

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/27419258>

Geology, Mining, Metallurgy

Article · June 2006

Source: OAI

CITATIONS

2

READS

1,215

6 authors, including:



Dieter Rammelmair

Bundesanstalt für Geowissenschaften und Rohstoffe

58 PUBLICATIONS 731 CITATIONS

[SEE PROFILE](#)



Karen Appel

European XFEL

215 PUBLICATIONS 2,695 CITATIONS

[SEE PROFILE](#)



Robert A. Schwarzer

Technische Universität Clausthal

147 PUBLICATIONS 1,035 CITATIONS

[SEE PROFILE](#)



Andreas Moeller

University of Kansas

153 PUBLICATIONS 2,225 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



High-Energy Density Instrument [View project](#)



MSKU Scientific Research Office (BAP-16/20) and Scientific and Technical Research Council of Turkey (TUBITAK - 117Y283). [View project](#)

7.6 Geology, Mining, Metallurgy

Methodological Developments and Applications

*D. Rammlmair, M. Wilke, K. Rickers, R.A. Schwarzer, A. Möller,
A. Wittenberg*

7.6.1 Introduction

Geology, mineralogy, exploration, and mining require an interdisciplinary approach involving geological mapping, tectonics, petrography, geochemistry, sedimentology, remote sensing, geophysics, microbiology, engineering, mineral treatment, and melioration. Within this frame geochemistry is one of the basic tools used in characterizing rocks of magmatic, metamorphic, and sedimentological origin, as well as soils and weathering products of these. The obtained geochemical information allows us to classify the rock either in terms of an internationally approved rock name classification [397] (Le Maitre et al. and references), genetic origin, such as the classification of magmatic rocks to geotectonic environments [398] (Pearce and references) or parental magma series. Moreover and more importantly, genetic processes like fractionation and/or mixing and/or assimilation during transport in the earth's interior become elucidated through the geochemical characterization of the source rock, the interim, and the final product. Even chemical changes within apparent homogeneous successions due to cryptic layering, metamorphism, metasomatism, alteration, weathering and/or mineralization can be visualized.

The characterization of soil samples is fundamental for understanding soil-forming processes and transport processes within soils and their contribution to the groundwater quality. Soil characterization on a regional scale is embedded and used in soil information systems. The data obtained are used for monitoring the amount and type of fertilizer to be adopted in the high-technology GPS (global positioning system)-controlled agricultural industry. For these applications, high accuracy of the obtained geochemical data is crucial. Regarding exploration and mining, the rapid characterization of prospective zones due to relative enrichment or even depletion of diagnostic or pathfinder elements is fundamental for finding and developing a mine site.

In the field of metallurgy, online quality control of the products is relevant at every point of the production process: starting at the mining site

itself, blocks of rock are selected and mixed properly to obtain a homogeneous ore concentration used in the treatment plant. Within the treatment plant, quality monitoring of the separation and concentration process, and the final products is crucial. For these applications, speed of analysis is of major importance. In situ online data acquisition is the optimal solution for decision-making processes. X-ray fluorescence (XRF) was [399,400] and is the method applied to solve these most basic problems of geologists, mining engineers, and metallurgists.

Several scales of chemical information are useful for the geoscientist.

- The macroscale involving direct field measurements, laboratory investigation of homogeneous bulk samples, and product online control.
- The mesoscale refers to the hand specimen size, down to a spatial resolution of 30–100 μm . Element 1D scans and 2D distribution maps provide zones of interest for further microanalytical research.
- The microscale focuses on single minerals, mineral zoning, single particles, fluid and melt inclusions, and compositions within experimental apparatus, e.g., diamond anvil cells (DAC).

The principles and advantages of wavelength-dispersive-(WDXRF), energy-dispersive-(EDXRF), nondispersive-(NDXRF), total reflection-(TXRF), and grazing emission X-ray fluorescence(GEXRF) have been described in detail by Bertin [401] and Lachance [402] and are the subject in some of the chapters (Chaps. 2–5) of this book. Hahn-Weinheimer et al. [403] and Weber-Diefenbach (and references) [404] refer in detail to the applicability to geosciences. Brill [405] compared WDXRF and EDXRF systems. Kramar [406] discussed the progress in EDXRF technology. Several manufacturers of XRF instruments provide basic information on instrumentation and applications via the internet. Depending on the field of application, the individual systems are designed to fulfill certain conditions. Spectral resolution, excitation conditions, and spatial resolution are thereby the most relevant aspects. A number of XRF instruments on the market meet the requirements of application in the field or outcrop, in the laboratory, and for online monitoring of technical processes.

Robust and highly accurate laboratory systems facilitate bulk analyses, fast online systems help to control production quality, handheld systems enable analysis in the field and help to reduce the number of samples by selective sampling, and high spatially resolving systems support meso- and microanalytical approaches. However, for each scientific application an adequate method should be chosen based on the need of qualitative, semiquantitative, or quantitative information and the required spatial resolution.

This chapter does not refer much to the methodological and instrumental background, tubes, filters, detectors, analyzer crystals, optics, evaluation and correction methods, since these are treated in detail in chapters 2–5 of this volume. However it aims to give an insight on the application of the XRF methods within the fields of geology, mineralogy, mining, and metallurgy. Among the

large variety of possible applications, special emphasis is laid on examples using EDXRF, and on analytical methods with spatial resolution that cover analyses on the hand specimen scale or even on the microscopic scale. Investigations on the microscopic scale have been strongly boosted by the use of synchrotron radiation. Hence, special treatments of such applications are given in Sect. 7.6.4 (Microanalysis using synchrotron radiation XRF). Since geologists study processes in the history of the earth's evolution, dating methods are crucial for the understanding of the earth's history, and an example of chemical dating using U–Th–Pb contents in monazite is presented in Sect. 7.6.4 (U–Th–Pb chemical dating). As a valuable extension to XRF methods, geological applications of X-ray absorption fine structure spectroscopy (XAFS) are shown in Sect. 7.6.4 (XAFS in earth sciences). Finally, the application of imaging XRF, combined with texture and lattice strain measurements in deformed metals, gives an insight on applications in metallurgical problems (Sect. 7.6.3 (Microanalysis using synchrotron radiation XRF)).

7.6.2 Macroscale

In Situ Analysis in the Field

The field geologist has to decide right in the field on the most adequate sample for the geological, stratigraphic, exploration, or tectonic work that has to be performed.

Portable EDXRF systems based on radioisotope sources (^{55}Fe , ^{109}Cd , ^{244}Cm , ^{241}Am) have been in use since decades. Recently handheld minute size laser induced X-ray sources equipped with energy-dispersive pin-diode detectors have been providing basic field information for a wide range of elements, simultaneously allowing to identify rock types for mapping purposes [407], differentiate within stratigraphic sequences by element finger-print patterns, and obtain geochemical information from areas where sampling is not possible. Heavy metals are especially suitable for this method as they have low detection limits. The development of minute-size low-energy consuming systems is motivated by the interest to obtain information from planets such as Mars. The prototype has landed on Mars' surface and has been providing information on the Martian geochemistry [408, 409].

Investigations of mine waste [410] and contaminated soils in the vicinity of industrial sites are also suitable applications of this type of rapid screening [411–414].

The method has been applied in a qualitative evaluation of heavy metals in soils by McCain [415] using an isotope-source energy-dispersive XRF analyzer for rapid onsite screening.

Onsite data acquisition has been used in addition to outline zones of interest in exploration areas previous to further detailed representative sampling

for accurate XRF analyses [416, 417]. Konstantinov et al. [418] developed a new indicator method as an effective exploration method for blind ore. The method takes advantage of the partial redeposition of ore and vein matter in the overlying rocks as a result of the magmatic, hydrothermal, and tectonic processes in the form of shears, veinlets, and/or dikes. A number of indicator elements are analyzed to localize anomalous zones. The indicator method uses special sampling of the post-ore uplift structures. The proposed technique was successfully used to prospect blind ore mineralization and new ore bodies in various geological environments and is applicable over a vertical range of more than 200 m. The resolution identifies individual blind ore bodies as well as groups of ore bodies.

The rapid element screening can further be applied to characterize ore types, drill cores, and hand specimens. The fast turnover of information is a very valuable contribution to improve decisions and save resources.

Within the metallurgical section the onsite characterization of stainless steel samples [419], metal alloys, and metal scrap allows gaining higher purity of the end products.

Sample preparation for the screening method in general is minimized. The best available surfaces are used. Analyses aiming for better reproducibility might use homogenization methods in the field. The data arrived at are qualitative to semiquantitative since comparable sample geometry and homogeneity cannot be provided in the field. Quantitative values are hard to be obtained by this fast method and are not really necessary since element fingerprint pattern and element ratios generally provide the necessary information needed for making decisions in the field.

Of late emphasis has been on the development of downhole-EDXRF systems [420] applied in drillholes to monitor in situ chemical patterns of the drilled soils and rock units.

Quantitative Analysis in the Laboratory and in the Field

After the selection of the most adequate sample, or a random or a grid-oriented sample series in the field, high-quality representative analyses are performed by standard XRF techniques in the laboratory or benchtop-equipped mobile field laboratories. Depending on the amount and type of sample, WDXRF, EDXRF, and for special occasions even TXRF are used to get the appropriate geochemical data for interpretation of the field data.

Various sample preparation techniques are used on geological samples to obtain the optimum results. Detailed descriptions of the individual techniques, and advantages and problems are available in literature [401, 402, 404], (van Grieken et al. Chap. 6) and internet (www.spectroscopynow.com; www.learnxrf.com). The most important requirements for excellent reproducibility are homogeneity, grain size and minimum thickness of the sample, and limitation of matrix effects.

Applications

Classification of Rocks and Plate Tectonic Implications

Identification and nomenclature of rock samples is usually done by the field geologist on the basis of macroscopic and microscopic observations. However, the magmatic equivalent of altered and metamorphosed rocks is generally identified by geochemical investigations. The classical schemes of Streckeisen [421], Le Bas et al. [422], and Le Maitre et al. (and references) [397] have a mineralogical background and are based on the relative proportions of minerals such as alkali feldspar, plagioclase, quartz and feldspatoids in volcanic rocks, and plutonic equivalents. There are various protocols (e.g., the Niggli values [423] and the CIPW norm [424, 425]) to convert the chemical raw data into classifications that relate the chemical composition to the mineralogy of the rocks. In these norms collective components or contents of normative minerals are calculated from the chemical composition that enables an improved classification of the rocks where mineral content is not directly determinable (e.g., fine grained or altered rocks). In parallel, some classifications directly use element concentrations to classify rocks as in the TAS diagram, where the total alkali content versus the silica content is plotted [422].

Classification schemes such as SEDNORM [426] and MINLITH [427] are applied for characterization of sediments.

Besides the classification of samples into rock types, a number of classification schemes on the basis of major and trace elements are available, which may be used to establish genetic features of a given rock unit, such as the geotectonic environment [398] (Pearce and references). These schemes have been applied in numerous cases to classical ophiolite sequences, komatiitic successions, and granitoid systems.

Field observations often reach their limits with regard to stratigraphy within sediments, salt successions, or layered intrusions due to the macroscopic conformity of the rock units. Detailed geochemical investigations - mainly XRF based - provide a fast tool for correlation of units from different localities (e.g., drill cores from marine environments, exploration targets) and even provide up and down criteria for overturned sequences in highly tectonized areas. The documentation of saw-teeth patterns in cryptically layered magmatic successions provides insight into magma-mixing episodes and processes. For example, investigations on the Bushveld and Stillwater complexes or the Skaergaard and Dufek intrusions have shown the importance of detailed geochemical approaches for the interpretation of their complex history [428, 429].

Mineral Chemistry

In combination with methods that provide insights into the crystallographic structure, such as X-ray diffraction analysis (XRD), XRF is used for characterizing the composition and purity of minerals and mineral concentrates [399].

Analyses of mineral concentrates are performed in the same way as for the whole rocks. Large single grains of micas, hornblendes, or zircons, to name a few, have been investigated by WDXRF for elements like K, Rb, Sr, Nd, Sm, U, and Th for classification or as a base for age-dating purposes. The beauty of this method is its nondestructiveness. Hence, the same samples can be used for further analyses. This application competes with electron microprobe analysis (EMPA) of minerals, which is also capable of simultaneous major and trace element analysis of multielement samples and has the additional advantage of achieving a high spatial resolution in the micrometer range. However, EMPA requires additional time-consuming preparation steps, as polished thin sections of mineral and rock samples are generally used for analysis.

More recently, multielement EDXRF designed for microprobes named XRF microprobe or EMMA (energy-dispersion miniprobe multielement analyzer) have been developed [430] for special applications (see U–Th–Pb chemical dating in Sect. 7.6.4).

The XRF, a fast, precise and low-priced method when compared to other multielement analytical techniques, is now a routine technique in industrial applications [431]. As an in- or rather on-time method for routine bulk analyses during industrial production, WDXRF is used [432]. In particular, it is the industrial manufacturing of high-quality products, which requires very pure minerals either of natural or synthetic origin [433]. For this purpose pressed pellets of either pure minerals or mineral concentrates are analyzed. While using pressed pellets most of the interesting trace elements can be analyzed due to the lack of dilution. The disadvantages of pressed pellets are related to grain effects and chemically zoned single grains. Since the last few years, problems related to grain effects seem to be fully understood and hence can be taken into account by corrections [434].

While ED and WDXRF are widely utilized it is especially the TXRF technique that is of great interest for the purest material chemical analysis, since the detection limits can be reduced to those of the very expensive and sophisticated inductively coupled plasma mass spectrometer (ICP-MS) technique. For further information, in particular about the TXRF used for wafer monitoring, see Sect. 7.3.6.

Geochemical Mapping, Prospection, and Exploration

Large-scale low-density geochemical surveys provide basic knowledge on geochemical provinces that can be used to outline prospective areas. A reliable and comprehensive database of the natural variability of the geochemical background of diagnostic elements is the basis for administrative and legal issues concerning sustainable long-term management of environmental and mineral resources [435].

Data acquisition by XRF is a valuable basis for geochemical mapping. Numerous element distribution maps have been produced in Europe and worldwide at regional and local scale for characterization of catchment areas,

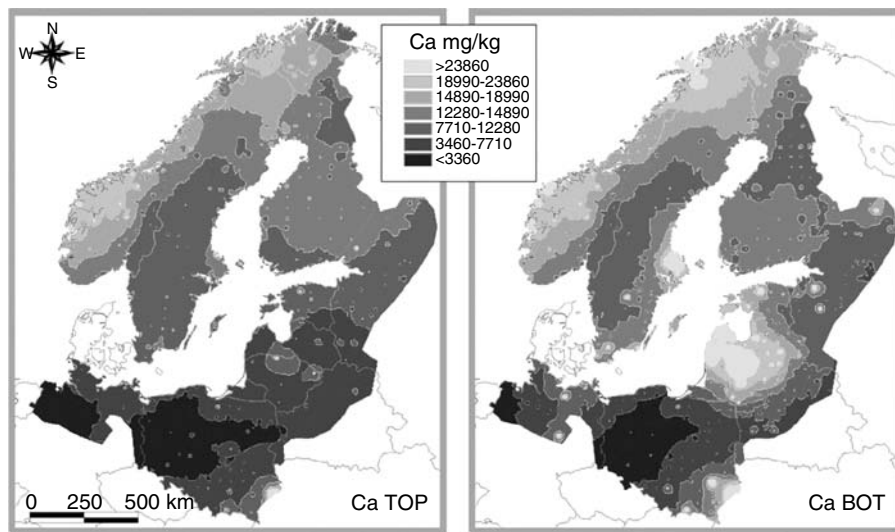


Fig. 7.126. Ca in agricultural soil, Ap (TOP) and B/C-horizon (BOT), total concentrations, WD-XRF (Courtesy of Reimann et al. [437] 2003).

soils, rock units, and mineralization for the support of mapping, exploration, and environmental investigations. Reimann et al [436, 437] have shown in the Baltic Soil Survey that top and bottom soil (TOP and BOT) provide basic information on regional distribution of major and trace elements. The Ca maps (Fig. 7.126) for example show that both TOP- and BOT maps contain the highest concentrations above the Caledonides, intermediate values for most of Sweden and Finland, which may be assigned to granitic rocks, and high Ca occurs above sediments in the SE of Sweden.

Chemical reconnaissance mapping and exploration used the same method as described earlier. In general, depending on the requirements a 2-mm and a 60- μ m fraction is obtained from the soil or stream sediments. Alternatively, heavy mineral concentrates, chip or channel samples, as well as hard rock samples along base lines, grids, and streams may be used to identify areas for detailed investigation. In special cases, plants (e.g., for Au, Cu, Ni) and termite hills (e.g., for kimberlites) are used for prospection to outline zones of interest under thick sedimentary cover [438, 439]. X-ray fluorescence analyses provide over 30 elements for purposes at reasonable costs and fast turnover, crucial for the exploration geologist. Anomalous zones are subsequently mapped in detail, including drilling at sites of major importance to increase the knowledge on the anomalous zone of interest.

Mining, Whole Rock, and Mineral Treatment

In the mining sector recognition of wallrock, subeconomic, economic, and high-grade ore portions within a mining site is done on a visual basis as long as

the lithology provides this information. However, significant differences often cannot be recognized this way onsite. Fast sampling has to be performed on an in situ basis via handheld EDXRF systems or by quick turnover via the laboratory. Often drill arrays are performed before the mining reaches the zone of interest. Detailed (1 m down to 10 cm) sampling of the drill core enables the mining engineer to outline blocks of similar ore content. In modern open pit mining the operators of trucks and Caterpillars are remote controlled onsite via GPS, with the adequate information of block mining in the proper ratio providing a continuous flow of the standard product for optimum recovery of the ore or other raw material of interest.

From mining to final product all processes have to be monitored by mineralogical and geochemical methods to enhance the recovery and the quality of the mineral products or concentrates. All steps are accompanied by sampling and eventually, like in the cement, glass, or ceramic industry, even online continuous measurement in the production chain of the components can be performed.

Coal, Oil, Bitumen

Coals, oil shales, hydrocarbons, bitumens, and ashes are analyzed by XRF for their carbon, sulfur, and trace element contents [440–442]. Genetic implications can be drawn from the chemical composition of coals as influenced by mineralogical changes in the primary environment of deposition, by epigenetic and supergene alterations. Only a few elements (e.g., P, REE) vary with the rank of coalification [443]. The trace elements are believed to be associated with either organic compounds (Mo, Hg, and U) or minerals such as aluminum-iron-silicates (Sc, Ge, and Bi), aluminum-silicates (Cs, Be, Th, Pb, Ga, and REE), iron-phosphates (Zn, Rb, and Zr), iron-sulfides (As, Cd, Cr, Cu, Hg, Ni, Tl, and V), and carbonates (Sr, Mn, and W).

Some coals are strongly enriched in the trace elements U, Pb, and Hg due to volcanic activity. Epigenetic sulfide and carbonate mineralization are common in some coalfields. Elements such as Zn, As, Sb, Hg can be enriched in micropores and microfractures [444]. Hence, the hazardous potential of a coal due to its combustion has to be estimated by analyzing the ashes in the laboratory and even onsite [445].

Potential Hosts for Nuclear Waste Depositories

The nuclear industry, basically the electric power industry, is in need of finding a lasting and durable depository for highly radioactive nuclear waste. Until now no location has been equipped. Rock salt sequences, clay formations, and granitoids have proved to fulfill the requirements. In part they do. Again detailed geochemical investigations in the underground and via drill cores are necessary to understand the stratigraphic background (PLATE II 2.1-2), recognize weak zones, learn about the behavior of the material in contact with

the nuclear waste bearing containers and about its neutralization potential for radionuclides that may have escaped from the container.

To check the possibility of final safe storage in former rock salt mines samples of rock salt have been analyzed by WDXRF for Rb, Sr, Br to characterize the contents of Br in view of primary distribution and redistribution due to recrystallization and tectonic overprint [446].

7.6.3 Mesoscale

Analyses of Inhomogeneous Samples

Hand specimen rock samples are usually heterogeneous and cannot be characterized in an appropriate way macroscopically. Therefore the samples are either homogenized for bulk analyses, or small parts are selected to be analyzed in detail by microanalytical methods such as microscopy, EMPA, scanning electron microscopy (SEM), cathodoluminescence (CL), infrared (IR) or Raman spectroscopy. With the adaptation of fast simultaneous EDXRF systems with high spatial resolution, hand specimen and drill cores of sample sizes of 10 cm by 10 cm and more can be analyzed in a relatively short time for major and trace elements at a spatial resolution of 100 μm to 10 μm . The obtained elemental scans provide a facility to select appropriate areas for further analyses by EMPA, SEM, and other microanalytical systems.

Time is the crucial part for sample characterization. Due to the application of powerful microfocus X-ray tubes and advanced X-ray optics such as mono- or polycapillaries, highly oriented pyrolytic graphite (HOPG) [447], and multilayers for EDXRF, the photon flux has been increased in such a way that even 8 W X-ray tubes provide enough flux when using sensitive detectors to allow reduction on the acquisition time to parts per second for qualitative and semi-quantitative measurements. Some instruments with fast scanning devices are able to provide an overview of major element distributions for large samples within minutes. Statistical improvements will be obtained by accumulation of repeated measurements. The application of pin diodes or Peltier-cooled silicon drift detectors enables continuous measurements at reasonable costs. Commercial scanning facilities generally work in air. Some benchtop systems can switch to vacuum conditions in order to lower the detection limits and to enable the analysis of light elements such as Na, Mg, Al. Zhdanov [448] provides details on manufacturers of micro-XRF systems in the internet.

Sample Preparation Techniques

In general, all types of samples are suitable for qualitative analyses, but to obtain semiquantitative or quantitative information, samples have to fulfill certain conditions. A relatively smooth polished surface is required. However, grain, pore and crystal size distribution, water and organic content, crystal orientations in the sample are properties that strongly influence the signal and may hinder the access of quantitative information [401].



