

## ONE CENTURY OF DISCOVERING THE X-RAYS – MODERN DEVELOPMENTS IN X-RAY ANALYSIS FOR THE CEMENT INDUSTRY

### Abstract

Ever since the discovery of X-ray radiation by Wilhelm Conrad Röntgen about 100 years ago, X-ray analytical measurement methods have gained considerable importance. In X-ray analysis, we principally differ structure and phase analysis via X-ray diffraction (XRD) from elemental analysis via X-ray fluorescence analysis (XRF). Minimal effort in sample preparation, short measuring times, analytical flexibility, high reproducibility and full integration into automation processes are the main advantages of modern analytical X-ray systems for process and quality control in the cement industry.

In the course of the past few decades, many innovative steps have been added to make modern X-ray analysis more effective and more universal. Due to optimized spectrometer technology, light element analysis by XRF can be employed as a fast, reliable and convenient analytical method in the cement industry, in addition to standard routine applications. Improved light element analysis, for example carbon or fluorine, is achieved by artificial multilayer analyzer crystals and very coarse collimators, but optimized by excitation using thin beryllium end-window X-ray tubes. When considering quality and process control by

modern X-ray analysis, it is important to also take into account X-ray diffraction (XRD) analysis for reliable qualitative and quantitative determinations of crystalline phases in raw materials or klinker (e.g. free lime).

Modern analytical X-ray spectrometers and diffractometers meet the user's need for convenient sample handling today and in the future by modular sample changer concepts with full compatibility to process automation. The basic units can be easily upgraded to the large sample magazines with the most flexible access from conveyor belts or robots. Large sample magazines and the automatic, safe measurement of large sample measuring sets ensure a maximum of measuring capacity and flexibility.

Modern X-ray analytical software packages are open for easy integration into customized software packages, e.g. user-specific programs for process and quality control and computer networks – without influencing the reliability of the standard software product. User-friendly XRF software also includes precalibrated analytical programs for semiquantitative analysis or reliable quantitative analyses of geological materials, e.g. sands, clays, rocks, minerals, slags and cements.



## Introduction

Ever since the discovery of X-ray radiation by Wilhelm Conrad Röntgen almost 100 years ago, analytical X-ray measurement methods have gained considerable importance. In X-ray analysis, structure and phase analysis is achieved by X-ray diffraction (XRD) whereas elemental analysis is the technique of X-ray fluorescence analysis (XRF). In the course of the past few decades, many innovative steps have been added to make modern X-ray

analysis more effective and more universal. In 1992, as a further step, the new SRS 3000 X-ray spectrometer, after an extremely short development time of less than two and a half years, was introduced into the market (Fig. 1). In 1993, the D 5000 matic X-ray process diffractometer followed, in 1995, the new MRS 4000 multichannel X-ray spectrometer, and in 1998 the SRS 3400 with 4 kW and SPECTRA<sup>plus</sup>.



Fig. 1: Modern sequential X-ray spectrometer (SRS 3400)

During the course of these developments, besides the increase in analytical effectivity, the innovation of the sample changer system had the highest priority. The number of applications in the field of process and quality control, where analytical X-ray systems are involved in a fully automated laboratory environment – from sampling, sample

preparation and analysis to evaluation and control of the production – has increased in years past. In years to come, this tendency will further increase. PC techniques have helped to develop more effective programs for measurement, system control and data evaluation, enabling entirely automated measurement routines.

### X-ray fluorescence analysis

Wavelength-dispersive X-ray spectrometry is a non-destructive and environmentally safe analytical method. All elements of the periodic table from beryllium to uranium can be determined using qualitative, semi-quantitative and quantitative measurements in solids, powders and liquids. In the cement industry, X-ray fluorescence (XRF) analysis is applied to control the quality of the very different raw materials (limestones, marls, sands, clays, industrial waste materials, iron ores, etc.) and the ground mixture forming the raw meal. The production process is controlled by XRF analysing the klinker. Finally, the quality of the final products, the different cement types, is controlled by determining the major, minor and trace compounds by XRF.

