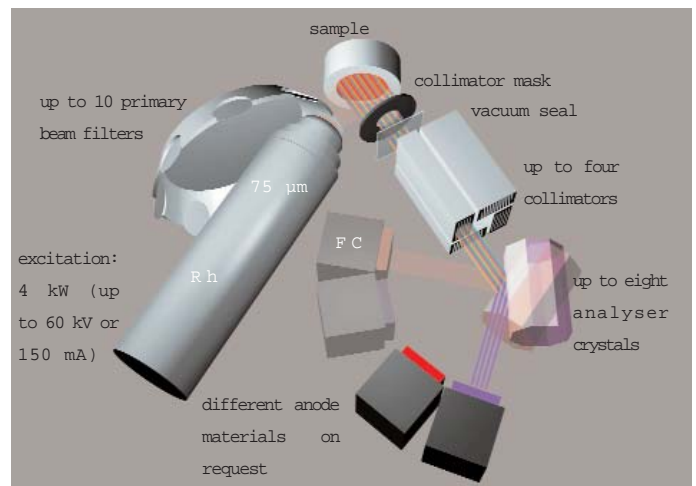


Figure 1. WD-XRF analysis is based on the optical dispersion of the element characteristic fluorescence radiation applying a highly precise goniometer and optics.

resolves the element characteristic fluorescence radiation. In ED-XRF, this is carried out directly in the detector, supported by state-of-the-art electronics and deconvolution algorithms. The unexcelled high resolution in WD-XRF is achieved by applying the optical properties of the element characteristic fluorescence radiation or wavelength. The element characteristic wavelengths are first collimated and then dispersed at an analyser crystal under well-defined angles realised by a highly precise goniometer positioning (Figure 1). 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 the total of intensities coming from all the different elements in a specimen. Therefore WD-XRF, in general, offers the highest res-



Figure 2. The new S4 EXPLORER WD-XRF spectrometer generation: small in terms of space, but gigantic in terms of analytical performance.

olution, 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 (WD) spectrometers and to improve the analytical capability of bench-top size energy-dispersive ED-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 1 m³ 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 better than 0.1 % relative for major compounds). 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 (Figure 2).

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 mini-

imum space requirements, single port connection, and fast installation and relocation (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 spacings d_{hkl} , which are characteristic for any crystallographic or mineralogic phase, can be obtained by measuring the reflection angles $2\theta_{qhkli}$ 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 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 (Figure 4). Modern process diffractometers feature a compact robust design, incorporating highly precise goniometers, innovative X-ray optics and detectors to ensure excellent analytical results.

Flexible sample handling

Modern analytical X-ray systems meet the user's immediate and future sample handling requirement by applying modular sample changer concepts with full access to process automation. This is an advantage in all industrial applications where a user-specific input of process samples is requested. Fully integrated, large sample magazines (over 50 positions) and automatic, safe measurement routines of large sample measuring sets ensure a maximum of unattended measuring capacity. Longer routine measurements can easily be interrupted for priority samples at any time, allowing 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 or belt or a robot (Figure 5). Modern compact X-ray instruments with small foot print and low requirements for installation also make containerised at-line, or even mobile, laboratories a reality.

XRF analytical software - an almost expert system



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

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, which can enter an XRF process and quality control laboratory in the minerals and mining industry. Any sample (coal cuttings, loose mineral powders, rock pieces, slags or ashes) 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.

The precalibrated OilQuant program was developed for the easy quality control of coal products. OilQuant is a calibration package for full quantitative XRF analysis of solid and liquid fuels (coal, coke, oils, diesel, gasoline, etc.). As it is optimised for liquid fuels, it can also be applied to other light matrix materials such as coals, lignites and even polymers, which also consist mainly of carbon. Twenty-four elements, from sodium to lead, are calibrated, a figure which can easily be extended by further element calibrations. Two different calibrations are available for sulphur and chlorine, one for trace contents (up to 1000 ppm) and one for contents in the percentage range (>1000 ppm). Table 1 summarises the most important calibration parameters for every element: concentration range, residual dispersion, detection limit and standard repeating deviation for 25 µg/g and 500 µg/g samples.

Latest developments in XRD software

Commonly used 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 con-

Table 1. Element and concentration ranges and calibration data of precalibrated OilQuant (measured with the S4 EXPLORER)

	Concentration range [µg/g]	Res. dispersion [µg/g]	LLD (3s; 25 s) [µg/g]	Abs. deviation (~25µg/g; n=15)	abs. deviation (~500µg/g; n=15) [µg/g]
Na	LLD - 500	7	7.1	9	9
Mg	LLD - 500	5	2.8	3	6
Al	LLD - 500	2	2	2	9
Si	LLD - 500	2	2.3	3	5
P	LLD - 2500	5	1.4	1	5
S	LLD - 1000	2	1.1	0.7	4
S	LLD - 5%	0.0047%	2.6	-	0.014% (1.13%)
Cl	LLD - 1000	3	2.7	4	-
Cl	LLD - 5%	0.0040%	6	-	0.020% (1.52%)
K	LLD - 300	2	1.3	-	-
Ca	LLD - 6000	5	1.2	1	5
Ti	LLD - 500	1	1	0.6	3
V	LLD - 500	2	0.8	0.3	5
Cr	LLD - 500	2	0.8	0.5	6
Mn	LLD - 500	3	0.7	0.3	3
Fe	LLD - 500	2	1	0.3	3
Ni	LLD - 500	1	1	0.6	3
Cu	LLD - 500	1	0.9	0.3	3
Zn	LLD - 2500	3	0.7	0.2	2
Br	LLD - 1000	0.6	0.7	-	-
Mo	LLD - 500	0.6	1.9	0.5	4
Ag	LLD - 500	3	6	1	6
Cd	LLD - 500	3	7.1	2	5
Sn	LLD - 500	4	3.7	2	4
Ba	LLD - 2000	3	3.8	1	5
Pb	LLD - 1000	2	1.2	0.2	3

tains 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 a unique technique for obtaining this crystallographic information. The width and shape of the reflections are characteristic of 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 (XRD) in combination with quantitative Rietveld analysis has been shown to offer new insights in the field of mineral phases. 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



Figure 4. The new generation of compact D4 ENDEAVOR X-ray diffractometer supports a wide range of industrial applications.



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

shortest time possible, but also a fully automated online 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 longer the 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 the latest Windows™ programs 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, 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 online 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 ana-

lytical X-ray instruments for elemental and phase analysis in process and quality control. User-friendly XRF software packages also include universal and specialised pre-calibrated 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 foot print and low requirements for installation perfectly fit the needs for elemental and phase analysis in the process and quality control of coals, lignites, ashes and slags. ■