Fig. 7.127. XRGs equipped with columns

Instrumentation and Methods

The applications shown later have been performed on two individual instruments, both designed by COX Analytical Systems AB, Sweden. The Itrax geo scanner (XRGs), a special design by the Bundesanstalt für Geowissenschaften und Rohstoffe (BGR), Germany (Figs. 7.127 and 7.128), operates with flat beam optics suitable for 1D profiles, while the standard ITRAX X-ray microscope using a 100- μm monocapillary is applicable for point measurements, 1D profiles, and 2D scans. Both systems are based on a Rich. Seifert & Co. ISO-DEBEYEFLEX 3003 HV-generator and the standard operation voltage for the data acquisition is 45 kV at 30 mA with long fine-focused Philips XRD Mo tube type PW 2275/20 (3 kW, 60 kV).

Within the XRGs the beam is focused by a glass slit capillary at 50 μm height and 2000 μm length. The detector is placed at an angle of 45° to the sample surface. It is an energy-dispersive, Peltier-cooled RÖNTEC

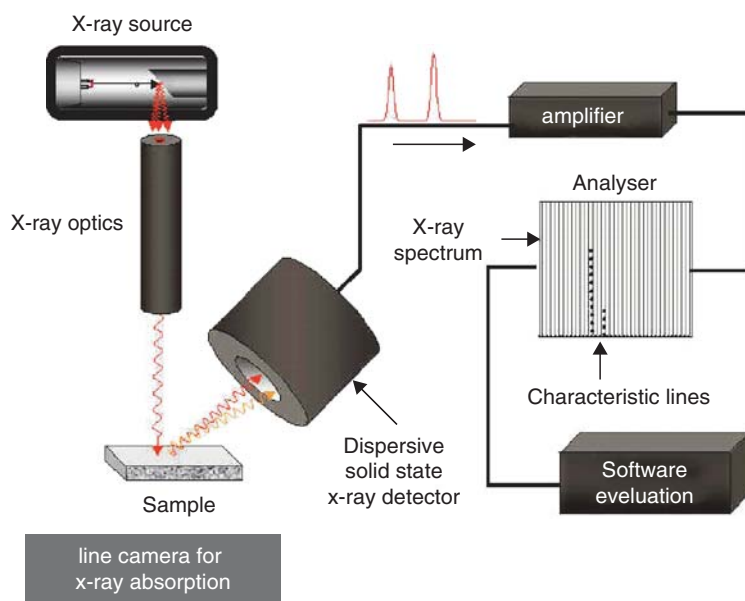


Fig. 7.128. Schematic view of the EDXRF geo scanner (courtesy of COX Analytical Systems AB, Sweden).

drift-chamber detector, with an energy resolution of 149 eV provided by a vacuum nozzle. The XRGS is further equipped with a rotating stage for 6 samples. The samples are scanned vertically by a line camera to find the area of interest, and after rotation to the measurement position, the sample is focused and scanned by moving the X-ray tube and detector unit. Step sizes range from 50 to 200 μm and time of exposure from 1 to 30 s according to the individual requirements.

A number of elements can be chosen to be displayed on the monitor showing the variation of elements during the XRF scan. For each step the complete energy-dispersive spectrum is stored in 1024 channels for later evaluation. The obtained spectra consist of the characteristic element lines of the sample, besides the tube characteristics, e.g., the Mo lines, the incoherent Compton radiation, and the Bremsstrahlung. Due to the glass slit capillary the intensity of the X-rays with higher energy is increased and the Bremsstrahlung at lower energies is minimized (up to the Fe $K\alpha$). Relative concentrations are calculated by the fundamental parameter method and are made available on a spreadsheet [449].

The ITRAX X-ray microscope is based on the same principle, but is equipped with a glass monicapillary of 100 μm diameter and an energy-dispersive RÖNTEC XFlash Si(Li) detector mounted at an angle of 45° to the sample surface with an energy resolution of 139 eV and a nozzle that may be evacuated. An optical camera and a sample stage complete the system.

The obtained spectra from either point, line scan or area scan measurements, are saved and elemental concentrations are determined using the fundamental parameter approach. A number of individual points, profiles, or areas can be selected for analysis using the optical camera. The elements of interest can be marked, and the time for each analysis (minimum 0.5 s) and the individual step size (100 μm standard) can be selected. The data from the selected element channels are stored as text files. The spatial distribution of each selected element can be viewed and printed. The data can be further processed in a spreadsheet or by image analysis [449].

Imaging is one of the key aspects of geochemical mapping. Visualization of chemical patterns at any scale provides a quick overview of huge amounts of data. The EDXRF images can provide a data cube of elements with x columns and x rows. An automated segmentation of EDXRF image sets previsualizes heterogeneities of samples in an adequate way [450]. Element mapping generally requires stepwise sequential data acquisition. With EDXRF the accumulation time can be reduced due to the simultaneous spectra acquisition. A new method for simultaneous X-ray imaging using a microchannel plate X-ray optics [451] has opened a new dimension of element mapping.

One aspect in EDXRF mapping is the data acquisition, which is dependent on a number of factors mentioned earlier, but major problems arise from the time-consuming data presentation, and manipulation and adaptation of the coordinate systems to other microanalytical systems to verify anomalies in the sample. Since the chemical data acquisition is free of distortion, the combination with optical scans achieved by optical desktop scanner or by slide scanner is a basic approach to interpret chemical and optical data.

Applications

Stratigraphic Control

Within uniform rock sequences the identification of characteristic marker horizons is generally a difficult task. Dating by absolute and relative methods might solve the problem, but it is time consuming and would require repetition for each locality. Chemical bulk analyses of samples taken in equidistant steps do not provide a continuous image but deliver bulk information on an integrated sample only. The adaptation of laser ablation (LA)-ICP-MS techniques along 1D profiles and micro-EDXRF 2D-mapping gives very detailed information for relatively small sample sets. Using the EDXRF scanner described earlier, meters of drill cores can be scanned almost continuously at a 50- μm spatial resolution with elevated statistical significance as compared to a point-like source. Within fine-grained laminated marine and lake sediments this method provides excellent spatial information on seasonal compositional changes of varves [452–454], turbidites, and flood-derived sediments [455].

Quantitative analyses are difficult to obtain, since geometry, grain size, and water content of the samples are in general unknown. On the other hand

it is not really needed since the semiquantitative information obtained reflects the variability of certain element concentrations for individual lamina. A comparison of sets of individual summer or winter layers shows that the differences in element contents are basically lithologically controlled. Tilting with respect to the horizontal X-ray beam of thin lamina appears to be a problem locally. Nevertheless, the information obtained from a 1-cm sample provides details of 10 to 30 years in finely varved sequences, composed of winter and summer layers [454]. The spatial resolution of 50 μm is high enough to outline even activities of algae and diatomea adding silica to the sediment in spring and summer, whilst Ca precipitates are related to summer, and Mn and Fe precipitates to autumn and winter (PLATE I 3). Sediment cores of the Lake Constance are used to reconstruct the environmental history and processes within the lake and its catchment area, such as heavy metal contamination, eutrophication, and climate history. The sediment input is governed by the annual runoff due to the melting of snow in the catchment area of the alpine Rhine River, which drains some 12000 km^2 off the Alps. This generates a maximum sediment input during the summer. Additionally, single events of heavy rainfall generate strong flood events that lead to annually laminated sediments. The sedimentary record is composed of flood events of the Rhine River system (grayish layers) and the molasse-catchment basin (yellowish-brownish layers), mixtures of both, as well as individual carbonate rich lamina (whitish layers), which can be observed within the background sedimentation (PLATE I 4).

Alteration, Mineralization, and Tectonic Overprint

The understanding of alteration and mineralization patterns in brecciated, hydrothermally altered rocks is a complex problem. Alteration and mineralization textures are often difficult to interpret by eye. Microscopy of thin and polished sections provide insight on the chemical composition of small portions only. The XRD patterns of the bulk or small selected areas give information on primary and secondary products but not much detail on the spatial distribution.

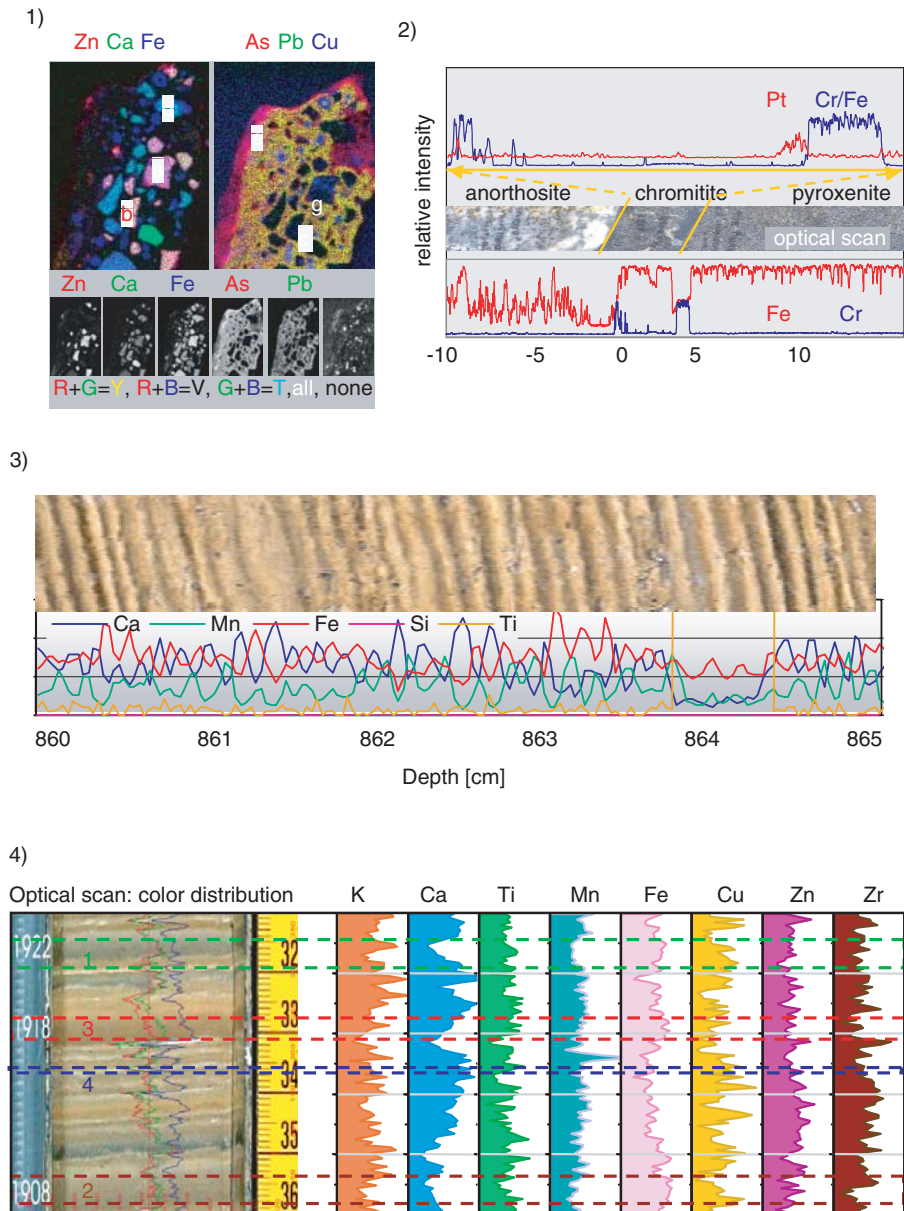
Micro-XRF enables the visualization of chemical composition distribution patterns on the hand specimen scale providing valuable data for understanding rock-water interaction processes. For example in andesitic rock units the fragmented rock might undergo all stages of degradation, namely propylitization, sericitization, alunitization, ferric and silicic alteration, and finally weathering. All these stages are documented by the redistribution of elements (i.e., Fe, Ca, K, Si, Cu) within the rock. Enrichment and depletion can be recognized (PLATE II 1.1-6) and related to respective alteration processes. Some elements such as Ti (1.3) remain immobile and outline the distribution of the andesite fragments. Alteration might go so far that only small relics (see 1.2: elevated Ca) or even traces of fragments enable the identification of the primary rock type. At the rim of the fragments potassic and ferric

alteration can be noticed by high K and Fe concentrations (1.2-3). Within the interfragmental area precipitation of sulfates, e.g., alunite (1b, d-g: K, Al, S) and sulfur (1.3, 1.5-6: S), takes place. Silica accumulates in small interstitial areas (1.4, 1.6).

A major field of interest is the distinct identification of mineralized zones in rock sequences, especially in drill core samples. This sample type provides considerable advantages for the 1D-EDXRF scanning devices: a more or less continuous succession, a relatively smooth surface, and in the case of a half-core even a flat surface. Depending on the desired detection limits one hour or a few days are needed for the analysis of a sample of 1 m length. For most exploration approaches 20-30 s per 50 μm step (20000 points/m) are sufficient. Scanning hard rock samples, for example chromite, chalcopyrite, or pentlandite distribution, focuses on the distribution of Cr, Cu, and Ni, respectively. Searching for anomalous zones of PGE or Au content is a quick and successful approach (PLATE I 2) to detect areas of element enrichment. While the localization of Cr, Cu, and Ni due to a good peak/background ratio can be quite easily attributed visually to zones of mineralization, the distribution of Au and PGE is frequently obscured by diffraction peaks due to low concentrations, grain size effects, and background noise variation because of porosity, etc., and requires more detailed information by microscopical follow up or 2D-EDXRF mapping to differentiate between point-like PGE anomalies or silicate-shaped diffusive patterns on the same energy level. Besides these difficulties the localization of PGE [456], Ge-bearing phases [457], or gold in banded iron formation (PLATE II 3.1-2) is possible within a short period of time.

A further aspect that deserves attention is the possibility of determining mineral ratios of/in the sample by identifying and attributing mineral specific element patterns based on element ratios (PLATE II 5.1-2). This approach has been applied for EDX-SEM systems for many years in the mining industry to monitor all steps within the treatment plants to obtain the best possible concentrate. The determination of the degree of liberation of a certain mineral, the inter-grown phases, the characterization of the size and shape and finally of the consequences for the mineral processing such as milling, screening, magnetic or gravitative separation and flotation, mainly forwarded by the QEM x SEM (quantitative evaluation of minerals by scanning electron microscopy), have been developed by Gottlieb and scientists of CSIRO, Australia [458, 459]. With some modifications such a system could be applied to the mesoscopic scale to identify individual minerals [460]. Michibayashi et al. [462] characterized silicate minerals from ductile shear zones by EDXRF microscopy.

Tectonization, fluid transport, alteration, and mineralization often interact in such a way that a proper attribution of the succession of the events appears to be difficult on a macroscopic scale. Often thin section work goes so much into detail that peculiarities are missed. By EDXRF mesoscale scanning this problem can be overcome. Zones of enrichment or depletion can be outlined,

**Plate I. 1–4**

1. Consists of silicate slag with sulfide spheres (g), fly ash (d), and roasted arsenopyrite have partly been altered and agglutinated by an As-Pb-rich gel phase (f) showing a rim effect (e). Zn occurs partly within the glass being highly dissoluble (a), and also in stable Zn spinel (b).

multiple tectonic or recrystallization events can probably be identified and used to identify a typical chemical signature (PLATE II 4.1-4).

In Situ XRF Analyses During Experiments

In many cases geological investigations require experiments under controlled laboratory conditions to understand natural processes. The XRGs setup was designed to run column tests accompanied by repeated EDXRF scans. The aim of the project is to obtain kinetic information on the behavior of certain elements within capillary force-driven transport in columns of sedimentary material and, of the result of this transport, to develop a newly formed hardpan. The experiment was performed to elucidate the transport conditions in slag heaps from metallurgical plants and fines from tailings dams, but it can also be applied to monitor transport in soils or weathering processes in sediments. Figure 7.129 shows the result of an experiment that was run for five months. The image exhibits mushroom-like features in the center of the sand-filled column, documented by both optical and chemical (Fe) images, respectively. These features are believed to be derived from pulse-like availability of the transported matter in solution from the water-saturated level filled with mining residues. At the capillary fringe at the top of the column, alternating hardpan layers of Ca- and Fe-rich precipitates (gels) can be observed.

The column material is filled in a polyethylene tube ($\varnothing = 5$ cm; 80 μ m thick) and is water saturated over a large part of the column. Due to these circumstances the fluorescence yield for Ca is reduced by 40–50% and for Fe by about 10%. However, enough information is provided to visualize the

Plate I. *Continued.*

2. XRGs profile across the anorthosite – chromitite – pyroxenite boundary of the Merensky Reef, Bushveld Complex, SA. Fe and Cr highlight the chromite and pyroxenite content. Low Fe values outline the plagioclase. The detailed view of the chromitite zone shows elevated pT values adjacent to the upper chromitite layer.
3. Laminated lake sediments (Belauersee, northern Germany) show alternate dark and bright layers, which are interpreted to document summer (Ca) and winter (Fe, organic) precipitation, respectively. Mn is slightly shifted to the autumn. Ti and Si indicate influence from other sources such as wind transported sand or dust.
4. Flood records: Example from Lake Constance showing various flood events with a distinct chemical signature. The 1922 flood of the Rhine river system (1) shows a typical increase of Fe and decrease of Ca in the beginning. The irregularities toward the top might be due to the contribution of other tributaries recruiting from the molasse-catchment (brown and yellowish layers). The 1908 flood (2) can be regarded as a mix of the Rhine River system and probably Bregenzer Ache River. The 1918 flood of the molasse –catchment (3) shows a strong increase of Ca, K, Ti, and Mn and a decrease of Fe. Between the flood events some whitish layers appear, which show elevated Ca due to precipitated calcite (4). Zr, Zn, Ti, Mn peaks will need more detailed investigation for proper explanation.

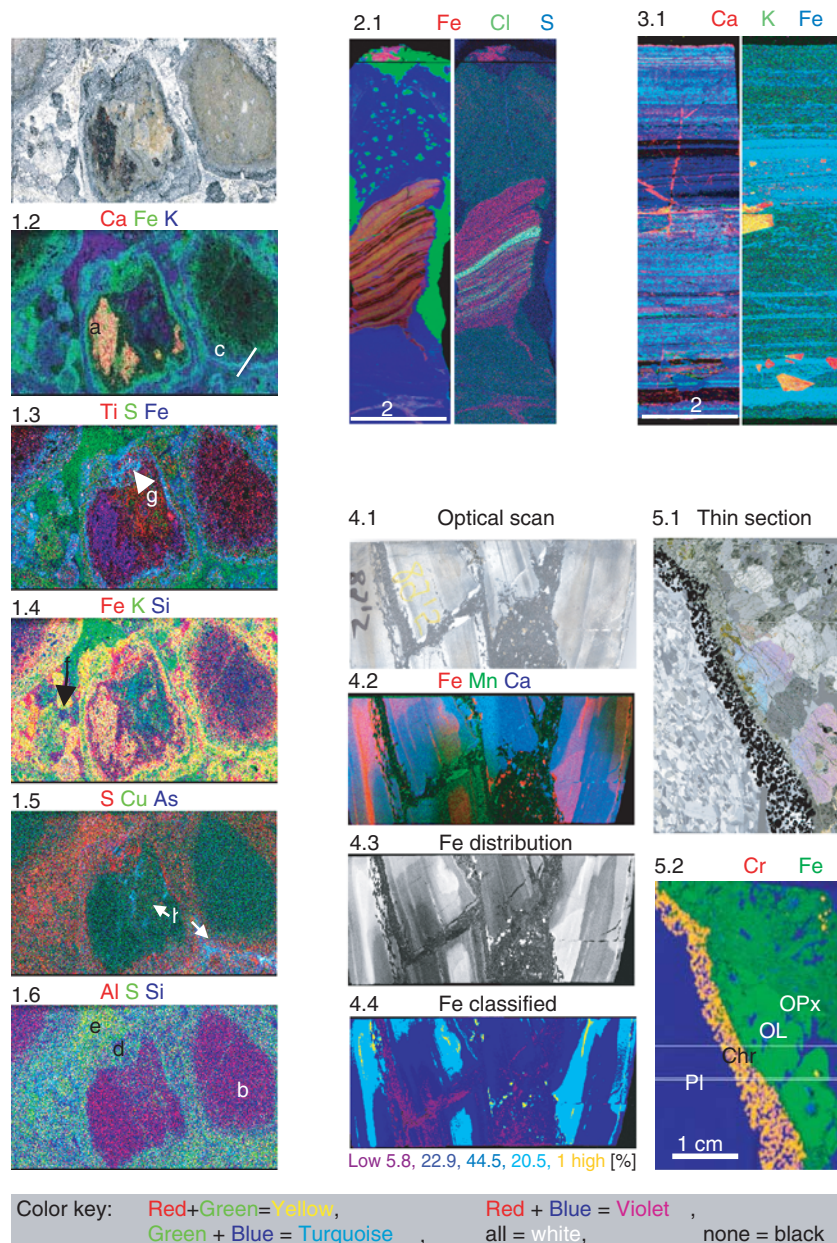


Plate II. 1–5. Visualization of chemical alteration pattern of andesitic breccia: **1.1–6** (a) relatively fresh Ca rich relic with ilmenite, (b) altered with Ti, (c) alteration rim with Si, Ca depletion, and Fe and K enrichment rims. The interstitial filling consists of (d) alunite with (e) some native sulfur and (f) silicified zones. (g) fragments contain Fe, S filled fractures, whilst (h) Cu-As-mineralization occurs along cross-cutting features. Some elements are enhanced relative to others. **2.1–2.** Ore genesis: Mn-bearing banded iron formation (a) with calcite (b) and quartz veinlets (c). Pyrite blasts (d) are concentrated in two zones with variable grain sizes. Some pyrite grains show elevated Au values (e).