For normal routine analysis of solid but inhomogeneous samples, e.g. sands, rocks, minerals and cements, etc., sample preparation is quite simple and rapid: crushing, grinding (size  $\ll 0.05$  mm) and pressing of powders to pressed pellets. Depending on the analytical demand, fused beads may be preferable. For analysing liquid samples of any kind, liquid cups or filter preparations can be used.

The measurement takes only a few seconds per element (using a sequential X-ray spectrometer), and the analysis runs fully automatically. Depending on the specific application (element and matrix), concentrations from the 0.1 ppm level up to 100 % can be analysed. High measurement accuracy and reproducibility (better than  $\pm 0.1$  % rel.) at maximum sensitivity are characteristics of the modern analytical XRF system. For this reason XRF analysis is a well established method for elemental analysis in process and quality control in the cement industry.

Modern X-ray spectrometers offer many new features for optimum analytical flexibility over the full elemental range from beryllium to uranium. Since the early eighties, most manufacturers of sequential X-ray spectrometers have used high-tech end-window X-ray tubes instead of the old side-window technology. Modern end-window X-ray tubes combined with medium frequency X-ray generators are the foundation of precise and highly reproducible elemental XRF analyses and a long service life. Improved light element analysis is based on multilayer analyzer crystals and very coarse collimators, but optimized by the innovative technology of 75  $\mu\text{m}$  thin end-window X-ray tubes for optimum excitation of the light elements with Rh-L radiation (Fig. 2).



Fig. 2: Very close optical coupling of X-ray tube and an extremely thin beryllium window improve light element analysis (Siemens end-window X-ray tube)

Using sequential X-ray spectrometers, primary beam filter changers offer sufficient positions to be equipped with an analytically useful choice of filters and masks to reduce the background and to suppress the spectral lines of the tube anode material. For all applications involving analysing liquids and also loose powders, a vacuum seal between the internal sample and the spectrometer chamber provide many advantages: higher analytical reproducibility, minimized helium consumption and safer operation.

Electronically controlled goniometers with separate  $\theta$  and  $2\theta$  stepper motors ensure high precision and automatic adjustment of the instrument. The mechanical construction and quality of the moving parts of a modern sequential X-ray spectrometer are so high that the overall reliability of a sequential spectrometer is practically as good as that of a simultaneous instrument. So, for example, the SRS 3400 uses the same goniometer drive as the well proven D 5000 X-ray diffractometer.

Collimator changers with up to four positions can be equipped with suitable collimators to provide the best measuring conditions for any application from increased sensitivity for light elements (for example boron) using the very coarse collimators to an improved resolution for rare earth elements (for example cerium) by applying super fine collimators. Sophisticated crystal changers enable the use of the most suitable analyzer crystal for the user's application, e.g. artificial multilayer crystals with 11 nm 2d spacing for the analysis of carbon.

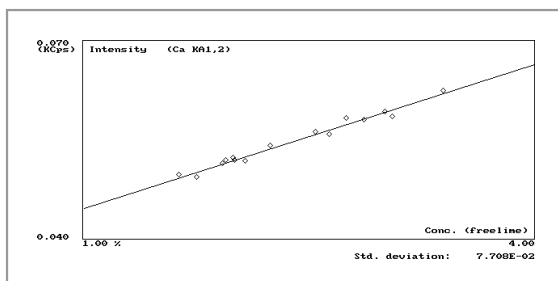


Fig. 3: Free lime calibration curve for klinker samples (XRD quantitative phase analysis)

The principal reason for the use of a sequential X-ray spectrometer for production control is that the sequential instrument is much more flexible, analytically (allowing measurement of additional elements and reliable background measurements, etc.) and normally less expensive. The measuring time of a modern sequential spectrometer is short enough for most process applications (e.g. 10 elements for cement analysis in less than 2-3 min). Also in routine operation a sequential spectrometer is as easy to operate as a simultaneous instrument.

When using multichannel X-ray spectrometers for very fast, simultaneous element analysis in process and quality control, analytical flexibility is limited to the quantitative analysis of up to 28 elements in solid or pressed powder samples. This analytical limitation may be accepted whereas a very fast feedback of analytical results or a high sample throughput is required in a continuous process routine. All chemical elements from Beryllium to Uranium (depending on the selection of fixed channels) are measurable in a few seconds with high precision from ppm to 100 % concentrations. Easy-to-use "pushbutton" measurement routines with automatic setting of all measuring parameters also support operation by un-skilled shift technicians. Modern multichannel X-ray spectrometers can be equipped with one or two scanners for fast, flexible quantitative and qualitative analysis to extend the analytical capability of the fixed channels.

### X-ray diffraction analysis

In the X-ray diffraction technique, a sample is exposed to monochromatic radiation from an X-ray tube causing X-ray diffraction patterns which are characteristic of the crystalline structure of the sample. After sintering of the raw meal in the kiln, the klinker consisting of different klinker phases is produced. Besides determining the minerals (quartz, calcite, dolomite, etc.) of the different raw materials, a very important X-ray diffraction analysis in the cement industry is used for determining the free lime content of the klinker to control the sintering process and the quality of the cement (Fig. 3). The D 5000 matic was especially developed to be applied in such industrial environments.

### 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. The basic units can be easily upgraded to the large sample magazines with the most flexible access to process automation. This achieves an advantage in all industrial applications where a user-specific input of process samples is requested, e.g. from a conveyor belt. Large sample magazines and automatic, safe measurement of large sample measuring sets ensure a maximum of measuring capacity over night or during the weekend.

For similar-sized samples, e.g. pressed powder pellets, fused beads or metal disks, there is an innovative approach to handle samples without sample holders. Instead of a sample holder catcher, the 100-position sample magazine of the SRS 3400 uses a low vacuum suction device to ensure direct, safe transport and loading requiring only two sample holders for the internal sample handling. For laboratory automation in the cement industry, spectrometers can be equipped with a process automation sample magazine to handle powder samples pressed into steel rings without sample holders and an inverting attachment to take process samples from a conveyor belt.

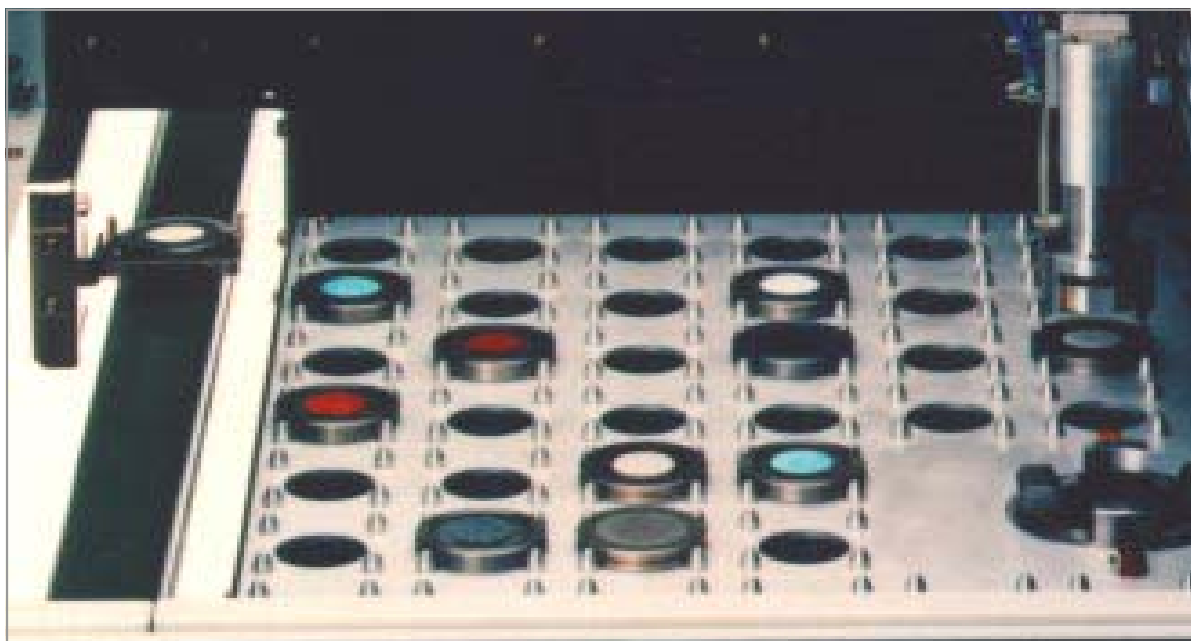


Fig. 4: Integrated large sample magazines ensure maximum measuring capacity and full integration into automation concepts (MRS 4000 sample changer to handle process cement samples pressed into steel rings coming from a conveyor belt)