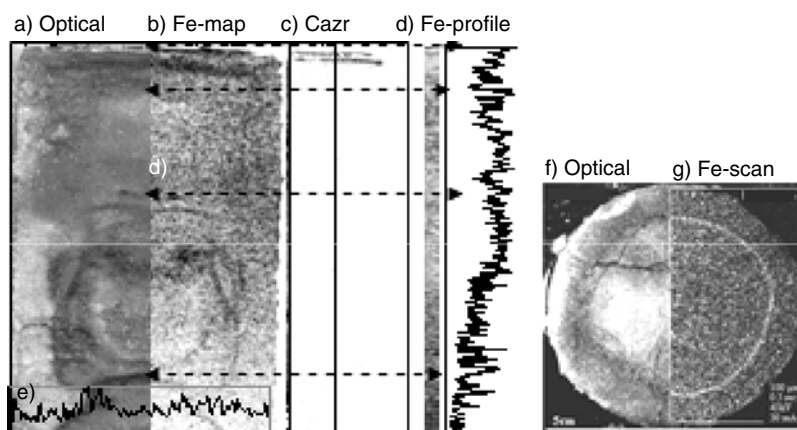


Fig. 7.129. a-g Visualization of transport conditions in a column experiment. Image of multiple mushroom-like oxidation fronts in a longitudinal section of the upper 9 cm quartz filling of a pyrite column showing favored transport pathways. The Fe distribution across the mushroom texture mirrors the photograph (a). The Ca distribution shows a crust with distinct layers (c). The upper crust bends around the edge and incrustates the outer wall for about 4 cm down the column. The black dots are isolated zircons (c) in the sand matrix. A central vertical profile (d) shows the intensities of the Fe distribution gaining toward the crust. The cross-section at 9 cm depth (e) outlines the dark Fe-rich zone. A horizontal section through the central part of the column (f) shows an outer rim in gray, a highly oxidized zone in black and a white core for the photo. The EDXRF Fe map (g) shows an enriched zone (white) about 0.5 cm from the rim (see black zone in a). White dots in the center and rim correspond to Fe-rich minerals in the quartz filling. The gray scattered distribution is attributed to Fe-gel coating of quartz grains.

Plate II *Continued.*

3.1–2. Stratigraphic control: Within salt diapirs a stratigraphic correlation of individual lamina is often complicated. Detailed EDXRF mapping provides a characterization of sequences. Folded anhydrite with rock salt cubes with laminated clay and salt injections. The clay sequence shows characteristic Zr-enriched layers. Tectonic injections of clay and rock salt into anhydrite and salt soaked clay layers can be observed.

4.1–4. Optical (4.1) and EDXRF scans of a mineralized breccia from Namibia₄ (Melcher [457]). A composite elemental map (4.2) shows the PbZnCu ore in black, and disseminated and patchy Fe sulfide in red. Mn forms a halo in the dolomite and precipitates as manganiferous-calcite in the ore zone. Earlier calcite veinlets had displaced pulse-like Fe-infiltration zones. The Fe distribution (4.3) shows when classified (4.4) several zones. Dolomite background (blue), infiltration turquoise (yellow highest concentrations), zones of leaching and Cu ore (dark blue), and very low values in Mn-carbonate veinlets and halo zones (purple) are seen.

5.1–2. EDXRF combined elemental distribution map mirroring the mineralogical distribution. For comparison an optical scan outlining plagioclase (Pl), chromitite (Chr), olivine (Ol), and orthopyroxene (OPx) is shown.

transport process. The main transport takes place in the center, but chemical signature at the rim follows the central trend except at a lower concentration.

Imaging micro-XRF, Texture, and Lattice Strain Mapping

XRF analysis determines the relative amounts of elements within the probed sample volume. Material properties of solids, however, not only depend on the concentration of elements, but also on the phases as well as on the arrangement of crystallites and their orientation distribution *crystal texture*. Polymorphism for instance, i.e., crystal forms of the same chemical composition but of different crystal lattices, cannot be detected by any analytical method. Therefore, analytical investigations must often be complemented by using additional techniques to reveal the morphology, the grain orientations, and the distribution of internal stress. In the 1990s, SEM in combination with elemental analysis by energy-dispersive spectroscopy (EDS) and backscatter Kikuchi diffraction (BKD, ACOM, also known as “Automated EBSD”) has evolved into the standard technique to provide conveniently these complementary aspects of microstructure [462]. Typical spatial resolutions are 5 nm in SEM images with secondary electrons, 0.5 μm in EDS microanalysis, and 50 nm in BKD. Better resolutions of about one order of magnitude are obtained from thin specimens in the transmission electron microscope (TEM) using EDS analysis and transmission Kikuchi diffraction [463].

Electron microscopy is not a universal technique to meet all requirements of microstructure characterization. Many applications in mineralogy only require, at a moderate resolution from macroscopic areas in the specimen surface or from cross-sections, the knowledge of the element distribution and the spatial distribution of certain crystal lattice directions (i.e., pole densities rather than the full crystal lattice orientation of each grain). In these cases, XRF and XRD are the methods of choice. These X-ray techniques are principally superior by about two orders of magnitude in accuracy over their electron microscopical counterparts, namely, EDS analysis and Kikuchi diffraction. Continuous background is almost negligible in XRF. The dispersion, $\Delta\vartheta/\vartheta$ s in XRD is excellent as compared to electron diffraction, since spectral linewidth, $\Delta\lambda/\lambda$, is extremely small and the characteristic X-ray wavelengths, λ , are in the range of the lattice spacings, thus producing large Bragg angles, ϑ .

Almost all X-ray analyses in the laboratory are nonimaging. Conventional lenses are not available for X-rays. To obtain microstructural images from a localized specimen region of the morphology, the spatial distributions of elements, the type of crystal lattice (i.e., phases), grain orientations, and residual stress rather than an average over the whole illuminated area, a mapping technique is required whereby a small spot-size X-ray beam is generated, and the specimen is mechanically scanned under the stationary beam spot. A synchrotron source is ideal for this purpose [464], but availability still demands using conventional X-ray generators as a more feasible alternative. X-ray microbeam scanning instruments for imaging XRF have demonstrated their

high potential for many years [465–468], and commercial systems have been developed [449, 469]. Modern X-ray texture goniometers are often equipped with a computer-controlled x-y specimen stage on the Eulerian cradle. They enable, in principle, texture mapping, if appropriate software for controlling the mechanical x-y sample scan, the acquisition, interpretation and representation of the diffraction data is available. Spatially resolved texture analysis has been demonstrated [470] on a commercial X-ray texture goniometer by calculating offline orientation densities, texture symmetry, texture index, and the Taylor factor in several raster points.

The X-Ray Scanning Instrument Based on a Conventional X-Ray Source and EDS

Inhomogeneities of morphology, element and phase distribution, texture and residual stress in the submillimeter range are quite common in geology and mineralogy. They have to be accessed in quantitative microstructural analysis since they bear information about the history of rock forming and sedimentation, and are often decisive in the reliability and performance of a product in metallurgy. Spatial resolutions of conventional XRF and XRD are insufficient for studying local features and gradients. To avoid some limitations of electron microscopy as well as conventional X-ray techniques, an X-ray scanning instrument (XSI), based on energy-dispersive X-ray spectroscopy (EDXRS) and diffraction (EDXRD), has been developed [471, 472]. The system is unique in that it combines four techniques: spatially resolved pole-figure measurement [472, 473] as well as, on a grain-specific level, imaging micro-XRF analysis, texture mapping, and lattice strain mapping. Although the initial applications have focused on metals and alloys, and their response to plastic deformation, a wide field regarding deformation of rocks and minerals, in general can be tackled.

In our design, shown schematically in Fig. 7.130, the XSI consists of a conventional X-ray source (PHILIPS generator PW 1830/25) equipped with a fine-focus tube, a two-circle goniometer base (PHILIPS PW 1835), and an open Euler cradle (PHILIPS X'Pert MRD goniometer). Most applications have been carried out with a tungsten anode in order to increase the continuous background. The *white* primary radiation is not filtered, thus enabling a wide range of elements to be excited for fluorescence emission and hence setting almost no practical restriction on the range of lattice spacings for diffraction. A circular pinhole collimator is used to produce a small primary beam spot. The diffracted secondary spectrum is detected with either a conventional proportional counter and postspecimen filter for pole-figure measurement or an energy-dispersive solid-state spectrometer system (SPECTRACE 6100 and TRACOR NORAN Si(Li) detector) for acquiring XRF spectra and texture maps.

The instrument is fully controlled by a personal computer. The specimen is translated step by step across a user-defined grid pattern in the x-y-z stage

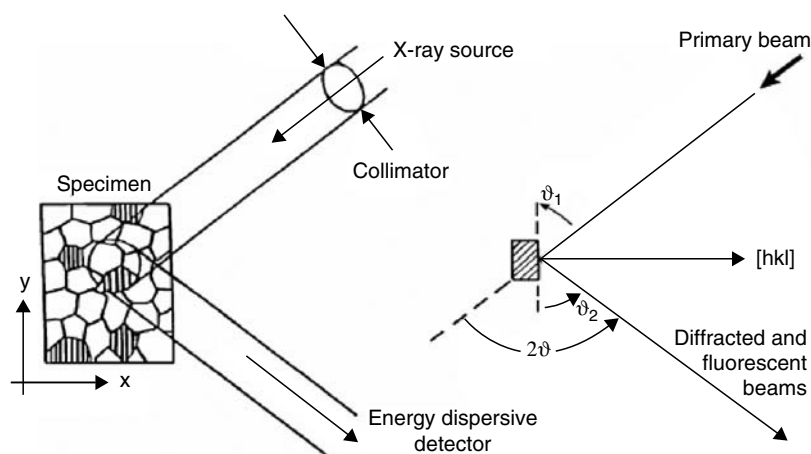


Fig. 7.130. Schematics of microbeam X-ray mapping

(Fig. 7.131). Grid patterns of any shape are possible, in order to match the scanned field to the area to be sampled, e.g., scans along a line, across rectangles or polygons in $1\text{-}\mu\text{m}$ wide steps over an area of 100 mm by 100 mm wide. The current sample position under the beam spot is monitored with a video camera, and so the corner points of the sampled region are easily defined.

Energy-Dispersive Spectroscopy and Data Acquisition

Identification of spectral components in the secondary beam must take into account the following features:

- a low background of continuous radiation

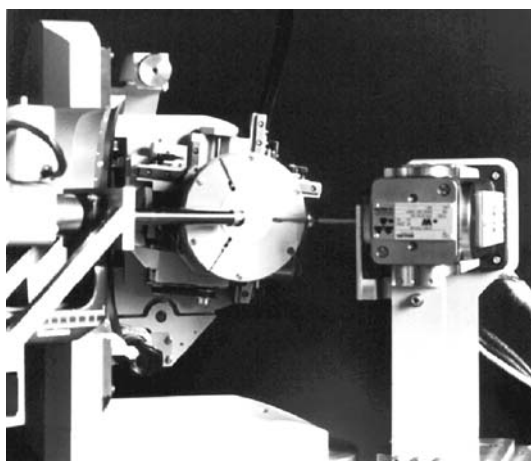


Fig. 7.131. The experimental setup of the X-ray scanning instrument

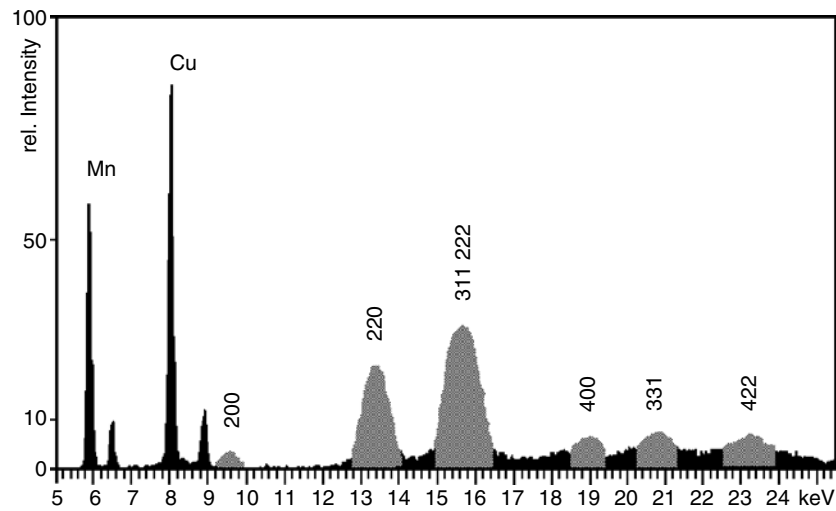


Fig. 7.132. Energy-dispersive X-ray spectrum from an AlMn 1% metal sheet

- sharp characteristic lines due to scattering from the primary beam
- sharp characteristic fluorescence lines from the specimen
- broad diffraction peaks from the specimen (Fig. 7.132)

Absorption in air has to be considered for quantum energies $E_x < 3 \text{ keV}$. Hence, a helium atmosphere or an evacuated specimen chamber will be indispensable if light elements are to be detected by ~~XRF~~ ^{XRF} materials with large lattice constants have to be studied by XRD. Very high quantum energies, on the other hand, are not adequate, since Bragg's angles decrease unduly up to grazing incidence with hard X-rays. Then the spot size is extremely foreshortened and spatial resolution is impaired. A high excitation of fluorescence lines is obtained with an overvoltage of the primary beam of about twice the energy of the characteristic lines of the elements to be detected. A good compromise is obtained for most samples with an angle of incidence of $\vartheta_1 \sim 45^\circ$ and quantum energies of the primary beam between 8 keV and 15 keV.

A comprehensive PC software package has been developed. One part contains the hardware control of the goniometer, the Eulerian cradle, the x-y-z sample stage and the proportional counter, as well as the EDS system. The other part has been developed for the graphical representation of measured pole figures and scanning data of selected sample areas. The experimental pole-figure data can be used for ODF analysis, irrespective of the chosen angular sampling grid and specimen symmetry, and for the calculation of average tensorial material properties by using a dedicated ODF program [474]. An analysis tool identifies the fluorescence and the diffraction peaks in the spectrum. Several XRF elemental as well as texture distribution maps of selected crystallographic directions can be obtained at the same time.

Regions of interest (ROI) are set on selected peaks for evaluating the fractions of counts in each window separately by integrating the ROI intensities. The spatial distribution of residual lattice strain is obtained by interpreting the widths and positions of diffraction peaks in the spectrum of every image point. For mapping the microstructure pixel by pixel, the count rates falling in a selected spectral window are represented on the digital image by attributing specific pseudocolors.

Basics of Energy-Dispersive X-Ray Diffraction

Energy-dispersive X-ray diffraction (EDXRD) is based on Bragg diffraction of a collimated *white* primary X-ray beam in dependence on the orientation distribution of the grains in the surface. If a grain fulfills the Bragg condition (7.40):

$$E_{\text{hkl}} = n \cdot h \cdot c / (2 \cdot d_{\text{hkl}} \cdot \sin \vartheta_{\text{hkl}}) \quad (7.40)$$

at an angle of incidence, ϑ_1 , due to an appropriate orientation of lattice planes at spacings d_{hkl} and for a photon energy E_{hkl} of the primary beam, a partial ray of this energy is reflected. It is collected with a solid-state Si(Li) detector at a take-off angle, ϑ_2 . $\vartheta_{\text{hkl}} = (\vartheta_1 + \vartheta_2)/2$ is known as Bragg angle (Fig. 7.130). In general, several sets of lattice planes will meet the Bragg condition at the same time for a broad *white* spectrum of primaries. They produce several diffraction peaks on the ED spectrum. If the illuminated specimen volume is composed of grains of different orientations, each crystallite may reflect its own set of partial beams of different energies into the take-off angle, ϑ_2 . All partial beams emitted under the same angle ϑ_2 merge in the secondary spectrum. So several diffraction peaks are produced whose intensities are a measure of the volumes of all grains that fulfill the Bragg condition for the corresponding hkl lattice directions, irrespective of their spatial arrangement in the irradiated sample volume. They resemble traditional hkl diffraction peaks. The intensity of an hkl diffraction peak corresponds to the pole density on the hkl reference sphere of texture at the particular angular setting, (α, β) , of the specimen with respect to a reference system.

The measured pole densities are proportional not only to the volume fractions of the related grains, but also to the intensities falling in the corresponding spectral windows of primary X-ray radiation. They are further affected by the spectral absorption of the X-rays on their way from the source to the detector (this is in particular the case within the sample), and by possible nonlinearities of the detector system. In quantitative texture analysis, corrections are applied to the measured pole densities.

If the Bragg angle is moved from ϑ_{hkl} to ϑ_{hkl}^* , the centers of the diffraction peaks on the ED spectrum shift from energy channels E_{hkl} to E_{hkl}^* , according to (7.40), whereas the characteristic X-ray lines that are scattered from the primary radiation, and the fluorescence lines from the specimen, stay on fixed positions on the energy scale. Diffraction peaks and characteristic lines can be

easily discriminated. A weak diffraction peak, due to a low pole density, can be enhanced considerably by adjusting the Bragg angle such that the energy of the diffraction peak coincides with a characteristic line in the primary beam spectrum.

Lattice strain is analyzed and mapped with the same setup, in addition to texture and elemental mapping, by evaluating the shift and width of diffraction peaks in the spectrum of each image point [475]. The shift $\Delta\vartheta$ of a diffraction peak, ϑ_{hkl} , as compared to the peak position ϑ_0 with a relaxed specimen with lattice spacing d_0 , follows from Bragg's equation:

$$\Delta\vartheta = \vartheta_{\text{hkl}} - \vartheta_0 = -\tan \vartheta_0 (d_{\text{hkl}} - d_0)/d_0, \quad (7.41)$$

or transformed to the scale of photon energy, E , which is more adequate for energy-dispersive diffraction:

$$\Delta E = E_{\text{hkl}} - E_0 = -E_0 (d_{\text{hkl}} - d_0)/d_0 \quad (7.42)$$

Line-profile analysis is performed by Gauss fitting after background correction. The width of a diffraction line reflects the variations of lattice spacing, Δd , residual strain from grain to grain in the diffracting volume, strain gradients across grains, or microstructural imperfections in the grains (residual stress of the second and third kind). For a (semi-) quantitative estimate of residual strain, it is common practice to take, under the same experimental conditions, the difference of the full widths at half maximum (FWHM) of the line profiles with the strained and with an annealed reference specimen, respectively. More sophisticated quantitative approaches are based on line-profile analysis by Fourier deconvolution or on profile-matching simulations. Peak broadening due to the finite primary beam and detector apertures, defocusing effects, small grain size, and limited spectral resolution of the detector have to be considered. A well-collimated parallel primary beam and a narrow (Soller slit) collimator on the diffracted beam side in front of the detector can drastically improve $\Delta a/a$ resolution, at the expense of intensity and necessary dwell time per pixel. Though being very intense, narrow characteristic lines are, unfortunately, inadequate to excite and enhance weak diffraction peaks for lattice strain analysis, since the primary beam has to supply a sufficiently broad and flat spectrum of primary radiation for ED diffraction. Otherwise the shape of the diffraction peak simply reflects the profile of the exciting characteristic primary beam line.

In the XSI, the sensitivity and the $\Delta a/a$ resolution of residual strain measurement are finally limited by the spectral resolution of the solid-state spectrometer system. A standard Si(Li) detector has been used here with a nominal spectral resolution of 140 eV at 8.4 keV (Mn $K\alpha$ line). A tradeoff has to be made between intensity and peak width by using rather wide primary beam and detector apertures. At $2\vartheta = 40^\circ$ (corresponding to $E_{\text{hkl}} \approx 10$ to 13 keV for low index planes of metals) apertures of 0.35° produce an FWHM between 400 eV and 500 eV, which is distributed over about 100 spectral channels. The apertures are adjusted by using appropriate pinhole diaphragms in

the primary beam and a sufficient distance of the Si(Li) detector from the specimen. Peak position is not affected by the aperture size in a symmetric goniometer setup ($\vartheta_1 = \vartheta_2$). By a Gauss fit, the peak center can be located to $\Delta E \leq 0.5 \text{ eV}$. Hence residual strains of the first and second kind are well resolved down to $\Delta a/a \approx \cdot 10^{-4}$.

A noticeable improvement in lattice strain analysis is expected from a reduction of the energy interval per spectral channel and a higher energy resolution of the detector system. However, a practical limitation still rests on the need of excessively large apertures for gaining sufficient peak intensity. A position sensitive detector (PSD) with a standard Bragg-Brentano setup and monochromatic radiation is still superior by one order of magnitude or more as far as high dispersion is concerned for residual strain analysis. This would enable a reliable peak-width analysis and also the mapping of residual strain distributions even of the third kind. The replacement of the ED system, however, is at the expense of simultaneous acquisition of several peaks/maps at the same time, and stringent restrictions would be imposed in addition to satisfy the Rowland-focusing condition for the Bragg-Brentano geometry.

Spatial resolution is limited by the size of the X-ray spot on the tilted specimen surface. Since no conventional lenses are available for white X-rays, a beam collimator has been used here, which consists of two small circular diaphragms of diameter d at distance a and b , respectively, from the sample. The effective spot size is then:

$$d_s = (1 + 2a/b) \times d \quad (7.43)$$

The main drawback of a diaphragm collimator is the loss of intensity. An increase in spot brightness is expected from glass capillary collimators [476, 477], which would enable a higher spatial resolution and a shorter acquisition time. The apertures, $\Delta\vartheta$, of the primary and secondary beams are less crucial, unless lattice strain mapping is of concern. Since texture in most materials is hardly sharper than a few degrees, a width of diffraction peaks in this range, according to $\Delta\vartheta$ in (7.41), is quite acceptable. The width of fluorescence peaks is not affected by the aperture of the beam spot.