### Data evaluation

Powerful and user-friendly analytical PC software packages characterize the spectrometer environment for control of the spectrometer, edition and evaluation of qualitative and quantitative programs and definition of measurement jobs. During measurement, Windows NT based multitasking techniques ensure control of both the system and the data collection process, freeing the PC for various other jobs such as data evaluation or display of the spectrometer status, system parameters and diagnostics, etc.

Using modern PCs, fundamental parameter programs provide fast and reliable calculation of the appropriate correction coefficients ("theoretical alphas") of interelement influences (matrix effects) from fundamental physical data such as absorption and secondary fluorescence. This allows universal calibrations over a wide concentration range. The fundamental parameter method is very effective for the reliable quantification of silicate samples with complex matrices, such as rocks, minerals and cements.

Modern XRF analytical software is open for easy integration into customized software packages, e.g. user-specific programs for process and quality control, and computer networks without influencing the reliability of the standard software product. All analytical results can be stored as a standard Excel worksheet and ASCII data files to be accessed by the most commercially available programs.

User-friendly XRF software packages also include precalibrated analytical programs. Of primary interest is a particular universal program which allows analysis of nearly all elements of the periodic table in all the different materials which can enter an XRF laboratory. Any sample – metal cuttings, plastic granulates, rock pieces or even used oil – can be analysed with a uniform program detecting all elements: the precalibrated analytical task of SPECTRA<sup>plus</sup> (Fig. 5).

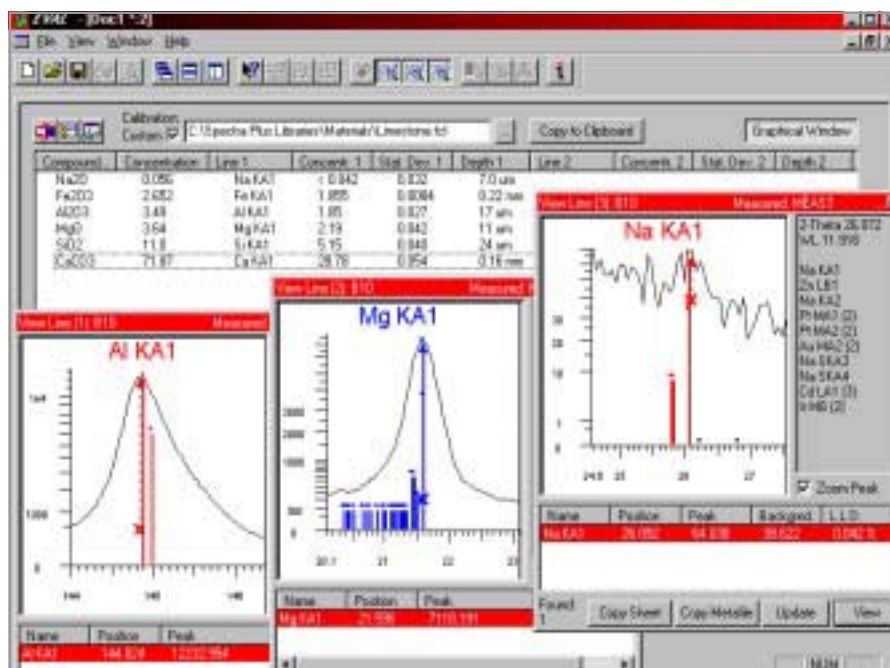


Fig. 5: Precalibrated analyses are based on fast scan measurements, automatic peak identification and quantification using net intensities. Transparent verification of evaluated concentrations is ensured by integrated scan presentation.