The oblique incidence of the primary beam results in an elliptical foreshortening of the spot on the sample surface. Spatial resolution decreases with angular tilt, γ , of the specimen with respect to the incoming beam. A circular primary X-ray spot is elongated by projection on the tilted specimen surface to an ellipse of aspect ratio $1/\cos\gamma$. The practical limit of spatial resolution is presently at 0.1 mm for pole-figure measurement and lattice strain mapping, and 0.05 mm for element and texture mapping, due to the low intensity of the collimated primary beam.

Pole-figure measurement has to precede texture mapping on the same specimen area in order to recognize significant texture components. Thinned angular grids, equal area grids, or relevant sections on the pole sphere, as well as areas of any shape on the specimen, can be selected to reduce acquisition time by the combination of pole-figure measurement with a

stepwise-controlled specimen tilt through the pole-figure grid and a controlled spatial x-y translation of the specimen. Large tilts, however, may result in inconsistent pole-figure data if the texture is not uniform in depth beneath the surface, since XRD becomes more surface sensitive with increasing incidence angle γ . Information depth decreases linearly with $\cos \gamma = \sin \vartheta \cos \alpha$.

Pole density can be measured alternatively in the conventional way with filtered - *monochromatic* - primary beam radiation and a proportional counter set to the appropriate ϑ - 2ϑ positions for each measured hkl pole figure, one after another. The specimen is tilted to the specified pole-figure points for intensity acquisition step by step. Energy-dispersive microdiffraction, however, using *white* (i.e., not filtered) primary beam radiation and a lightweight Peltier-cooled solid-state detector [478] enables a significantly faster and more accurate acquisition of several pole figures at the same time.

Any specimen reference direction (α , β) can be used for mapping provided that pole density (i.e., diffracted intensity) is high enough – which of course depends on local texture. It is worth noting that texture, as well as residual strain, is probed exclusively only for those grains that satisfy the Bragg condition for the chosen specimen-fixed reference direction, e.g., the specimen normal direction in the case of the symmetric goniometer setup with the specimen not tilted. There is no information acquired on grains at other orientations.

Examples of Application

As a test specimen for spatial resolution, regular gold patches ($420 \times 420 \mu\text{m}$ wide) have been deposited on a glass substrate by sputtercoating through a TEM specimen support grid. Using $30\text{-}\mu\text{m}$ wide apertures and the Au L α fluorescence lines for imaging, the free bars ($<60 \mu\text{m}$ wide gaps) between the patches are clearly resolved in two perpendicular directions in the XRF map (Fig. 7.133) [462]. A spatial resolution of approximately $30 \mu\text{m}$ is thus demonstrated.

A deformation pattern has been formed by impressing the jaws of a mechanical testing machine into the coarse grain surface of a recrystallized aluminum sheet metal. Finally, the sample surface was ground and mechanically polished such that the pattern was no longer visible. The stamp process, however, has changed the local texture. In the texture maps (Fig. 7.134), high pole densities can be recognized in regions where the corrugating teeth of the jaws caused a high deformation, while the grooves in the jaws induced a deformation low enough to preserve the original matrix texture. The texture maps of Fig. 7.134 were acquired simultaneously from the same sample area at symmetrical diffraction settings ($\vartheta_1 = \vartheta_2$). Hence, the pole densities in the sample normal direction are shown. The matrix texture did not contribute to these selected diffraction peaks. If a texture component of the matrix is of interest, the specimen has to be tilted off the symmetrical geometry to an

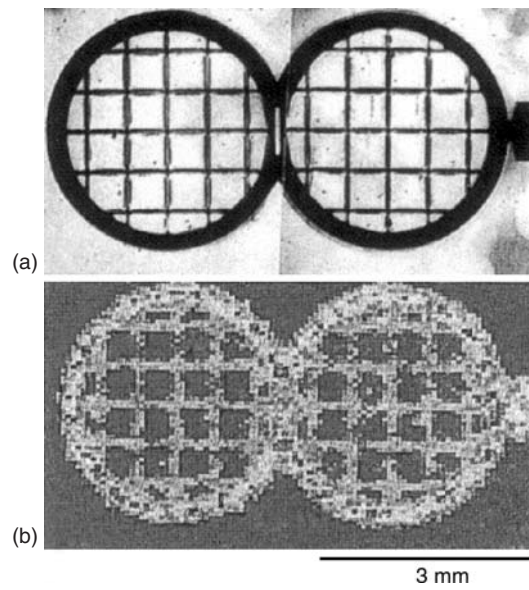


Fig. 7.133. Gold pattern sputtered through a TEM support grid on a glass substrate.

a. Image in the light microscope.

b. X-ray micro-fluorescence map with the Au $L\alpha$ line.

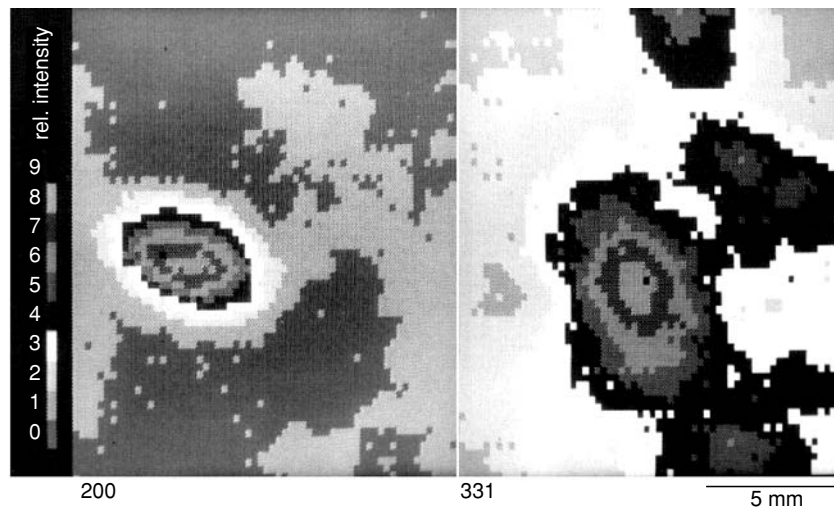


Fig. 7.134. Texture maps of a deformation pattern in aluminum revealing local plastic deformation. Left: $\{200\}$ reflections; right: $\{331\}$ reflections

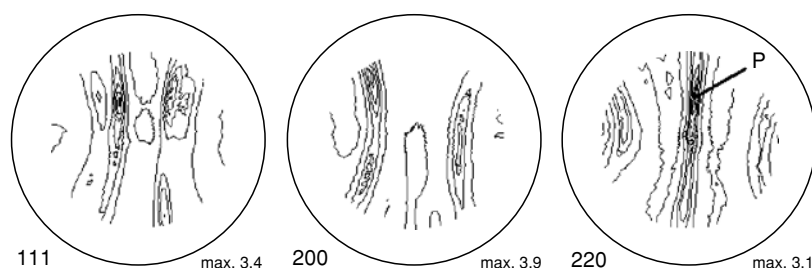


Fig. 7.135. Pole figures acquired across the rivet bolt of Fig. 7.136. The polar specimen direction P ($\alpha = 35^\circ$, $\beta = 83^\circ$) has been used for texture and residual strain mapping

appropriate pole-figure point. The corresponding angles of tilt can be read from X-ray pole figures that have to be acquired in advance.

The X-ray spectrum (Fig. 7.135) contains two sets of characteristic lines: a set of Cu $K\alpha$ and Cu $K\beta$ of scattered primary beam radiation (Cu anode, 40 keV), as well as a strong set of Mn $K\alpha$ and Mn $K\beta$ fluorescence radiation, which has been emitted from the rather small content of manganese in the AlMn 1% alloy. Al-K fluorescence radiation, as a possible characteristic line from an Al sample, is not present. The Al-K fluorescent line is excited rather weakly by Cu K radiation and, furthermore, is strongly absorbed in air on the way from the sample to the EDS detector. In contrast to the sharp characteristic lines, the diffraction peaks are broad, due to the wide beam aperture (see (7.41)). In Fig. 7.132, the windows of the diffraction peaks (200), (220), (311)/(222), (400), (331), and (422) are marked by hatching. The (311) and (222) reflections are coincident, but the contribution of (222) is negligible in this particular point on the sample because the (111) peak is missing.

A cross-section of an aluminum rivet was carefully polished flat by gentle mechanical grinding and finishing. A final electrochemical polishing was applied to remove any mechanical damage introduced during preparation. Before mapping, several pole figures had been acquired in steps along lines across the head and the bolt of the rivet to recognize relevant texture components. A strong fiber texture has been found in the bolt region (Fig. 7.135) [475]. The (220) diffraction peak P ($\vartheta_1 = \vartheta_2 = 20.1^\circ$, $E_{220} = 12.62$ keV; $\alpha = 35^\circ$ and $\beta = 83^\circ$) has been used for evaluating at the same time the spatial distributions of pole density (texture map) and strain (residual strain map). Dwell time extended over ~~240 s/pixel~~ to yield a sufficient count statistics in view of the low intensity. At a step width of $120\ \mu\text{m}$ 2,232 image points had been acquired.

A clear inhomogeneity is revealed in the texture (Fig. 7.136a) as well as in the strain maps (Fig. 7.136b). Two almost parallel strips of high pole density run along the axis of the bolt with a slight shift to the right-hand side. They are supposed to form a tube of about one-third of the bolt diameter in the

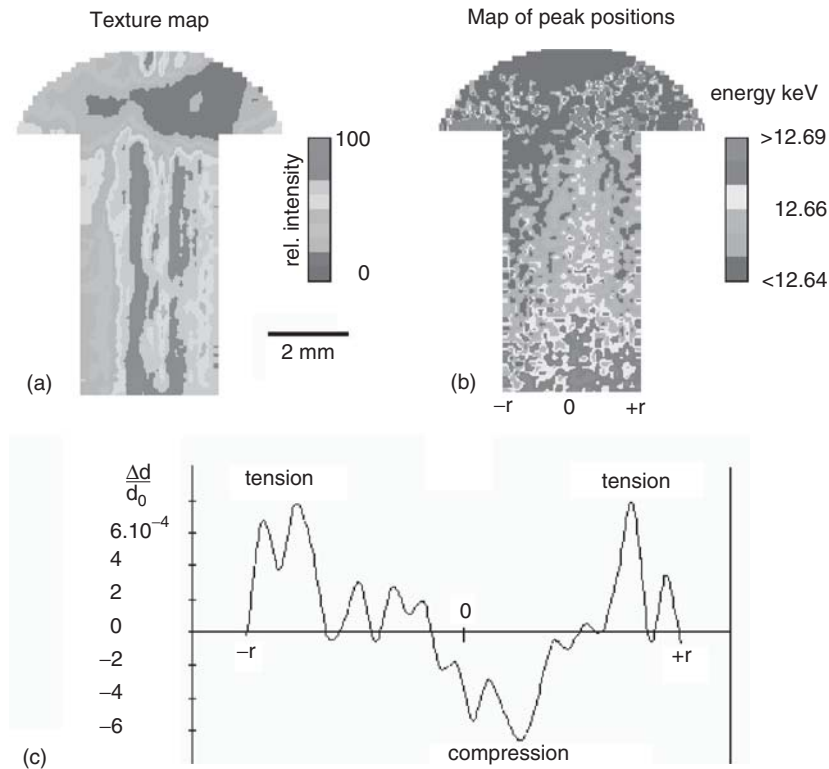


Fig. 7.136. Cross-section of an aluminum rivet. Distribution maps (a) of the intensity (pole density, texture) and (b) of the shift (residual strain) of the 220 peak at pole P ($\alpha = 35^\circ$, $\beta = 83^\circ$). (c) The lattice strain $\Delta d/d$ across the bolt.

3-dimensional rivet. The head of the rivet shows a much lower density of this pole. It is worth noting that it forms a butterfly-shaped minimum, which might result from punching the head during production.

Along the bolt is a gradient in compressive residual strain to the head. A dish-shaped maximum of compressive strain (dark) is found in the head, which is related to the butterfly-shaped minimum in the (220) texture map. There is an increased compressive residual strain in the interior of the texture tube (dark) and a tensile strain (bright) to the bolt surface. Statistics has been improved by averaging the peak shifts along a section of the shaft. So the radial distribution of residual strain across the bolt is clearly seen in the graph line (Fig. 7.136c).

7.6.4 Microscale

Chemical analyses with high spatial resolution are of major interest in geological applications as minerals are often chemically heterogeneous on the

microscopic scale and these compositional variations are of major importance for understanding the formation processes. Most of this microanalytical work is performed by EMPA due to the spatial resolution in the micrometer range, well-established quantification procedures, and the widespread availability of instruments. While this method is well suited for the determination of major elements it is not sensitive enough to detect trace elements at levels below approximately 100 ppm. To fill this gap, micro-XRF instruments using X-rays for excitation for multielement EDXRF analyses may be used and an instrument has been developed especially for trace element analyses on single mineral grains [430]. The detection limit of such an instrument is about 5–10 times better than with EMPA but the spatial resolution is about 10–100 times lower. A promising application is the U–Th–Pb dating of grains of monazite as described later. For trace element analyses with higher spatial resolution and/or element contents in the lower ppm range synchrotron-based micro-XRF methods have to be applied.

Sample Preparation

For trace element analysis with XRF at high spatial resolution sample preparation is of major importance. For positioning the beam exactly on the sample and precisely defining the analyzed sample volume, its surface should be smooth or even polished. The X-ray beam penetrates deep into most geologic materials. For an exact quantification of the XRF spectra it is crucial to know the thickness of the analyzed sample volume. For those two reasons, double-sided polished samples of consistent thicknesses are most favored for micro-XRF analysis. Another consequence of the penetrative nature of the beam concerning the sample preparation is that the spatial resolution is controlled by the sample thickness. Any backing of the sample should be minimized or avoided since the backing material will contribute to the scattered radiation and will increase the background of the spectra leading to higher detection limits and potential additional peaks. Samples should be prepared as thin as possible while mechanically stable. Typical thicknesses of geological samples for microanalysis vary between 30 and 100 μm .

U–Th–Pb chemical dating

Radiometric dating provides absolute constraints on the timing and duration of (long-lived) geological processes and is therefore of fundamental importance within the geosciences. U–Th–Pb dating is one of most used tools for radiometric dating. It is based on the decay of radioactive U and Th isotope to stable isotopes of Pb in three independent decay schemes (see later). Chemical dating, the calculation of the age from elemental abundances of U, Th, and Pb, is one of the earliest absolute geochronological techniques. It was even used on minerals containing abundant U or Th (e.g., uraninite – UO_2 ; [479]) before the development of mass spectrometry. Geochronology by isotope analysis is a

modern and more accurate technique allowing the comparison of the three differently calculated ages and corrections for nonradiogenic Pb in the mineral, but it is expensive and labor intensive.

Renewed interest in chemical dating techniques arose from the application of relatively cheap and readily available EMPA [480, 481], which has the additional advantage of a spatial resolution in the range of 2–3 μm . This spatial resolution allows the study of complexly zoned minerals. The application of nondestructive analyses on Th- and U-rich accessory minerals, especially monazite, became the focus of these studies because in situ microanalysis in geological samples allows the correlation of age data with the textural development of the main rock constituents.

Monazite (CePO_4) combines several characteristics that make it very favorable for chemical U–Th–Pb dating. First, it is a common accessory mineral in many crustal rocks, granitoids, gneisses, as well as metasediments. Second, it typically incorporates little Pb upon crystallization, but contains very high amounts of ThO_2 (up to 30 wt%) and UO_2 (up to 3 wt%), which leads to a fast accumulation of significant amounts of radiogenic Pb. Quite importantly, radiation damage that could cause loss of Pb by diffusion is usually negligible because the crystal lattice anneals quickly. Zoning within monazite can be controlled with backscatter electron images due to the large compositional variability (heavy elements like Th, U, Y, and REE) in the monazite solid-solution series toward huttonite (ThSiO_4) or brabantite ($\text{CaTh}(\text{PO}_4)_2$). Monitoring trace elements in monazite (e.g., Y, REE) has been used to link monazite ages with specific metamorphic episodes [482] and pressure-temperature paths of its host rock [483]. This has made in situ monazite studies a versatile tool in the interpretation of complex metamorphic rocks. Chemical U–Th–Pb dating may also be applied to other minerals, such as xenotime, zircon, or allanite, but most of them do not fulfill all requirements for a suitable geochronometer or just contain much less radiogenic Pb than monazite.

Comparison of Analytical Approaches

In chemical dating, an age can be calculated iteratively, by assuming that the total amount of Pb can be divided into thorogenic and uranogenic portions of the same age (e.g., [480]) or by calculating independent Th–Pb and U–Pb ages based on the algorithm of Rhede et al. [484]. The most commonly used analytical method for chemical U–Th–Pb dating is wavelength dispersive X-ray detection with an electron microprobe (e.g., [480, 481, 484–487]). At 20 kV acceleration voltage and 50–100 nA intensity the electron beam can be focused to give an excitation volume of approximately 2–3 μm width and 3–5 μm depth. However, the long half-lives of U ($^{238}\text{U} = 4.47 \times 10^9$ a, $^{235}\text{U} = 0.704 \times 10^9$ a) and Th ($^{232}\text{Th} = 14.01 \times 10^9$ a) mean that accumulation of significant amounts of radiogenic Pb takes a long time and the typical detection limits of approximately 100 ppm for Pb prohibit precise determination of ages younger than approximately 200 Ma on the EMP.

Bruhn et al. [488] used a proton microprobe (PIXE) to date monazite, with lateral spot size of 20-30 μm but high penetration depth (30 μm), and they were able to reproduce isotopic ages of monazite standard material. A 1.5-nA sample current and acquisition times of 5-10 min yielded detection limits of approximately 10-20 ppm for Pb, Th, and U and < 1000 ppm for the REE. Frei et al. [489] have shown the feasibility of micro-PIXE chemical dating on a 1 Ga old high uranium (265 ppm) titanite. Structural damage to the minerals due to the large mass of the protons in PIXE analyses has not been investigated but cannot be ruled out.

Analytical techniques using X-ray induced excitation of fluorescence (XRF) also have good potential in providing lower detection limits due to the better peak-to-background ratio of this technique. A micro-XRF method was developed by Cheburkin et al. [430] with a set-up using monochromatic X-ray radiation. Scherrer et al. [490] modified this technique, using it to date monazite with a lateral resolution between 38 and 90 μm in doubly polished sections. These methods use EDX detection, enabling the acquisition of the complete XRF spectrum at once in a relatively short time. However, at the energies needed (approximately 17-20 keV), the beam transects the complete thickness of a 30- μm -thick thin-section (i.e., thickness of the sample determines the analyzed volume) and therefore spatial control is limited. Detection limits of approximately 10 ppm were achieved with a beam of 50 μm on whole grains at 40-min data collection times, sufficient to date monazite grains as young as 15 Ma [491] (Engi et al. 2002).

Additional improvements may be achieved by the use of synchrotron radiation XRF (SRXRF). The higher photon flux and brilliance of such X-ray sources provide the possibility of focusing the beam down to 2-3 μm lateral diameter or less. The high photon flux of the beam still ensures very low detection limits down to ppm range or better, thus pushing the theoretical limits for the youngest datable monazite below 1 Ma even for monazite with low contents of ThO_2 (4 wt%). In other words monazite with an average ThO_2 of 10 wt%, yielding 20 ppm of radiogenic Pb within approximately five million years could be dated relatively precisely. However, small amounts of nonradiogenic Pb may cause some concern at this level of detection.

The lower detection limits in PIXE, micro-XRF, and SRXRF analyses make the investigation of other phases or minerals with lower concentrations of U and Th that accumulate less radiogenic Pb viable (e.g., zircon, titanite), of course only if nonradiogenic Pb is negligible.

Microanalysis Using Synchrotron Radiation XRF

The use of SR as a photon source in contrast to a lab source has enabled studies on trace element contents and compositional changes scale of trace elements in minerals and glasses on the micrometer. The high flux of synchrotron radiation X-rays additionally enables analyses of buried materials

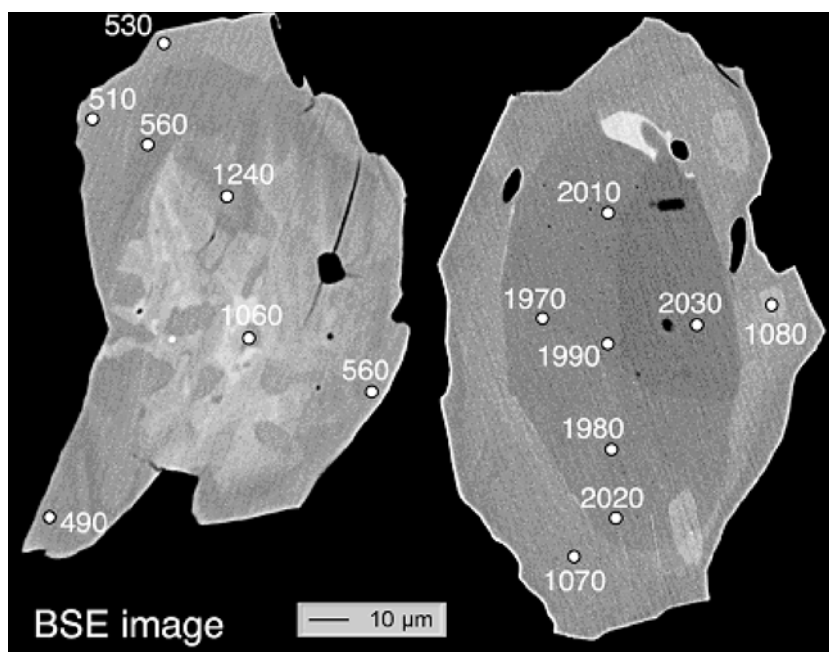


Fig. 7.137. Monazite from the Zambezi Belt, Zambia. Brightness of the backscatter-electron (BSE) images is a measure of the average atomic number of the material. The images are used to detect compositional zoning of target minerals prior to analysis. Areas with higher Th and U enclose internally complex grain cores with highly variable Th in the left image and lower U contents in dark zones in the right image. Lobate boundaries of the rims impinging on the inner parts of grains are typical for fluid-assisted recrystallization. Areas analyzed by electron microprobe are indicated by circles of approximately $3\mu\text{m}$ diameter, with the approximate calculated ages given in million years.

like fluid and melt inclusions and in situ studies in sample volumes inside an experimental apparatus like a DAC. The wide continuous energy spectrum provides multielement information.