The usual requirements for such a universally precalibrated analysis are a classification into major and minor elements and “nearly” quantitative results. 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 massive glass or metal samples and a more or less rough chemical characterization for extremely small, bulky or untreated samples.

The quality of an XRF analysis depends on the counting statistics. Therefore the reduction of the measuring time to achieve a very fast semi-quantitative analysis will be limited by the user’s demand on the analytical quality. Concentration calculations in XRF analysis are based on fluorescence intensities from a layer at the surface of a sample, whose thickness may vary depending on the element and basic material, to a few layers of atoms lying a few centimeters down. Thus, the limit of accuracy in semi-quantitative analysis also depends on the surface quality of the sample.

A further example of new precalibrated analytical programs is the new GeoQuant program for exact quantitative analyses of geological materials, e.g. sands, clays, rocks, minerals, slags and cements, etc. This precalibrated program can be most helpful for quality control of the cement industry’s raw materials.

### Specific XRF applications

The reliable determination by XRF analysis of major, minor and trace compounds is a well proven analytical routine of modern X-ray spectrometers. Modern applications are the determination of environmentally relevant trace elements (Pb, Cd; (Fig. 6), control the content of chlorine or fluorine, the analysis of carbon, or the sulphur content differentiation originating from sulfates or sulphides.

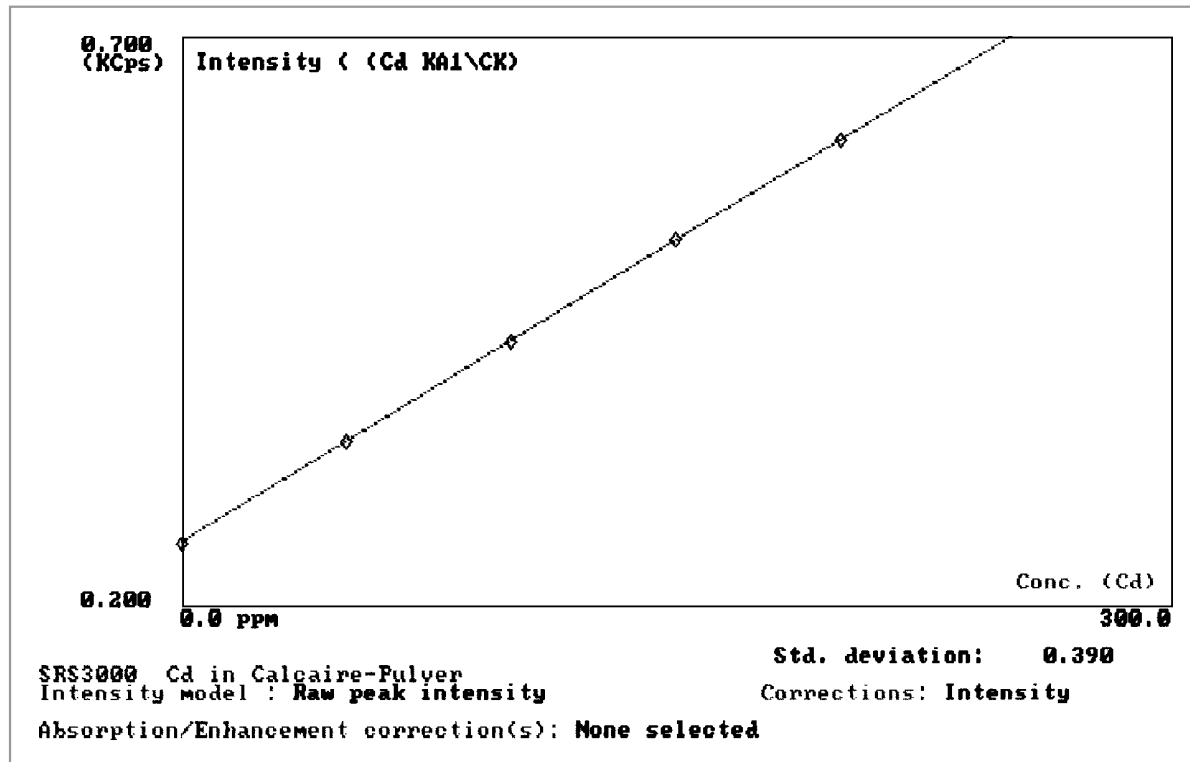


Fig. 6: Calibration curve of Cd determination by XRF analysis in limestone prepared as pressed pellets (uncorrected raw intensities)