Elements of interest are dependent on the given geological question and may cover the whole periodic table. While major element compositions in glasses and minerals are easily accessible by EMPA, trace element studies with high spatial resolution of as many elements as possible are a major application of $\mu\text{-SRXRF}$. As the synchrotron radiation spectrum is continuous the excitation spectrum may be efficiently adjusted to the sample and the given analytical problem by the use of filters or monochromators. Additionally, elements with Z up to 82 may be detected via K-shell excitations (Fig. 7.138), which is a significant improvement compared to conventional X-ray tubes (maximum excitation conditions generally below 20 keV), e.g., solving the problem of strong overlaps of REE-L lines with K-lines of lower Z elements. In order

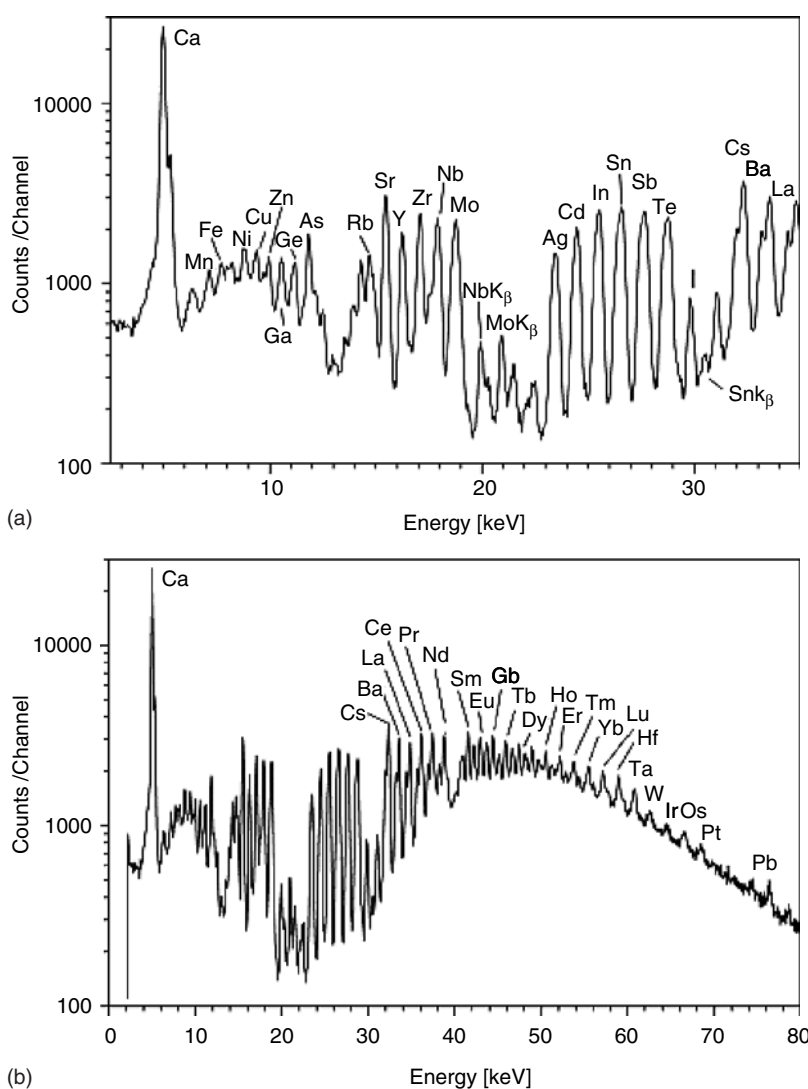


Fig. 7.138. a-b. Fluorescence spectrum of multielement 100 μm thick doubly polished standard reference material NIST612. The glass matrix is doped with trace elements with Z between 22 and 92 in the concentration range between 30 and 80 ppm. The most important K-lines are labeled. Note that Pb may be detected via K-shell excitation. A 20-mm thick Al absorber was inserted for spectrum acquisition to adjust excitation conditions for elements with Z around 45-60. The live time was 300 s and the beam size 50 $\times$ 50 μm^2 . Figure 7.138a shows an enlarged view of the low energy part of the spectrum displayed in Fig. 7.138b.

to achieve efficient simultaneous excitation toward high-energy K-shells, the polychromatic beam is generally used to achieve satisfactory flux. However, the elastically scattered photons contribute to the background at all energy levels resulting in lower sensitivity and may lead in some cases to detector overloading. Peak-to-background ratios of the low-energy part of the spectra may be improved by inserting absorbers for low-energy cut-off. Another, more effective, method to reduce the background contribution is the use of monochromatic or small bandwidth excitation resulting in lower background and thus higher sensitivities an additional advantage is the possibility of selecting the optimum excitation conditions for the element of interest, i.e., an excitation just above it is absorption edge. Because of the lower photon flux when using just a small bandwidth of the spectrum only, the detection of heavy elements via K-shell excitation is limited to third-generation synchrotron radiation sources and beamlines optimized for hard X-rays. Nakai et al. [493] have shown an example of using 116-keV X-rays as an excitation source of X-ray fluorescence analyses. The detection limits were minimal for W with 0.1 ppm in the SRM NIST612. Those measurements, however, were not achieved with a microbeam. This is a future option, which can be achieved by use of compound refractive lenses (CRL) that enable focusing even of hard X-rays down to the 100 nm scale (at 24 keV, [494]) or to the micrometer scale or better (up to 120 keV, Schroer, pers. com.) at third-generation synchrotron sources.

Applications

Mineral, Particle, and Glass Compositions. In cases when especially low limits of detection at high spatial resolution are needed, XRF analysis using synchrotron radiation is applied. Quantitative information is generally obtained by using fundamental parameter approaches or Monte Carlo simulations [495]. However, the quantification via comparison to standard reference materials is also a common approach. Recently, a new set of standard reference glasses from representative geological rock types has been produced and found to be suitable for use in μ -SRXRF [496]. The achieved accuracy of quantitative trace element analysis by using iterative Monte Carlo simulations may reach 8–10% even at concentration levels as low as 50 ppm [495].

Synchrotron radiation microanalysis was applied to run products of experimental geochemistry to determine trace element diffusivities in andesite melts [497, 498] and trace element partitioning behavior between garnet and melt [498]. Trace elemental maps on manganese nodules were determined with μ -SRXRF to investigate long-term environmental changes as evidenced by trace element compositions [499]. Feldspar trace element compositions determined with μ -SRXRF in combination with textural observations were studied, e.g., on ignimbrite “A,” Gran Canaria, Canary Islands, and used to reconstruct dynamic processes such as magma mixing and contamination in evolving rhyolitic magma chambers [500]. Analyses of chevkinite and co-existing glass using μ -SRXRF revealed the importance of chevkinite as an

accessory phase for the REE budget of evolving felsic peralkaline magmas as it concentrates Zr, Nb, and the LREE [501]. Trace element analysis of minerals and interstitial glasses in xenoliths from the East Eifel, Germany, revealed Pleistocene underplating and metasomatism processes of the lower continental crust [502]. By μ -SRXRF determinations on microtektites of the Cretaceous-Tertiary boundary from various localities, the tektites could be linked to their probable source within the Chicxulub impact crater by trace element fingerprints [503]. Besides analyses of glass and minerals another growing field of application for SRXRF is major and trace element analysis of particles from aerosols or dust in the light of their environmental health potential. The quantitative analysis of particles, however, is difficult due to their complexity in terms of chemical heterogeneity, crystallinity, and surface topology [504]. Vincze et al. [505] have shown that the accuracy of quantitative analysis of coal fly ash particles using μ -SRXRF and Monte Carlo simulations ranges between 5 and 30%. Typical airborne particles like fly ash particles [505] and fuel particles [506] were analyzed for potentially toxic elements. Another field of application that also has the aim of tracing environmental problems is the analysis of sediment-derived particles. Osán et al. [507] were able to learn about the origin of the toxicity of river sediment pollution particles by combined μ -SRXRF and μ -XANES (X-ray absorption near-edge structure). Salbu et al. [508] determined the oxidation states of uranium in depleted uranium particles (average size: 2 μm or less) from soil samples by μ -XANES and μ -SRXRF. The results are fundamental for understanding the potential remobilization of U within the contaminated area. The combined study of chemical composition and speciation is of major importance in particle research as the speciation has a major influence on the transport and dissolution behavior of the metal ions from the particle, biological uptake, and the toxicity of the particle. To identify the areas of interest for μ -XANES, μ -SRXRF is commonly applied.

Fluid and Melt Inclusion Analysis. Fluid and melt inclusions in mineral hosts are formed during crystal growth or crack annealing and - if their composition is conserved after the time of trapping - uniquely record directly the fluid and melt phase that was present during the rock genesis. Typically, many generations of fluids are included within the same mineral host (e.g., Roedder [509]). Thus, the analysis of single inclusions allows studying the evolution of crustal rocks, element transport in the crust, and enrichment processes of economically important elements. Analysis of single inclusions is ambitious because of their small size in the micrometer range and the fact that they are shielded by their host mineral. Trace element analysis of single inclusions is possible with PIXE, LA-ICP-MS, and SRXRF. Laser ablation ICP-MS allows the multi-element analysis of major and trace elements with very high accuracy and low limits of detection [510,511]. The sensitivity varies from very high to low. Typical spot sizes have a diameter from a few to tens of micrometers. Audétat et al. [512] have used LA-ICP-MS of single fluid inclusions to trace the formation of a magmatic-hydrothermal ore deposit. Heinrich et al. [513] were able to retrieve information on the metal fractionation between magmatic brine and

vapor using the same method. However, LA-ICP-MS is destructive and does not permit reproducibility measurements that are possible with PIXE and SRXRF. For inclusion studies, both methods have been proven to be complementary. The proton microprobe was shown to be best for near-surface inclusions and light elements ($Z < 22$; e.g., Ménez et al. [514, 515]). With a spatial resolution of about $2\mu\text{m}$, it is well suited for element distribution maps (e.g., Kamenetsky et al. [516], Ryan et al. [517, 518]). Detection limits are in the 10 ppm range which is significantly higher than those for SRXRF. Synchrotron radiation XRF facilitates multielement analysis of major and trace elements for heavy elements with Z between 15 and 92 at a high spatial resolution. The determination of light elements in most geological samples is mainly semiquantitative because the fluorescence is strongly absorbed in the dense geologic materials. Possible beam sizes are extremely variable with cross-sections between 1 and 2 mm and diameters in the micrometer range and can easily be adjusted to the size of the inclusion of interest. Minimum sensitivities are in the sub-ppm range. Element distribution maps of multiphase single inclusions enable to study the element distribution among vapor, liquid, and crystals. Bühn et al. [519] used a beam diameter of only $2\mu\text{m}$ and were able to distinguish between different optically identical carbonates in three different types of fluid inclusions. With this information they could reveal the complex heterogeneous entrapment and necking-down process in an evolving carbonatitic fluid system. The capability of 2D SRXRF elemental maps of fluid inclusion studies is also documented in Fig. 7.139.

Area scans display an enrichment of Sn and Sb within the inclusion, which may be correlated to a tiny opaque daughter phase, possibly SnO_2 . Philippot et al. [520] as well as Ménez et al. [515] pointed out the possible identification of optically invisible minerals within individual fluid inclusions by performing 2D SRXRF scans of single inclusions using a beam in the micrometer range (size of beamspot on the sample: $2 \times 7 - 10\mu\text{m}$). This demonstrates the importance of the analysis of complete inclusions either by 2D scans or by using a beam size covering the complete inclusion for exact quantitative analysis. Using 2D elemental maps Ménez et al. [515] could demonstrate the preferential partitioning of Br into the vapor phase (beamspot $2 \times 7\mu\text{m}$) of a liquid- and vapor bearing inclusion. This finding supports the results of Ryan et al. [521], Damman et al. [522], and Heinrich et al. [513] using PIXE analysis and – as Br has the capability of complexing metals – is of major importance in the study of segregation and enrichment processes in ore-forming systems. Recent developments of a confocal set-up of SRXRF [523] have enabled 3D imaging of single inclusions that significantly improves the possibilities to distinct elemental distributions between different phases within inclusions.

Besides the potential for qualitative analysis of trace elements in fluid and melt inclusions and element distributions, the method allows quantitative analyses of the inclusion fluorescence spectra. One peculiarity of inclusion analyses is the heterogeneous geometry of the samples. This means that the primary beam as well as the fluorescence radiation is absorbed in the

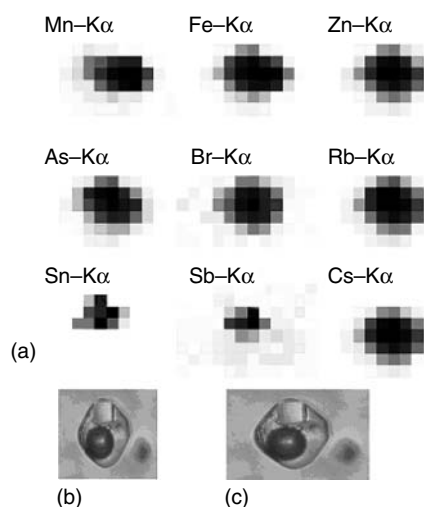


Fig. 7.139. (a) Example of 2D measurement of single fluid inclusion. Step sizes are $7\mu\text{m}$ in both directions, the diameter of the beam is $10\mu\text{m}$. The spatial resolution, however, is lower than step sizes due to the thickness of the sample and the alignment of sample to detector in 45° geometry. For each element, the relative $K\alpha$ line intensities are shown; maximum and minimum values refer to black and white pixels, respectively. Manganese, Fe, Zn, As, Br, Rb, and Cs display a rather uniform distribution throughout the inclusion. Antimony and Sn display clusters that may be related to a black daughter crystal within the inclusion. (b) Photomicrograph of the inclusion. (c) Projection of the inclusion onto a plane parallel to the detector surface.

sample and air surrounding the inclusion. This absorption is energy- and consequently element-specific (Fig. 7.140). Therefore, for inclusion analysis, the thickness and composition of the top layer has to be exactly known for accurate depth correction and quantification. A second peculiarity of inclusion analyses is that internal standardization is generally not applicable as there is no possibility to determine the concentration of one element within the inclusion, which is at the same time sensitive for SRXRF by an alternate method. One exception is Cl in high-salinity flat-lying inclusions, which may be quantified by cryometric measurements of inclusions. However, Vanko et al. [524] demonstrated that an error in the thickness estimation of only $1\mu\text{m}$ of the overlaying matrix yields an error of several tens of percentages for elements with $Z < 20$. This means that results from an internal calibration to Cl, which has a Z of 17, are highly dependent on precise thickness estimation. In cases where internal calibration is impossible, the spectra may be calibrated externally by the use of thin-film NIST reference materials [524, 525] or synthetic fluid inclusions [515]. Quantitative results may also be obtained in a standardless mode [526] by comparison of peak areas of measured spectra and full XRF spectra simulated using a Monte Carlo code [527–530] that is applicable to a multilayer geometry. The achieved accuracy for this approach tested on

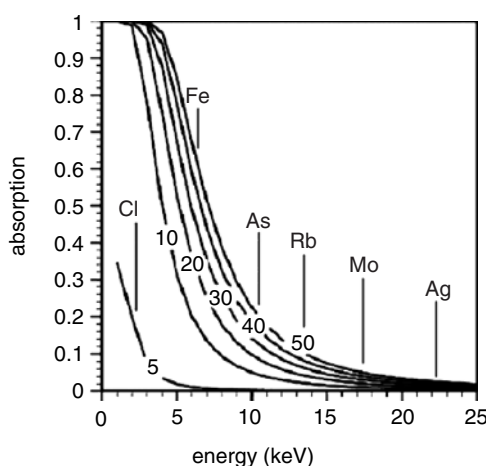


Fig. 7.140. Energy-dependent X-ray absorption in quartz of different thicknesses. The numbers on the lines refer to thicknesses in micrometer. The position of some interesting $K\alpha$ lines is marked.

synthetic fluid inclusions was better than approaches determining absolute concentrations by using a calibration on reference materials (17% error for concentrated inclusions and (30%) close to the lower limit of detection [526].

Single inclusion analyses are extremely powerful in ore deposit studies and allow the tracing of enrichment processes. One recent example is the study of the chemical evolution of an ore-forming pegmatite-hydrothermal system at the Ehrenfriedersdorf Complex, Germany, which is genetically related to important tin-tungsten deposits [526]. Arsenic and Cu were found to preferentially fractionate into the aqueous phase during phase separation of silicate melts and coexisting aqueous fluids. The enrichment processes relevant for the tin deposit take place in the hydrothermal stage at temperatures around 460°C. Early hydrothermal fluids are enriched in Cu, As, and Sn. The Rb/Cs ratios are low as are the contents of Zn, Fe, and Mn. Later fluids (inclusion temperature around 430°C) are brines and display extreme enrichments of Zn, Fe, Mn, Rb, and Cs (Fig. 7.141).

In Situ Determination of Mineral Solubilities. One recent application of XRF with synchrotron radiation has been the determination of mineral solubilities at high temperatures and pressures using a hydrothermal diamond anvil cell (HDAC) [531]. Several experimental methods have been used to study fluid-mineral equilibria that control the mobility of elements during geological processes. All those techniques, however, rely on indirect observation. The HDAC method is the first to allow real in situ measurements of the solubility of solid phases by observation of the XRF signal of dissolved elements in a fluid inside the sample volume with temperature and pressure. The fluorescence signal is calibrated against standards, and concentrations of the element

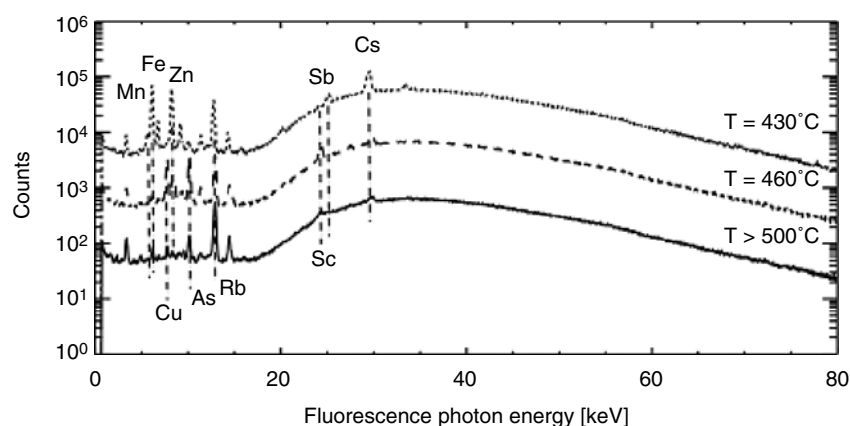


Fig. 7.141. Fluorescence spectra of three fluid inclusions representing the chemical stages relevant for ore enrichment processes of the pegmatite-hydrothermal system of the Ehrenfriedersdorf complex. The important elements are marked. The indicated temperatures refer to the approximate inclusion temperatures of the fluids from which the succession of the fluids may be deduced. For better representation, the spectra have been shifted along the y axis.

of interest may be determined at discrete P-T conditions. Up to now, two different cell set-ups have been proposed: both suggestions rely on externally heated DAC. One experimental setup was suggested using a Bassett-type HDAC [532], which was adapted to allow recording of the fluorescence of the sample volume in optimum geometry that is at an angle of 90° to the incident beam. Detection limits are below 80 ppm for elements with $Z = 37 - 65$ even for experiments performed in a second-generation synchrotron source [533]. The method is thus applicable to relatively low solubilities and at pressures up to 1.1 GPa and temperatures to 800°C . A first example of application was the determination of the solubility of AgCl in water at 300 to 450°C and pressures to 0.76 GPa [531].

A second experimental set-up has been proposed without modifying the original design of the Bassett-type cell achieving higher pressures of up to 3.6 GPa [534]. However, the conservative set-up of the HDAC demands for collection of the fluorescence spectra in forward scattering geometry at an angle of only 15° to the incident beam, which dramatically increases the detection limit to approximately 6 ppm for Sr [534] for experiments in a third-generation synchrotron source. Using this set-up, Sanchez-Valle et al. [534] investigated the P-T dependence of strontianite solubility in H_2O and found an increase of at least a factor of 2 between 0.4 and 3.6 GPa.

These data help to constrain better models on quantitative mass transfer processes in subduction zones. A second, extremely useful, application of DAC and SRXRF is the time-dependent measurements of the solubility of minerals at high P and T. The initial experiments were performed with this technique

on strontianite [534] and monazite [535]. These studies help in understanding the dissolution kinetics of minerals at conditions in the earth's crust.

X-Ray Absorption Fine Structure Spectroscopy (XAFS) in Earth Sciences

While XRF analyses provide information on the concentration of elements in a given sample, XAFS is able to add information on the chemical state or structural environment of these elements in the sample. The following is intended to give a brief overview on the technique of XAFS together with a few examples of applications relevant to geological problems. For a more thorough introduction to the field of XAFS and applications in earth sciences, the reader is referred to more comprehensive articles and books (e.g., Brown et al. [535, 536], Schulze et al. [537], Fenter et al. [538], Henderson and Baker [539]).

XAFS is performed by scanning the energy of the incident X-ray beam across a certain energy threshold needed for excitation of a core-level electron, typically at K- or L-edge of a given element. If the energy bandwidth of the incoming beam is small enough, small variation or a fine structure present in the otherwise smoothly varying X-ray absorption coefficient are observed, which are dependent on the chemical state and structural environment of the absorbing element. The observed fine structure arises from transitions of the photo-electron to higher bound-state energy levels (before or at the edge) or from backscattering of the photoelectron from the atoms surrounding the absorbing element (at the edge and after the edge). The method is basically grouped into two methods (see also Fig. 7.142):

- XANES: using the fine structure occurring just before and up to approximately 100-150 eV after the edge. This region in the spectrum is sensitive to the valence state of the absorbing element and to the geometry and the type of surrounding atoms.
- EXAFS (extended X-ray absorption fine structure): the fine structure occurring far beyond the edge (starting from approximately 100 up to 1000 eV or further) provides quantitative information on the distances and number of atoms surrounding the absorbing atom.

Because XAFS works as a local probe, the aforementioned information is also accessible in systems lacking long-range order as silicate glasses and melts or aqueous solutions and hydrothermal or even supercritical fluids. As XAFS is element specific it also allows investigation of elements that are only near or at the surface of a mineral or phase, thus providing a helpful tool for the investigation of processes at the mineral-water interface.

XAFS spectrometers usually rely on the continuous spectrum at high photon flux available at synchrotron radiation facilities. In order to detect the fine structure at the absorption edge a monochromatic beam with a sufficiently small bandwidth is needed. Typically used in the energy regime suitable for investigations of the 3d-transition elements are Si (111) based double-crystal

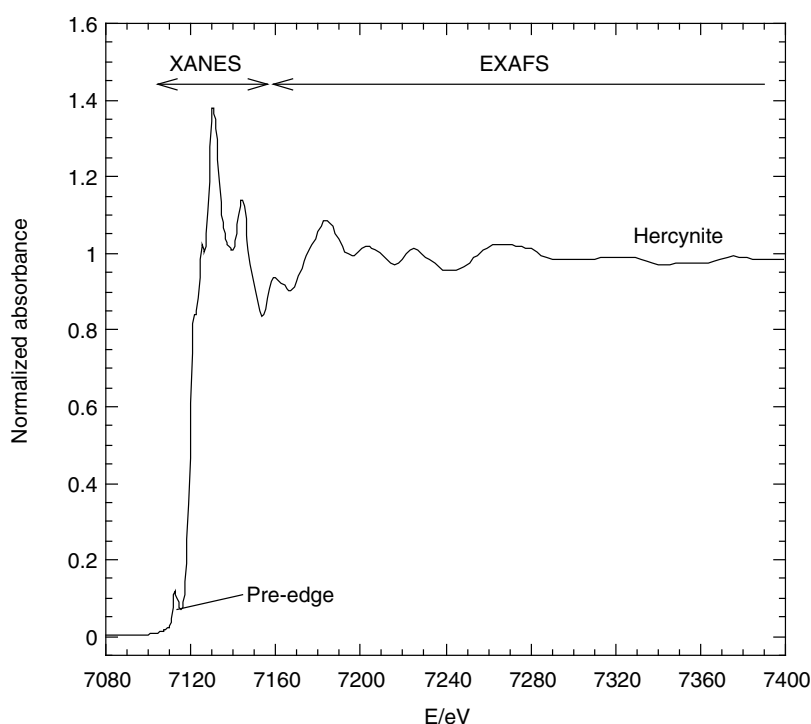


Fig. 7.142. XAFS-spectrum at the Fe K-edge of hercynite (Fe-Al-spinel) showing the respective regions within the spectrum as explained in the text. Note that the EXAFS region extends much further than shown here.

monochromators providing a resolving power $E/\Delta E$ of approx. 4000 at 7 keV. While such a resolution is adequate enough for investigations of the EXAFS region it may be insufficient to resolve all spectral features present in the XANES region so that monochromator crystals with higher intrinsic resolution have to be used, e.g., Si (220) or Si (311). The actual resolution needed is determined by the energy width of the transitions that are probed. The width is a function of the core-hole lifetime and increases with increasing atomic number. Use of a small bandwidth monochromator, however, may be limited due the accompanied loss in photon flux that potentially makes high-resolution measurements unfeasible due to low counting rates at the detector.

XAS and Fluorescence Yield

Originally X-ray absorption spectroscopy was performed by measuring the intensity of the X-ray beam before and after the sample (I_0 and I_{tr} , respectively), so that the absorption coefficient $\mu = \ln I_0/I_{tr}$. A further possibility is the indirect measurement of μ through detection of the fluorescence yield

as $\mu \approx I_f/I_0$. This relation holds as long as the concentration of the absorbing element is low or the sample is very thin. For thick and concentrated samples the oscillations and resonances above the edge are significantly damped, and peaks in the pre-edge region artificially are enlarged due to self-absorption of the incoming beam. These effects are dependent on the detection angle and are minimized by detection in grazing exit geometry (see Tröger et al. [540]; Manceau et al. [541]).

Detection of the fluorescence can be performed in several ways. The simplest way is by using a gas-filled ionization chamber [542]. Such a detector enables the detection of a large solid angle although the dynamic range is limited. The sensitivity for the energy used can be adjusted by the use of the appropriate gas filling. Use of this detector is only possible if only the element of interest is excited due to the low-energy resolution of this type of detector. In a similar way silicon pin diodes can be used to provide a higher sensitivity and much larger dynamic range [543] although the solid angle of detection is smaller. Use of solid-state detectors such as Si(Li), high-purity Ge, or Si-drift detectors provide additional advantages due to the high-energy resolution that can be achieved with these devices. Processing of the detector signal by a multichannel analyzer provides the possibility of separating the fluorescence signal from the elastically scattered background or from fluorescence radiation produced by other elements contained in the sample. Sophisticated treatment of each XRF spectrum that is saved at each energy position of a XANES scan enables the collection of XANES even at very low concentration levels [544]. In such a data treatment the fluorescence yield is separated from the background by fitting of the XRF spectrum. This procedure provides a much better separation of background and signal and reduces the noise contribution from elastic and Compton scattering.

Micro-XAFS

Use of a microbeam enables the investigation of samples that are inhomogeneous even on a microscopic scale. Analyses can be performed at specific sites, grains, etc. of a given sample or even mappings of the chemical state can be performed. Combined with concentration-distribution maps (from micro-XRF or EMPA) this will provide information on the distribution of the chemical state or structural environment of the mapped element in the sample. The synchrotron beam is usually strongly polarized. Therefore, spectra acquired by micro-XAFS on single crystals of minerals as occurring in rock thin-sections may be affected by the orientation of the crystal toward the beam, especially in strongly anisotropic phases [545, 546]. This additional uncertainty has to be taken into account for a robust interpretation of micro-XAFS data.

If elements show gradual lateral change in oxidation state within a sample the distribution of the oxidation state can be mapped by superimposition of XRF maps excited by X-ray energies at prominent maxima of the XANES of each oxidation state. The position of these maxima varies with oxidation state

by a few electron volts and therefore setting the energy at either position will lead to preferential excitation of either oxidation state (e.g., compare spectra in Fig. 7.143a). Normalization of the intensity at these energy positions to the height of the edge jump and subtraction of the two maps collected at the two energies will yield the distribution of oxidation state within the sample. Thus, for each position on the sample, the fluorescence yield at three energies has to be measured: one before the edge, one after, and one at the redox-sensitive maximum (see also Sutton et al. [547]).

Applications

As the position of the absorption edge is dependent on the oxidation state XANES spectra can be used for the determination of the valence state. This can be done by using the edge position, i.e., determination of position in comparison to the variation observed for the end member valence states. However, the observed position of the edge may be affected by resonances occurring in the edge region that are due to multiple scattering or transitions of the photoelectrons to localized energy levels (these features are very sensitive to the local geometry around the absorber and therefore structure dependent). Another possibility is the use of the whole XANES spectra: if the end member spectra of each oxidation state are clearly known from available model compounds the oxidation state of the unknown sample can be determined by linear combinations of spectra of the model compounds (e.g., Garvie and Buseck [548]).

As the structure of the XANES is also a “fingerprint” of the absorbing element in a given phase (e.g., examples in Fig. 7.143a), linear combinations of end member spectra can be used to determine the host phase of a given element and its relative abundance in a sample (e.g., Welter et al. [549]; Calmano et al. [550]; Vincze et al. [551], Salbu et al. [508]).

The pre-edge feature that probes $1s \rightarrow 3d$ transitions (especially sensitive to oxidation state) is only affected by the first co-ordination shell around the absorber (usually oxygen). Thus, it will show much less dependence on changes in the medium-range environment or bulk structure than the structure of the spectra occurring at the main edge. The pre-edge position varies significantly with oxidation state and shows variation in intensity due to the geometry of oxygen-coordination polyhedron (octahedral, tetrahedral, etc. see Fig. 7.143b; Wilke et al. [552]). In the case of Fe, the difference between the pre-edge position (measured as centroid) of ferric and ferrous Fe does not vary with the coordination geometry. Therefore, a linear variation of the position with redox ratio can be expected if the coordination does not change with oxidation state. Exploiting this effect, it was shown to give moderately precise estimates for the oxidation state (approx. $\geq 10 - 15\%$ error) by the use of general calibration curves (Fig. 7.143c) (Bajt et al. [553] 1995; Wilke et al. [552]). These calibrations were applied to several geological problems where knowledge of Fe^{3+} was essential (e.g., Dyar et al. [554]; Schmid et al. [546]). In these studies

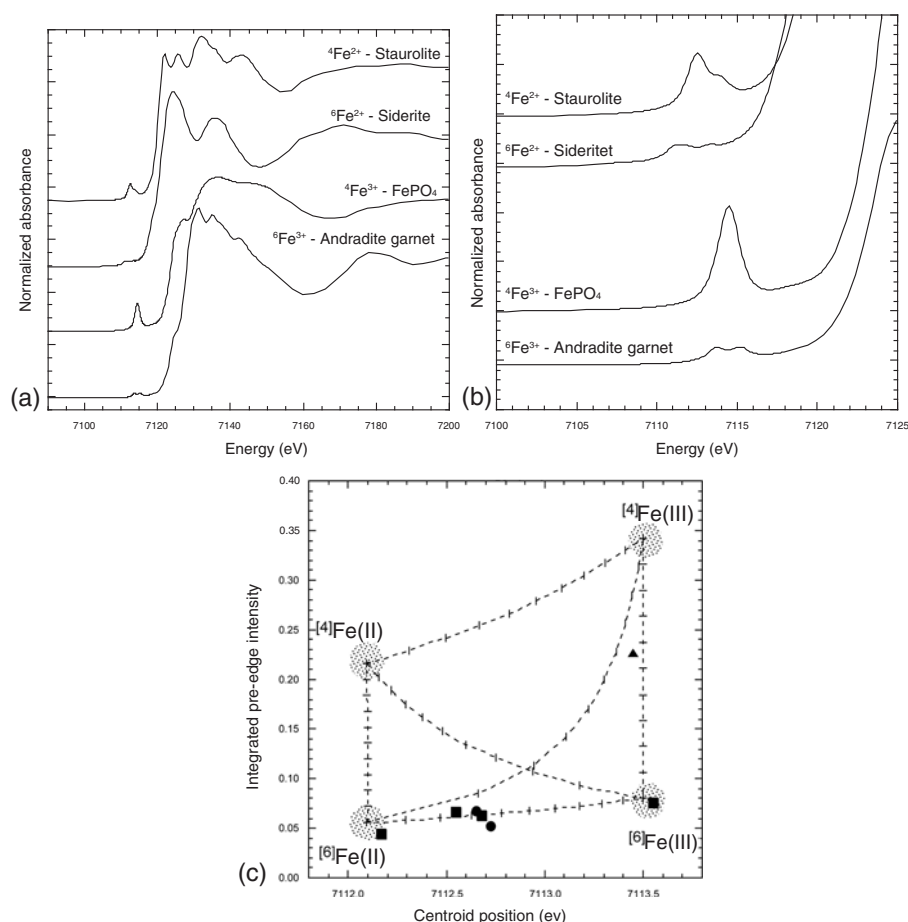


Fig. 7.143. (a) XANES spectra collected at the Fe K-edge of several model compounds (staurolite: Fe-Mg-Al nesosilicate; siderite: Fe-carbonate; andradite garnet: Ca-Fe nesosilicate) containing ferrous and ferric iron in various coordination geometries as indicated. The position of the main edge is dependent on the oxidation state, and the fine structure, observed at the main crest of the edge, provides a fingerprint of the local and medium-range structural environment of Fe in these phases.

(b) A zoom of the pre-edge region: The position of the pre-edge depends on the oxidation state while the structure and intensity of the pre-edge is mainly dependent on the geometry of the first coordination shell of Fe (oxygen in these examples).

(c) Variation diagram after Wilke et al. [552] showing the systematics of the pre-edge variation with oxidation state and coordination geometry, taking into account tetrahedral and octahedral site geometries. Integrated intensity and centroid position are determined on background corrected pre-edges. Plotted are examples of pre-edges of several other phases: Triangle: Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) with $2/3$ 4Fe^{3+} and $1/3$ 6Fe^{3+} ; Circles: Amphiboles with 6Fe , $\text{Fe}^{3+}/\sum\text{Fe}=0.4$; Squares: Clinopyroxenes with 6Fe , $\text{Fe}^{3+}/\sum\text{Fe}=0, 1$ and 0.3 (Data taken from Wilke et al. [552] and Schmid et al. [546])

the Fe^{3+} content of minerals was determined by micro-XAFS on 30- μm -thick thin sections of rock samples, providing information on the oxidation state of Fe that was not available from the chemical microanalysis with the electron microprobe.

Apart from investigations at ambient conditions XAFS also provides the possibility of characterizing samples at high temperatures and/or high pressures. Such studies are important if the samples are not stable at ambient conditions. For example, it was shown by high-temperature XANES and EXAFS that the speciation of elements in silicate melts at high temperature may differ from the one found in glass (Jackson et al. [555]; Farges et al. [556, 557]; and Fig. 7.144). Such differences have strong implications in the relationship between melt structure and macroscopic physical properties such as viscosity. Investigation of aqueous solutions at high temperature and high pressure using X-ray-transparent pressure cells (e.g., Bassett et al. [558]; Anderson et al. [559]; Seward et al. [560]) provides a direct view on the speciation of elements in such systems. Such data are important for the understanding of the processes involved during mass transport by fluids and fluid-rock interactions in the earth's crust, or in any physico-chemical process occurring at high temperatures and pressures.

To improve the results as compared to the examples by Dyar et al. [554] and Schmid et al. [546] a high-resolution monochromator should be used in order to better separate the pre-edge feature from the edge background (in case of Fe: Si(220) or (311) monochromator). Using high-resolution spectra and phase/mineral-specific calibrations errors below 10% can probably be achieved.

XAFS may also be used to perform time-dependent investigations to study the dynamic behavior of chemical and physical processes, such as redox reactions or phase transitions. For rather slow reactions this can be achieved by acquiring a time series of normal XAFS scans (10-20 min/spectrum). Such a study not only provides data on the kinetics of a reaction but may also reveal information on transient intermediate states that might be formed during reaction (e.g., Bargar et al. [561] 2000). For fast reactions in the minute or even second regime, so-called QEXAFS methods have to be used, where spectra are collected continuously within seconds or even fraction of a second (e.g., Frahm [562], Lützenkirchen-Hecht et al. [563])

7.6.5 Conclusions

XRF analysis is one of the most important analytical methods for geoscientists. The method can be applied manually, in automated mode, and even by remote control in space, at any scale, on other planets, in the field, in boreholes, at industrial sites, in the laboratory and even under submicroscopic conditions in all fields of geoscience: geological mapping, tectonics, petrography, geochemistry, sedimentology, remote-sensing, geophysics, microbiology,

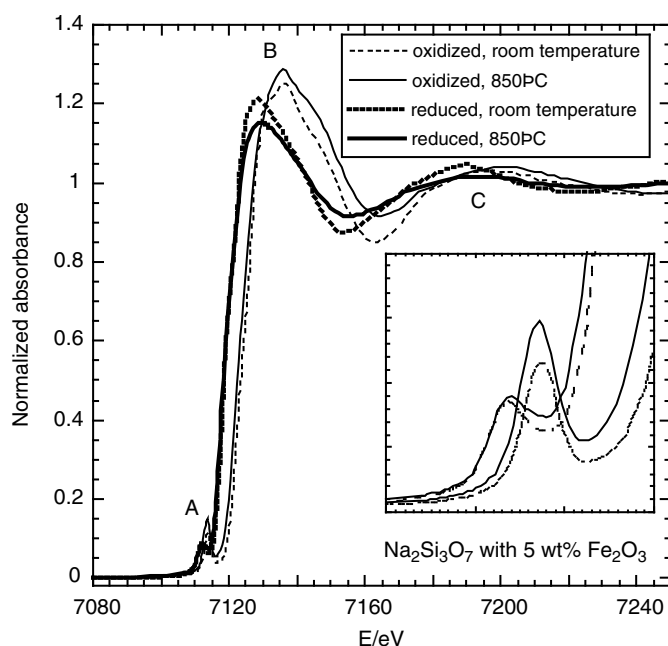


Fig. 7.144. XANES at Fe K-edge acquired on glass at room temperature and on melt at 850°C at oxidizing and reducing conditions in fluorescence mode (see Brown et al. [536] for experimental setup). Note the changes occurring at pre-edge (A), main crest (B) and first EXAFS-oscillation (C). Pre-edge intensity of the high-temperature spectrum of the oxidized sample is significantly higher than the one of the room temperature spectrum, indicating change in coordination toward tetrahedral geometry at high temperature. This interpretation is consistent with an observed shift of the first EXAFS-oscillation toward higher energies that indicate shortening of the Fe-O distance (as expected for change from higher to lower oxygen coordination number). The change in the pre-edge of the reduced sample between high and room temperature is much smaller and almost negligible after background subtraction. This indicates only small changes in the local structure at reducing conditions consistent with only a small shift of the first EXAFS oscillation. The loss in the EXAFS amplitude of high temperature is related to the thermally induced vibrational disorder at high temperature.

engineering, exploration, mining, mineral treatment, melioration, and metallurgy. Standard quantitative analyses by WDXRF, EDXRF, and TXRF are well developed for homogenized samples, but have to be individually modified for materials of anomalous chemical composition such as ores, salt, minerals, crude raw oils, fluids, and plants.

The method, if modified properly, is suitable for the analysis of all elements from carbon to uranium depending on the analytical conditions. Besides the

analysis of homogeneous samples, geoscientists require spatially resolved information of inhomogeneous samples. Knowledge of the type, shape, and frequency of an anomaly that may appear as a certain mineral (Au, PGM, etc.), a lamina (winter/summer), or a hot spot of a contaminant (Pb, Cu, Zn) is crucial for the interpretation of mineralization, climate impact/influence, contamination, etc. During industrial processes like mining and metallurgy the online control of the product at all stages of the production line is a key parameter since costs can be reduced, and the performance and quality of the end product is improved. Besides the manual specimen acquisition, in situ online systems are installed to monitor the flow at sensitive steps of the treatment process.

The miniaturization of systems that may be used within drill cores bore holes and as handheld instruments in the field and the advancement in element mapping and imaging systems provide very detailed information for the geoscientist onsite for fast adequate decision and precision sampling.

On the other hand, the improvement of X-ray optical systems at reasonable costs and highly sensitive detectors will push forward micro-XRF systems in the laboratory to solve analytical problems at any fields.

The scanning X-ray instrument based on energy-dispersive spectroscopy enables a comprehensive material characterization. It combines simultaneous imaging of element distributions by X-ray microfluorescence analysis, texture mapping, and residual lattice strain mapping on a grain specific scale, as well as quantitative texture analysis.