Due to improved spectrometer techniques, light element analysis by XRF is applied as a fast, reliable and handy routine in cement analysis, but don't forget the high reproducibility of the XRF analysis. A typical example is the analysis of carbon in cement. Modern wavelength-dispersive X-ray spectrometers have the analytical capability to analyse carbon in cement samples below 150 ppm (Fig. 7). XRF analysis of the very light elements is based on fluorescence intensities from

a layer of a few atoms at the surface of the sample. For this reason the quality of analysis strongly depends on the grain size (fine milling!) and the surface quality of the sample (clean, smooth surface). Due to improved spectrometer techniques, light element analysis by XRF is applied as a fast, reliable and handy routine in cement analysis, and don't forget the high reproducibility of the XRF analysis.

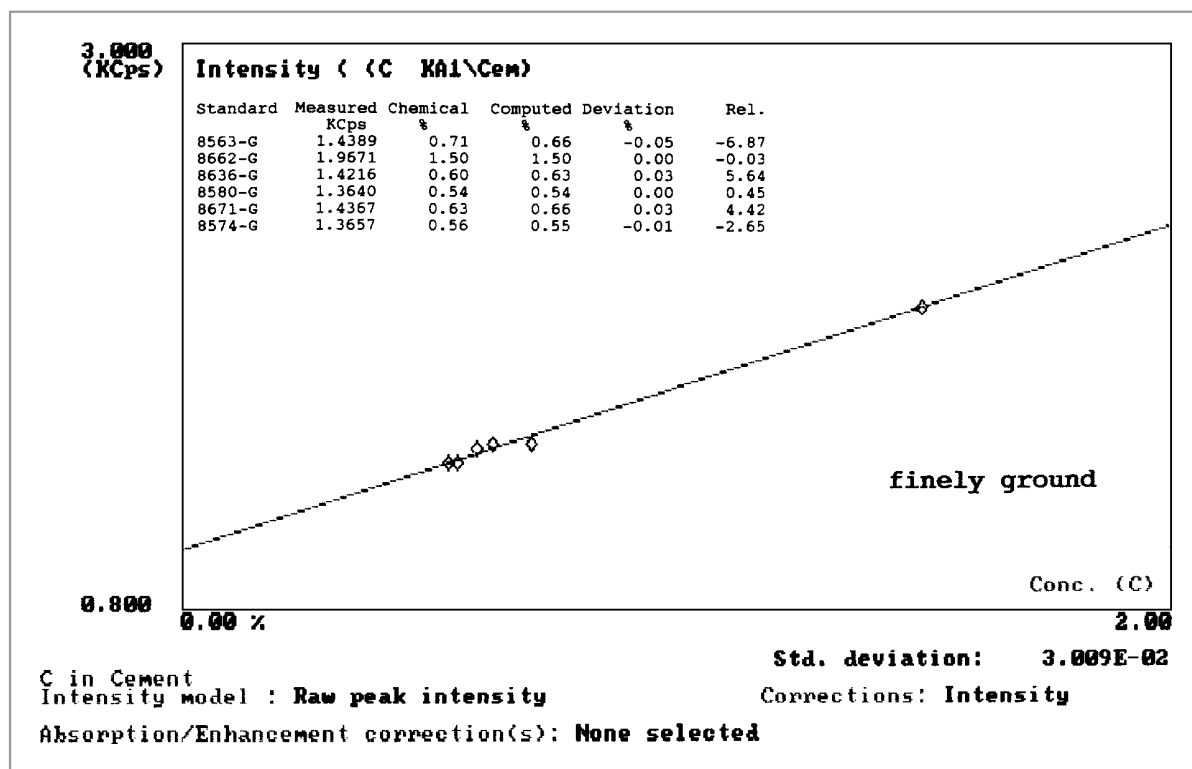


Fig. 7: Calibration curve for carbon in pressed pellets of cement samples (uncorrected raw intensities)

For the quantitative analysis of non-metallic materials requiring the highest degree of accuracy, the conversion of sample material into homogeneous fused glass beads using lithium borate is a universal and well proven method to overcome mineralogical effects of inhomogeneity and grain size. The fusion preparation method, diluting the sample matrix by the lighter flux material, is also preferred in order to minimize interelement effects (absorption and secondary fluorescence).

Modern, PC-based fundamental parameter programs provide a fast, easy calculation of appropriate correction coefficients ("theoretical alphas") to compensate interelement influences (matrix effects). This allows the definition of universal calibrations over a wide concentration range also in samples prepared as pressed powders. To minimize the mineralogical effects fine, careful grinding is fundamental. An example is given for the SiO<sub>2</sub> analysis of geological samples prepared as pressed powders (Fig. 8).

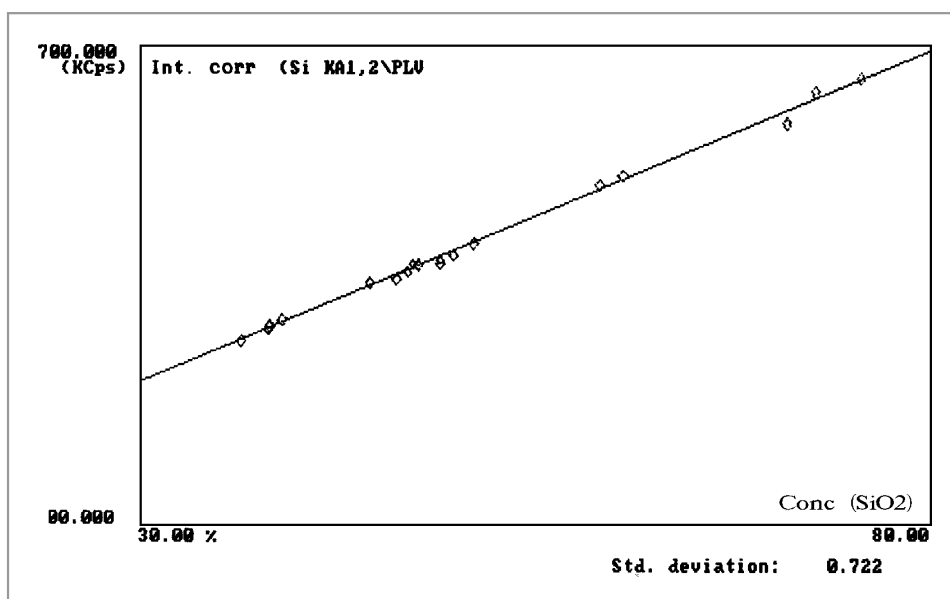


Fig. 8: Calibration curve for  $\text{SiO}_2$  in geologic samples with a large concentration range applying fundamental parameter matrix corrections (theoretical "alphas")

### Conclusion

Modern X-ray fluorescence analysis is a very flexible analytical method for the full range of element determinations in research and production laboratories in the cement industry. Inexpensive and fast sample preparation and low costs per sample/element determination compensate for the investment of an X-ray spectrometer system – not to forget the advantages of an environmentally safe, fast and operator-friendly analytical system. Through transparent hardware and data interfaces, process analytical X-ray systems can be integrated – easily and almost limitlessly – into customer-specific laboratory automation processes of quality and process control. An additional interface from the system microprocessor allows a fast and economic remote diagnosis via modem.

### Literature

- Neff, H.: Forecasting the technological characteristics of Portland cement by X-ray analysis. – Siemens Application Note 256, 5 pp., 1979.
- Schlotz, R.: Methods for determination of the sulfate and sulphide content in cement samples using X-ray fluorescence analysis (XRF). – Siemens Analytical Application Note 322, 8 pp., 1990.

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