References

1. Carpenter, D.A., x-Ray Spectrom. 18, 1989, 253
2. Yamamoto, Y., Hosokawa, Y., J. Appl. Phys. 27, 1988, L2203

3. Wittry, EMSA/MAS, Boston 1992, Focussing X-rays for microprobe X-ray fluorescence analysis
4. Janssens, K.H.A., Adam, F.C.V., Rindby, A., Wiley & Sons, Chichester, 2000, Microscopic X-Ray Fluorescence Analysis
5. Rindby, A., Janssens, K., in: Handbook for X-Ray Spectrometry (second edition), ed. by R.E. van Grieken, A.A. Markowicz, Marcel Dekker Inc, New York, 2002
6. Yinming, Y., Xunliang, D., Nucl. Instrum. Methods B52, 1993, 126
7. Carpenter, D.A. et al., Adv. X-Ray Anal. 32, 1989, 115
8. Wherry, C.D., Cross, B.J., Adv. X-Ray Anal. 31, 1988, 93
9. Rindby et al., Nucl. Instrum. Methods B, 124, 1997, 591
10. Haschke, M. et al., J. Phys. IV. 12, 2002
11. Bjeoumikhov, A.A., Langhoff, N., et al., Proc. of SPIE, 3444 (1998) 430
12. XOS company information, <http://www.xrayoptics.com/analyzer/Sindie%20Bench-top%2010-15.pdf>
13. Heckel, H., Ryon, D., in: Handbook for X-Ray Spectrometry (second edition), ed. by R.E. van Grieken, A.A. Markowicz, Marcel Dekker Inc, New York, 2002
14. Spectro, Geräteinformation XEPOS, <http://www.spectro-ai.com/pages/e/p010503.htm>
15. Haschke, M., Haller, M., X-Ray Spectrom., 2003; Holynska, B., Ostachowicz, J., Ostrowski, A., Ptasinski, D., Wegrzynek, D., Trace Microprobe Tech. 13(2), 1995, 163
16. Holynska, B. et al., J. Aerosol Sci. 28, 1997, No. 8, 1455
17. Bichlmeier, S. et al., X-Ray Spectrom. 30, 2001, 8
18. Longoni, A., NIM A, 1998, 407
19. IfG, IMOX instrument information, <http://www.ifg-adlershof.de/imoxs.pdf>
20. IXRF, fx option instrument information, <http://www.ixrfsystems.com/whatsnew.html>
21. Rindby, A., X-Ray Spectrom. 25, 1996, 39
22. Rödel, C., Diplomarbeit TU Berlin, 2000
23. Rödel, C., Bronk, H., Haschke, M., X-Ray Spectr. 2001
24. Haschke, M., Klein, J., Stichert, W., Vietze, U., GIT, 7, 2002, 780
25. Haug, G. et al., Science 299, 2003, 1731
26. de Stasio, et al., Cancer Research 61, 2001, 4273
27. Ioele, M., Instituto Centrale per il Restaurio, personal communication
28. Meltzer, C., King, B.S., Adv. X-Ray Anal. 34, 1991, 41
29. Miller, T.C., Havrilla, G.J., X-Ray Spectr. 33, 2004, 101
30. Kanngießer, B., Malzer, W., Reiche, I., Nucl. Instrum. Methods B 211/2, 2003, 259–264
31. Kumakhov, M.A., X-Ray Spectrom. 29, 2000, 343
32. Ding, X., Gao, N., Havrilla, G., SPIE Proc. 2000
33. Fiorini, C., Longoni, A., Bjeoumikhov, A., IEEE T Nucl. Sci. 48,3, 2001, 268
34. Proost, K., Janssens, K., Vincze, L., Falkenberg, G., Gao, N., Bly P., HASY-LAB Jahresbericht 2002
35. Vincze, L., Vekemans, B., Brenker, F.E., Falkenberg, G., Rickers, K., Somogyi, A., Kersten, M., Adams, F., Anal. Chem. 76, 2004, 6786–6791
36. Kanngießer, B., Malzer, W., Rodriguez, A.F., Reiche, I., Spectr. Chim. Acta B 60, 2005, 41–47
37. Elam, W.T., Ravel, B.D., Sieber, J.R., A new atomic database for x-ray spectroscopy calculations, Rad. Phys. Chem. 2002

38. Henke, B.L., Gullikson, E.M., Davis, J.C., *At. Nucl. Data Tables* **54**, 1993, 181
39. McMaster, W.H., Kerr del Grande, N., Mallet, J.H., Hubbel, J.H., *Compilation of x-ray cross sections*, Lawrence Radiation Laboratory, University of California 1969
40. Boisseau, P., Ph.D. thesis, Massachusetts Institute of Technology 1986
41. Janssens, K., Vincze, L., Vekemans, B., Adams, F., Haller, M., Knöchel, A., *J. Anal. At. Spectrom.* **13**, 1998, 339
42. Simionovici, A.S., Chukalina, M., Schroer, C.G., Drakopoulos, M., Snigirev, A., Snigireva, I., Lengeler, B., Janssens, K., Adams, F., *IEEE Trans. Nucl. Sci.* **47**, 2000, 2736
43. Golosio, B., Simionovici, A.S., Somogyi, A., Lamelle, L., Chukalina, M., Brunetti, A., *J. Appl. Phys.* **94**/1, 2003, 145
44. R. Castaing, G.J. Slodzian, *Microscopie* **1**, 395, 1962
45. F. Michiels, W. Van Hoolst, P. Van Espen, F. Adams, *J. Am. Soc. Mass. Spectrom.* **1**, 37, 1990
46. E. Denoyer, R. Van Grieken, F. Adams, D. Natush, *Anal. Chem.* **26A**, 54, 1982
47. F. Adams, T. Mauney, *Adv. Mass. Spectrom.* **10**, 507, 1986
48. S.I. Goldstein, D.E. Newbury, P. Echlin, D.C. Joy, C. Fiori, E. Lifshin, *Scanning electron microscopy and X-ray microanalysis*, Plenum Press, New York, 1984
49. J.A. Cookson, *Principles & Applications of High-energy Ion Microbeams*, eds. F. Watt and G.W. Grime, Adam Hilger, Bristol, 1987
50. G.W. Grime, M. Dawson, M. Marsh, I.C. McArthur, F. Watt, *Nucl. Instr. & Meth.* **B 54**, 52–63, 1991
51. D.N. Jamieson, *Nucl. Instr. & Meth.* **B 181**, 1–11, 2001
52. D. Bilderback, S.A. Hoffman, D. Thiel, *Science* **263**, 201, 1994
53. S.A. Hoffman, D.J. Thiel, D.H. Bilderback, *Nucl. Instrum. & Meth.* **A 347**, 384, 1994
54. P. Kirkpatrick, A. Baez, *J. Opt. Soc. Am.* **38**, 766, 1948
55. Y. Suzuki, F. Uchida, *Rev. Sci. Instrum.* **63**, 578, 1992
56. O. Hignette, G. Rostaing, P. Cloetens, A. Rommeveaux, W. Ludwig, A. Freund, In I. McNulty, ed., *X-ray Micro- and Nano-Focusing: Applications and Techniques II*, **4499** of *Proceedings of the SPIE*, 105, 2001
57. O. Hignette, P. Cloetens, W.K. Lee, W. Ludwig, G. Rostaing, *J. Phys. IV* **104**, 231, 2003
58. B. Niemann, G. Rudolph, G. Schmahl, *Opt. Commun.* **12**, 160, 1974
59. B. Lai, W. Yun, D. Legnini, Y. Xiao, J. Chrzas, P. Viccaro, V. White, S. Bajikar, D. Denton, F. Cerrina, E. Fabrizio, M. Gentili, L. Grella, M. Baciocchi, *Appl. Phys. Lett.* **61**, 1877, 1992
60. V.V. Aristov, Y.A. Basov, G.N. Kulipanov, V.F. Pindyurin, A.A. Snigirev, A.S. Sokolov, *Nucl. Instrum. Meth. A* **274**, 390, 1989
61. P. Chevallier, P. Dhez, F. Legrand, A. Erko, Yu. Agafonov, L.A. Panchenko, A. Yakshin, *J. Trace & Microprobe Tech.* **14**(3), 517–539, 1996
62. A. Snigirev, V. Kohn, I. Snigireva, B. Lengeler, *Nature (London)* **384**, 49, 1996
63. B. Lengeler, C.G. Schroer, M. Richwin, J. Tümmeler, M. Drakopoulos, A. Snigirev, I. Snigireva, *Appl. Phys. Lett.* **74**, 3924, 1999
64. B. Lengeler, C.G. Schroer, M. Kuhlmann, B. Benner, T.F. Günzler, O. Kurapova, C. Rau, T. Weitkamp, A.S. Simionovici, A. Snigirev, I. Snigireva, “Beryllium parabolic refractive x-ray lenses for full field imaging and scanning microscopy with hard X-rays”, *J. Phys. IV* **104**, 221–224, 2003

65. B. Nöhammer, C. David, H. Rothuizen, J. Hoszowska, A. Simionovici, "Deep reactive ion etching of silicon and diamond for the fabrication of planar refractive hard X-ray lenses", *Microelectr. Eng.* **67–68**, 453–460, 2003
66. C.G. Schroer, M. Kuhlmann, U.T. Hunger, T.F. Gunzler, O. Kurapova, S. Feste, F. Frehse, B. Lengeler, M. Drakopoulos, A. Somogyi, A.S. Simionovici, A. Snigirev, I. Snigireva, C. Schug, W.H. Schröder, "Nanofocusing parabolic refractive X-ray lenses", *App. Phys. Lett.* **82**, Nr. 9, 1485–1487, 2003
67. I.G. Grigorieva, A.A. Antonov, *X-Ray Spectr.* **32**, 64–68, 2003
68. P. Chevallier, P. Populus, private communication, LURE, 2000
69. B. Mason, *Principles of Geochemistry*, Wiley, 1952
70. S. Bohic, A. Simionovici, R. Ortega, A. Snigirev, "Synchrotron hard X-Ray microprobe for fluorescence imaging of single cells", *App. Phys. Lett.* **78**, 3544, 2001
71. B. Vekemans, K. Janssens, L. Vincze, F. Adams, P. Van Espen, *X-ray spectrometry* **23**, 278, 1994
72. See previous chapter on "Synchrotron Radiation Sources". Package available at <http://www.esrf.fr/machine/support/ids/Public/index.html>
73. R. Ortega, P. Moretto, A. Fajac, J. Benard, Y. Llabador, M. Simonoff, *Cell. Mol. Biol.* **42**, 77 (1996)
74. P. Boisseau, Ph.D Dissertation, M.I.T. Cambridge, 1986
75. G.-F. Rust, J. Weigelt, *IEEE Trans. Nucl. Sci.* **45**, 75, 1s998
76. A. Simionovici, M. Chukalina, Ch. Schroer, M. Drakopoulos, A. Snigirev, I. Snigireva, B. Lengeler, K. Janssens, F. Adams, "High resolution X-ray fluorescence tomography on homogenous samples", *IEEE Trans. Nucl. Sci.* **47**, Nr.6, 2736, 2000
77. M. Chukalina, A. Simionovici, A. Snigirev, T. Jeffries, "Quantitative characterization of microsamples by X-ray fluorescence tomography", *X-Ray Spectrometry* **31**, Nr. 6, pp. 448–450, 2002
78. B. Golosio, A. Simionovici, A. Somogyi, L. Lemelle, M. Chukalina, A. Brunetti, *J. Appl. Phys.* **94**, 145–157, 2003
79. C. Kak, M. Slaney, *Principles of Computerized Tomographic Imaging*, IEEE Press, New York, 1988
80. J.P. Hogan, R.A. Gonsalves, A.S. Krieger, *IEEE Trans. Nucl. Sci.* **38**, 1721, 1991
81. A. Brunetti, B. Golosio, *Comp. Phys. Comm.* **141**, 412, 2001
82. V. Sautter, J.A. Barrat, A. Jambon, J.P. Lorand, Ph. Gillet, M. Javoy, J.L. Joron, M. Lesourd, *Earth & Planet. Phys. Lett.* **195**, 223, 2002
83. L. Fabry, Y. Matsushita, *Silicon Materials Science and Technology*, H.R. Huffs, H. Tsuya, U. Gösele eds., *Proc. Vol. 98-1*, The Electrochemical Society, 1998, p. 1459
84. L. Fabry, *Fresenius J. Anal. Chem.* **337**, 148, 1997
85. L. Fabry, L. Köster, S. Pahlke, L. Kotz, J. Hage, *IEEE Transactions on Semicond. Manuf.* **9**, 428, 1996
86. P. Wobrauschek, P. Kregsamer, W. Ladisich, C. Streli, S. Pahlke, L. Fabry, S.A. Garbe, M. Haller, A. Knöchel, M. Radtke, *Nucl. Instr. Meth. A*, **363**, 619, 1995
87. J. Fucsko, S.H. Tan, M.K. Balazs, *J. Electrochem. Soc.* **114**, 1105, 1993
88. L. Fabry, *Accreditation and Quality Assurance*, Springer, Berlin Heidelberg New York, **1**, 99, 1996

89. M. Thompson, *Analyst* 124, 991, 1999
90. A. Huber, G. Böhm, S. Pahlke, J. Radioanal. Nucl. Chem. 169, 93, 1993
91. Ch. Schnürer-Patschan, W. Hrosch, S. Pahlke, L. Kotz, L. Fabry, Crystalline Defects and Contamination: Their Impact and Control in Device Manufacturing, 192nd ECS Meeting, Paris, Aug 30-Sep 5, 1997, B.O. Kolbesen, C.L. Claeys, P. Stallhofer, F. Tardif eds., Proc. Vol. 97-22, The Electrochemical Society, 1997, pp. 496
92. B. Wenz, M. Sperling, Atomabsorptionsspektrometrie, Wiley-VCH, 1997
93. P. Wobrauschek, R. Görgl, P. Kregsamer, Ch. Strel, S. Pahlke, L. Fabry, M. Haller, A. Knöchel, Radtke, *Spectrochim. Acta, Part B* 52, 901, 1997
94. International Technology Roadmap for Semiconductors, Semiconductor Industry Association, San Jose CA, 95110, 1999
95. Y. Yoneda, T. Horiuchi, *Rev. Sci. Instrum.* 42, 1069, 1971
96. C. Strel, *X-Ray Spectrom.* 29, 203, 2000
97. P. Kregsamer, *Spectrochim. Acta B* 46, 1333, 1991
98. H. Aiginger, *Spectrochim. Acta B* 46, 1313, 1991
99. H. Aiginger, P. Wobrauschek, *Nucl. Instrum. Methods* 114, 157, 1974
100. J. Knoth, H. Schwenke, *Fresenius' Z. Anal. Chem.* 291, 200, 1978
101. H. Schwenke, J. Knoth, *Nucl. Instrum. Methods* 193, 239, 1982
102. R.S. Becker, J.A. Golovchenko, J.R. Patel, *Phys. Rev. Lett.* 50, 153, 1983
103. Ch. Strel, P. Wobrauschek, V. Bauer, P. Kregsamer, R. Görgl, P. Pianetta, R. Ryon, S. Pahlke, L. Fabry, *Spectrochim. Acta, Part B* 52, 861, 1997
104. R. Klockenkämper, A. von Bohlen, *Spectrochim. Acta B* 54, 1385, 1999
105. L. Fabry, S. Pahlke, L. Kotz, P. Wobrauschek, Ch. Strel, P. Eichinger, *Fresenius' J. Anal. Chem.* 363, 98, 1999R Klockenkämper, A. von Bohlen, *Spectrochim. Acta B*, 54, 1385, 1999
106. X. Xiao, S. Hayakawa, Y. Goshi, M. Oshima, *Anal. Sci. (Jpn)* 14, 1139, 1998
107. P.K. deBokx, S.J. Kidd, G. Wiener, H.P. Urbach, S. De Gendt, P.W. Mertens, M.M. Heyns, I: *Silicon Mater. Sci. & Technol.*, H. Huff, H. Tsuya, U. Gösele eds., The Electrochem. Soc., 1998, PV 98-1, p. 1511
108. H. Schwenke, J. Knoth, *Eur. Patent Appl.*, 199.24 204.6 05/27/2000
109. P. Wobrauschek, C. Strel, *Advanced Light Sources, ADLIS*, TU Wien, 1999, p. 284
110. K. Yakushiji, S. Ohkawa, A. Yoshinaga, J. Harada, *Jpn. J. Appl. Phys.* 32, 1191, 1993
111. K. Yakushiji, S. Ohkawa, A. Yoshinaga, J. Harada, *Jpn. J. Appl. Phys.* 33, 1130, 1994
112. B.W. Liou, C.L. Lee, *Chin. J. Phys.*, 37, 623-30, 1999
113. R. Klockenkämper: *Total-Reflection X-Ray Fluorescence Analysis*, Vol. 140 *Chem. Anal.*, J.D. Winefordner ed., Wiley, 1997
114. ATOMIKA, Sales Department, Bruckmannring 40, D-85764 Oberschleissheim, Germany
115. I. Szaloki, Sz.B. Török, Chul-Un Ro, J. Injuk, R.E. Van Grieken, *Anal. Chem.* 72, 211R, 2000
116. L. Struder, N. Meidinger, D. Stotter, J. Kemmer, P. Lechner, P. Leutenegger, H. Soltau, F. Eggert, M. Rohde, T. Schulein, *Microscopy Microanal.* 4, 622-31, 1998
117. K. Tsuji, T. Yamada, T. Utaka, K. Hirokawa, *J. Appl. Phys.* 78, 969, 1995
118. J. Knoth, P. Beaven, H. Schwenke, M. Dobler, U. Reus, to be published in *Microchim. Acta*

119. Standard Test Method M 33: Test Method for the Determination of Residual Surface Contamination on Silicon Wafers, Semiconductor Equipment and Materials International, San Jose, CA 95134, attached to Chapter 8
120. Ch. Streli, P. Kregsamer, P. Wobrauschek, H. Gatterbauer, P. Pianetta, S. Pahlke, L. Fabry, L. Palmetshofer, M. Schmeling, *Spectrochim. Acta Part B*, 54, 1433, 1999
121. K. Yakushiji, S. Ohkawa, A. Yoshinaga, J. Harada, *Anal. Sci. (Jpn)* 11, 505, 1995
122. J. Knoth, H. Schwenke, P. Eichinger, In: *Proc. 2nd International Symp. Ultra Clean Processing of Silicon Surfaces (UCPSS '94 IMEC, Sept. 19-21, 1994, Bruges)*, M. Heyns, M. Heuris, P. Mertens eds., ACCO Leuven, 1994. p. 107
123. R. Klockenkämper, A. von Bohlen, *Spectrochim Acta B*, 44, 461, 1989
124. Y. Mori, K. Shimano, T. Sakon, *Anal. Sci. (Jpn)* 11, 499, 1995
125. I. Rink et al, of 12 TXRF Laboratories to be published in *Spectrochim. Acta B*, 2000
126. Y. Mori, K. Shimano, *Anal. Sci. (Jpn)*, 12, 277, 1996
127. R. Hölzl, K.-J. Range, L. Fabry, D. Huber, *J. Electrochem. Soc.* 146, 2245, 1999
128. B. Hackl, K.-J. Range, P. Stallhofer, L. Fabry, *J. Electrochem. Soc.* 139(5) 1495, 1992
129. L. Fabry, S. Pahlke, L. Kotz, E. Schmemmel, W. Berneike, *Crystalline Defects and Contamination: Their Impact and Control in Device Manufacturing*, B.O. Kolbesen, P. Stallhofer, Cor Claeys, F. Tardif eds., *Proc. Vol. 93-15*, 1993, p. 232
130. A.C. Diebold, *J. Vac. Sci. Technol. A* 14, 1919, 1996
131. R.S. Hockett, *Anal. Sci. (Jpn)* 11, 511, 1995
132. P. Eichinger, H.-J. Rath, H. Schwenke, In: *Semicond. Fabrication: Technology and Metrology*, ASTM STP 990, D.C. Gupta ed., ASTM 1989, p. 305
133. V. Penka, W. Hub, *Fresenius Z. Anal. Chem.* 333, 586, 1989
134. J.A. Sees, L.H. Hall, *J. Electrochem. Soc.* 142, 1238, 1995
135. H. Schwenke, J. Knoth, U. Weisbrod, *X-Ray Spectrom.* 20, 277 1991
136. U. Weisbrod, R. Gutschke, J. Knoth, H. Schwenke, *Fresenius' J. Anal. Chem.* 341, 83, 1991
137. W. Berneike, *Spectrochim. Acta B* 48, 269, 1993
138. H. Schwenke, R. Gutschke, J. Knoth, M. Kock, *Appl. Phys. A* 54, 460, 1992
139. M. Yamagami, M. Nonguchi, T. Yamada, T. Shoji, T. Utaka, S.Y. Mori, Nomura, K. Taniguchi, H. Wakita, S. Ikeda, *X-Ray Spectro.* 26, 451, 1999; *Bunseki Kagaku*, 48, 1005, 1999
140. H. Schwenke, J. Knoth, *Total Reflection XRF in Handbook on X-Ray Spectrometry*, R. van Grieken, A. Markowicz eds., *Practical Spectroscopy Ser. Vol. 14*, Dekker, New York, 1993, p. 453
141. H. Schwenke, L. Frey, S. Pahlke, L. Fabry, *J. Electrochem. Soc.* 144, 3979, 1997
142. R. Klockenkämper, A. von Bohlen, H.W. Becker, L. Palmetshofer, *Surface Interface Anal.*, 27, 1003, 1999
143. R. Klockenkämper, A. von Bohlen, *J. Anal. At. Spectrom.* 14, 571, 1999
144. R. Klockenkämper, A. von Bohlen, *Anal. Commun.* 36, 27, 1999
145. H. Schwenke, J. Knoth, *Handbook on X-Ray Spectrometry*, pp. 453-488, ed.: Van Grieken, Marcel Dekker, New York 1993
146. U. Weisbrod, R. Gutschke, J. Knoth, H. Schwenke, *Fresenius Z. Anal. Chem.* 341, 83, 1991

147. U. Weisbrod, R. Gutschke, J. Knoth, H. Schwenke, *Appl. Phys.* A53, 449, 1991
148. J. Knoth, H. Schwenke, U. Weisbrod, *Spectrochim. Acta* 44B, (5), 477, 1989
149. H. Schwenke, R. Gutschke, J. Knoth, *Adv. X-Ray Anal.* 35, 941 1992
150. J. Knoth, R. Bormann, R. Gutschke, C. Michaelsen, H. Schwenke, *Spectrochim. Acta* 48B, 285 1993
151. H. Schwenke, R. Bormann, J. Knoth, A. Prange, *Spectrochim. Acta* 48B, 293 1993
152. D.K.G. De Boer, W.W. Van Den Hoogenhof, *Adv. X-Ray Anal.* 34, ? 1991
153. D.K.G. De Boer, W.W. Van Den Hoogenhof, *Spectrochim. Acta* 46 B, 1323 1991
154. D.K.G. DeBoer, Leenaers, W.W. VanDenHoogenhof, *Appl. Phys* A58,169, 1994
155. D.K.G. DeBoer, Leenaers, W.W. VanDenHoogenhof, *X-Ray Spectrom.* 24, 91 1995
156. L. Torcheux, B. Degraeve, A. Mayeux, M. Delmar, *SIAJ* 21, 192, 1994
157. Y. Mori, K. Shimanoe, T. Sakon, *Adv. X-ray Chem. Anal. Jpn.* 26s, 69, 1995
158. L. Fabry, S. Pahlke, L. Kotz, Y. Adachi, S. Furukawa, *Adv. X-ray Chem. Anal. Jpn.* 26s, 19, 1995
159. R. Gutschke, Diploma Thesis, University of Hamburg, 1991
160. H. Schwenke, J. Knoth, *Adv. X-ray Chem. Anal. Jpn.* 26s, 137, 1995
161. U. Weisbrod, R. Gutschke, J. Knoth, H. Schwenke, *Appl. Phys. A* 53, 449, 1991
162. H. Schwenke, R. Gutschke, J. Knoth, *Adv. X-Ray Anal.* 35, 941, 1992
163. DKG de Boer, *Spectrochim Acta B* 46, 1433, 1991
DKG de Boer, WW van den Hoogenhof. *Adv. X-ray Anal.* 34, 35, 1991
164. DKG de Boer, WW van den Hoogenhof, *Spectrochim Acta B* 46, 1323, 1991
165. DKG de Boer. *Phys. Rev. B* 44, 498, 1991
166. DKG de Boer, WW van den Hoogenhof, *Adv. X-ray Anal.* 34, 35, 1991
167. WW van den Hoogenhof, DKG de Boer, *Spectrochim. Acta B* 48, 277, 1993
168. K.N. Stoev, K. Sakurai, *Spectrochim. Acta B* 54, 41, 1999
169. Standard Test Method E 45: Test Method for the Determination of Inorganic Contamination form Minienvironments, Semiconductor, Semiconductor Equipment and Materials International, San Jose CA 95134
170. T. Shiraiwa, N. Fujino, S. Sumita, Y. Tanizoe, In: *Semiconductor Fabrication: Technology and Metrology ASTM STP 990*, D.C. Gupta ed., ASTM, 1989, p. 314
171. A. Huber, H.-J. Rath, P. Eichinger, T. Bauer, L. Kotz, R. Staudigl, *Diagnostic Techniques for Semicon Mater and Devices*, T.J. Schaffner, D.K: Schroder eds., The Electrochem. Soc., PV 88-20, 1988, p. 109
172. C. Neumann, P. Eichinger, *Spectrochim. Acta B*, 467, 1369, 1991
173. G. Buhner, *Spectrochim. Acta B*, 54, 1399, 1999
174. A.C. Diebold, P. Maillot M. Gordon J. Baylis, J. Chacon, R. Witowski, H.F. Arlinghaus, J.A. Knapp, B.L. Doyle, *J. Vac. Sci. Technol A*, 10, 2942, 1992
175. S. Metz, G. Kilian, G. Mainka, C. Angelkort, C. Rittmeyer, H. Stelter, A. Fester, B.O. Kolbesen, In: *Crystalline Defects and Contamination*, B.O. Kolbesen, C. Claeys, P. Stallhofer, F. Tardif eds., The Electrochem. Soc., PV 97-22, 1977, p. 458
176. L. Fabry, S. Pahlke, L. Kotz, H. Rüfer, T. Ehmann, K. Bächmann, *Crystalline Defects and Contamination: Their Impact and Control in Device Manufacturing*, 192nd ECS Meeting, Paris, Aug 30–Sep 5, 1997, B.O. Kolbesen, C.L. Claeys, P. Stallhofer, F. Tardif eds., *Proc. Vol. 97-22*, The Electrochemical Society, 1997, pp. 468

177. GeMeTec GmbH, D-81379 München
178. L. Fabry, S. Pahlke, L. Kotz, Fresenius' J. Anal. Chem. 354, 266, 1996
179. H. Kondo, J. Ryuta, E. Morita, T. Yoshimi, Y. Shimanuki, Jpn. J. Appl. Phys., Part 2, 1A/B, 31, L11, 1992
180. G. Tölg, Analyst, 112, 365, 1987
181. H. Yamaguchi, S. Itoh, S. Igarashi, K. Naitoh, R. Hasegawa, Anal. Sci. (Jpn), 14, 909, 1998
182. C. Streli, P. Wobrauschek, V. Bauer, P. Kregsamer, R. Görgl, P. Pianetta, R. Ryon, S. Pahlke, L. Fabry, Spectrochim. Acta 52B(7), 861 (1997)
183. C. Streli, V. Bauer, P. Wobrauschek, Adv. X-ray Anal. Vol. 39, 771–779 (1997)
184. T. Fukuda, T. Shoji, M. Funabashi, T. Utaka, T. Arai, K. Miyazaki, A. Shimazaki, R. Wilson, Adv. X-ray Anal. 39, 781 (1997)
185. <http://www.rigaku.com/Semi-XRF/txrf3750>
186. M. Funabashi, M. Matsuo, N. Kawada, M. Yamagami, R. Wilson, Spectrochim. Acta B543, 1409, 1999
187. [http://www. Gemetec.de](http://www.Gemetec.de)
188. Proceedings of the 8th Conference on TXRF and related Techniques, Vienna, September 2000
189. R.W. Ryon, J.D. Zahrt, Polarized Beam X-ray Fluorescence, Handbook of X-ray Spectrometry, p. 491, Marcel Dekker, New York 1993
190. H. Aiginger, P. Wobrauschek, C. Brauner, Nucl. Instrum. Methods 120, 541, 1974
191. P. Wobrauschek, C. Streli, X-ray and Inner-Shell Processes, Ed. R.L. Johnson, H. Schmidt-Böcking, B. Sonntag, AIP Conference Proceedings 389, 233, 1997
192. D.H. Bilderback, B.M. Lairson, T.W. Barbee Jr., G.E. Ice, C.J. Sparks Jr., Nucl. Instrum. Methods 208, 251, 1983
193. P. Pianetta, T. Barbee, Nucl. Instrum. Methods A266, 441 1988
194. R. Rieder, P. Wobrauschek, W. Ladisich, C. Streli, H. Aiginger, S. Garbe, G. Gaul, A. Knöchel, F. Lechtenberg, Nucl. Instrum. Methods 355(2,3), 648, 1995
195. P. Wobrauschek, P. Kregsamer, W. Ladisich, R. Rieder, C. Streli, Adv. X-ray Anal. 39, 755 1997
196. R. Görgl, P. Wobrauschek, P. Kregsamer, C. Streli, M. Haller, A. Knöchel, M. Radtke, X-ray Spectrometry 26(4), 189, 1997
197. M. Madden, D. Wherry, P. Pianetta, S. Brennan, Mat. Res. Soc. Symp. Proc. 307, 125, 1993
198. C. Streli, P. Wobrauschek, W. Ladisich, R. Rieder, H. Aiginger, R. Ryon, P. Pianetta, Nucl. Instr. Meth. A345, 399 1994
199. C. Streli, P. Wobrauschek, V. Bauer, P. Kregsamer, R. Görgl, P. Pianetta, R. Ryon, S. Pahlke, L. Fabry, Spectrochim. Acta. 52B (7), 861, 1997
200. C. Streli, P. Kregsamer, P. Wobrauschek, Gatterbauer, P. Pianetta, S. Pahlke, L. Fabry, Palmethofer, Schmeling, Spectrochim. Acta 54B,(10), 1433, 1999
201. C. Streli, P. Wobrauschek, P. Kregsamer, G. Pepponi, P. Pianetta, S. Pahlke, L. Fabry, Spectrochim. Acta 56B, 2085–2094 2001
202. B. Beckhoff, R. Fliegau, G. Ulm, G. Pepponi, C. Streli, P. Wobrauschek, L. Fabry, S. Pahlke, Spectrochim. Acta B 56, 2073–2083, 2001
203. S. Brennan, W. Tompkins, N. Takaura, P. Pianetta, S.S. Laderman, A. Fischer-Colbrie, J.B. Kortright, M.C. Madden, D.C. Wherry, Nucl. Instrum. Methods 347, 417, 1994

204. S.S. Laderman, A. Fischer-Colbrie, A. Shimazaki, K. Miyazaki, S. Brennan, N. Takaura, P. Pianetta, J.B. Kortright, *Anal. Sci.* **11**, 515, 1995
205. P. Pianetta, N. Takaura, S. Brennan, W. Tompkins, S.S. Laderman, A. Fischer-Colbrie, A. Shimazaki, K. Miyazaki, M. Madden, D.C. Wherry, J.B. Kortright, *Rev. Sci. Instrum.* **66**, 1293 1995
206. A. Singh, K. Baur, S. Brennan, T. Homma, N. Kubo, P. Pianetta, *Proc. Mat. Res. Soc.* (in press)
207. H. Winick, S. Doniach, *Synchrotron Radiation Research*, Plenum, New York 1979
208. N. Takaura, S. Brennan, P. Pianetta, S.S. Laderman, A. Fischer-Colbrie, J.B. Kortright, D.C. Wherry, K. Miyazaki, A. Shimazaki, *Adv. X-ray Chem. Anal.* **26s**, 113, 1995
209. J. Wang, M.K. Balazs, P. Pianetta, K. Baur, S. Brennan, T. Bonne, J.M. Rosamilia, *Semiconductor Fabtech - 16th edn* (in press)
210. A. Bianconi in *X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES*, edited by D.C. Koningsberger, R. Prins (Wiley, New York) 618–624, 1988
211. T. Homma, W. Chidsey, *J. Phys. Chem.* **B102**, 7919, 1998
212. K. Baur, J. Kerner, S. Brennan, A. Singh, P. Pianetta, *J. Appl. Phys.* **88**, 4642, 2000
213. K. Baur, Brennan, B. Burrow, D. Werho, P. Pianetta, *Spectrochim. Acta B* **56**, 2049, 2001
214. L. Ortega, F. Comin, V. Formoso, A. Stierle, *J. Synchr. Radat.* **5**, 1064–1066, 1998
215. B. Beckhoff, R. Klein, M. Krumrey, F. Scholze, R. Thornagel, G. Ulm, *Nucl. Instrum. Meth. A* **444**, 480–483, 2000
216. F. Senf, F. Eggenstein, U. Flechsig, W. Gudat, R. Klein, H. Rabus, G. Ulm, *J. Synchr. Rad.* **5**, 780–782, 1998
217. C. Streli, P. Wobrauschek, B. Beckhoff, G. Ulm, L. Fabry, S. Pahlke, *X-Ray Spectrom.* **30**, 24–31, 2001
218. B. Beckhoff, R. Fliegauf, G. Ulm, J. Weser, G. Pepponi, C. Streli, P. Wobrauschek, Th. Ehmann, L. Fabry, C. Mantler, S. Pahlke, B. Kanngießer, W. Malzer, *Electrochemical Society*, In: *Proc. 'Analytical and Diagnostic Techniques for Semiconductor Materials, Devices, and Processes'* 2003-03, 120–128, 2003
219. F. Scholze, M. Procop, *X-Ray Spectr.* **30**, 24–31 (2004)
220. B. Beckhoff, R. Fliegauf, G. Ulm, *Spectrochim. Acta Part B* **58**, 615–626, 2003
221. S. Bechstein, B. Beckhoff, R. Fliegauf, J. Weser, G. Ulm, *Spectrochim. Acta Part B* **59**, 215–221, 2004
222. C. Streli, G. Pepponi, P. Wobrauschek, B. Beckhoff, G. Ulm, S. Pahlke, L. Fabry, Th. Ehmann, B. Kanngießer, W. Malzer, W. Jark, *Spectrochim. Acta B* **58**, 2113–2121, 2003
223. G. Pepponi, B. Beckhoff, T. Ehmann, G. Ulm, C. Streli, L. Fabry, S. Pahlke, P. Wobrauschek, *Spectrochim. Acta B* **58**, 2245–2253, 2003
224. S. Török, J. Osán, B. Beckhoff, G. Ulm, *J. Diffraction J.* **19**, 81–86, 2004
225. M. Kolbe, B. Beckhoff, M. Krumrey, G. Ulm, *Spectrochim. Acta Part B* **60**, 505–510, 2005
226. N. Broll and R. Tertian, *X-Ray Spectrom.* **12**, 1983, 30
227. P.M. Van Dyck, S. Török, and R. Van Grieken, *Anal. Chem.* **58**, 1986, 1761

228. E.P. Bertin, "Principles and Practice of X-ray Spectrometric Analysis," Plenum, New York, 1970
229. R. Jenkins, R.W. Gould, and D. Gedcke, "Quantitative X-Ray Spectrometry," Marcel Dekker, New York, 1981
230. H.H. Behncke, Metal Finishing **83**, 1984, 33
231. F. Ferrandino, Metal Finishing **85**, 1986, 29
232. R. Shan and A. Sandberg, "Advances in X-ray Analysis" vol. 26, Plenum, New York, 1983
233. C. Colliex, Proc. 8th European Congress on Electron Microscopy 1984, 57
234. T.B. Pierce, J. Trace Microprobe Techn. 2, 1984, 85, 291
235. L. Palmetschöfer, in "Surface and Thin Film Analysis," Wiley-VCH, Weinheim, 2002
236. Product of Helmut-Fischer GmbH + Co. KG, Sindelfingen, Germany
237. D.K.G. de Boer, X-Ray Spectrom. **19**, 1990, 145
238. P. Van Espen and K. Janssens, "Spectrum Evaluation," Chap. 4 of the "Handbook of X-ray Spectrometry," (R. Van Grieken, A. Marcowicz, eds.), Marcel Dekker, New York, 1992
239. W.H. Press, S.A. Teukolski, W.T. Vetterling, and B.P. Flannery, "Numerical Recipes in C," Cambridge University Press, 1992
240. V. Rößiger and K.-H. Kaiser, in "Jahrbuch Oberflächentechnik 1998," Metall Verlag Heidelberg 1998, p. 313
241. Fischer Application Report vr9605
242. Fischer Application Report vr0227
243. V. Rößiger, Galvanotechnik **92**, 2001, 8, 2070
244. B.N. Taylor and C.E. Kuyatt, NIST Technical Note 1297, 1994 Edition (Supersedes 1993 Edition)
245. DIN 1319, Part 3, Grundbegriffe der Messtechnik
246. DIN 55350-13, "Begriffe zur Genauigkeit von Ermittlungsverfahren und Ermittlungsergebnissen"
247. L.B. Barrentine, "Concepts for R&R Studies," ASQ Quality Press, 2003
248. K. Weise and W. Wöger, "Messunsicherheit und Messdatenauswertung," Wiley-VCH, Weinheim 1999
249. Fischer Application Report vr0103
250. Fischer Application Report vr0213
251. P. Neumaier, QZ **48**, 2003, 5
252. R. Jansen and P. Preischkat, Metalloberfläche München **56**, 2002, 4, 26
253. P. Hülser, Metalloberfläche München **57**, 2003, 7–8, 18
254. V. Rößiger, JOT, 2002, Issue 7, 62
255. D. Stöckert, Stahl, 2002, Issue 6, 70
256. F. Simon u. U. Manz, Galvanotechnik **94**, 2003, 2169
257. H. Kaiser (Hrsg.) "Edelmetallschichten," Leuze Verlag, Bad Saulgau 2002, 47
258. Fischer Application Report vr0223
259. P. Wingenfeld, Galvanotechnik **94**, 2003, 11, 2664
260. Fischer Application Report vr0304
261. V. Rößiger and M. Haller, Metal finishing ...
262. V. Rößiger, Metalloberfläche München **53**, 1999, 4
263. N. Kallithrakas-Kontos, X-Ray Spectrom. **33**, 2004, 12
264. Van Espen P, Nullens H, Adams F (1977) Method for accurate description of full energy peaks in nonlinear least-square analysis of X-ray spectra. Nucl Instrum Methods 145:579–582

265. Van Espen P, Janssens K, Nobels J (1986) AXIL-PC, software for the analysis of complex X-ray spectra. *Chemom Intell Lab Syst* 1:109–114
266. Johansson TB, Akselsson KR, Johansson SAE (1970) X-ray analysis: elemental trace analysis at the 10^{-12} g level. *Nucl Instrum Methods* 84:141–143
267. Injuk J, Van Grieken R (2003) Literature trends in X-ray emission spectrometry in the pe-riod 1990–2000 – a review. *X-Ray Spectrom* 32:35–39
268. Török SB, Lábár J, Schmeling M, Van Grieken RE (1998) X-Ray Spectrometry. (review) *Anal Chem* 70:495R–517R
269. Szalóki I, Török SB, Ro CU, Injuk J, Van Grieken RE (2000) X-ray Spectrometry. (review) *Anal Chem* 72:211R–233R
270. Szalóki I, Török SB, Injuk J, Van Grieken RE (2002) X-ray spectrometry. (review) *Anal Chem* 74:2895–2918
271. Potts PJ, Andrew TE, Kregsamer P, Marshall J, Streli C, West M, Wobrauschek P (2002) Atomic spectrometry update. X-ray spectrometry. *J Anal At Spectrom* 17:1439–1455
272. Potts PJ, Andrew TE, Kregsamer P, Marshall J, Streli C, West M, Wobrauschek P (2003) Atomic spectrometry update. X-ray spectrometry. *J Anal At Spectrom* 18:1297–1316
273. Tölg G, Klockenkämper R (1993) The role of total-reflection X-ray fluorescence in atomic spectroscopy. *Spectrochim Acta* 48B:111–127
274. Potts PJ, Webb PC (1992) X-ray-fluorescence spectrometry. (review) *J Geochem Explor* 44:251–296
275. Stumm W, Morgan JJ (1996) *Aquatic Chemistry*. Wiley, New York
276. Salbu B, Steinnes E (1995) *Trace elements in Natural Waters*. CRC Press, Boca Raton
277. Chapelle FH (2001) *Ground-Water Microbiology and Geochemistry*. Wiley, New York
278. Horowitz AJ, Lum KR, Garbarino JR, Hall GEM, Lemieux C, Demas CR (1996) Problems associated with using filtration to define dissolved trace element concentrations in natural water samples. *Environ Sci Technol* 30:954–963
279. Nozaki Y (1997) A Fresh Look at Element Distribution in the North Pacific, Eos, Transactions, American Geophysical Union, Electronic Supplement, <http://www.agu.org/eos.elecas97025e.html> [Posted May 27 1997]
280. Livingstone DA (1963) Chemical composition of rivers and lakes. In *Data of Geochemistry: U.S. Geol. Survey Prof.* (ed. M. Fleischer), paper 440, pp. G1–G64
281. Reimann C, Caritat CD, Halleraker JH, Volden T, Äyräs M, Niskavaara H, Chekushin VA, Pavlov VA (1997) Rainwater composition in eight arctic catchments in Northern Europe (Finland, Norway and Russia). *Atmos Environ* 31:159–170
282. Lacey RF, Shaper AG (1984) Changes in water hardness and cardiovascular death rates. *Int J Epidemiol* 13:18–24
283. Camel V (2003) Solid phase extraction of trace elements. *Spectrochim Acta* 58B:1177–1233
284. Benoit G (1994) Clean technique measurement of Pb, Ag, and Cd in freshwater: A redefinition of metal pollution. *Environ Sci Technol* 28:1987–1991
285. Bowman HR, Hyde EK, Thompson SG, Jared RC (1966) Application of high-resolution semiconductor detectors in X-ray emission spectrography. *Science* 151:562–568

286. Luke CL (1968) Determination of trace elements in inorganic and organic materials by X-ray fluorescence spectroscopy. *Anal Chim Acta* 41:237–250
287. Kinrade JD, Van Loom JC (1974) Solvent extraction for use with flame atomic absorption spectrometry. *Anal Chem* 46:1894–1898
288. Schwarzenbach G (1960) Relationships between metal complex stability and structure of complexing agents. *Anal Chem* 32:6–9
289. Green TE, Law SL, Campbell WJ (1970) Use of selective ion exchange paper in X-ray spectrography and neutron activation. Application to the determination of gold. *Anal Chem* 42:1749–1753
290. Vassos BH, Hirsch RF, Letterman H (1973) X-ray microdetermination of chromium, cobalt, copper, mercury, nickel and zinc in water using electrochemical preconcentration. *Anal Chem* 45:792–794
291. Van Grieken R (1982) Preconcentration methods for the analysis of water by x-ray spectrometric techniques. *Anal Chim Acta* 143:3–34
292. Tissue T, Seils C, Keel RT (1985) Preconcentration of subnanogram amounts of metals from natural-waters for X-ray-energy spectrometric determination using pyrrolidinecarbodithioic acid. *Anal Chem* 57:82–87
293. Ellis AT, Leyden DE, Wegscheider W, Jablonski BB, Bodnar WB (1982) Preconcentration methods for the determination of trace elements in water by X-ray-fluorescence spectrometry. 1. Response characteristics. *Anal Chim Acta* 142:73–87
294. Alvarez MA, Alvarez JR, Alvarez RP (2000) Heavy metal analysis of rainwaters by nuclear related techniques: Application of APDC precipitation and energy dispersive X-ray fluorescence. *J Radioanal Nucl Chem* 245:485–489
295. Clanet F, Deloncle R, Popoff G (1981) Chelating resin catcher for capture, preconcentration and determination of toxic metal traces (Zn, Cd, Hg, Pb) in waters. *Water Res* 15:591–598
296. Braun T, Abbas MN, Török Sz, Szokefalvi-Nagy Z (1984) Radioisotope-induced X-ray fluorescence determination of phenylmercury, methylmercury and inorganic mercury in water after preconcentration on diethylammonium diethyldithiocarbamate-loaded polyurethane foam discs. *Anal Chim Acta* 160:277–282
297. Török Sz, Braun T, Dyck PV, Grieken RV (1986) Heterogeneity effects in direct XRF analysis of traces of heavy metals preconcentrated on polyurethane foam sorbents. *X-Ray Spectrom* 15:7–11
298. Hou XD, Peters HL, Yang Z, Wagner KA, Batchelor JD, Daniel MM, Jones BT (2003) Determination of trace metals in drinking water using solid-phase extraction disks and X-ray fluorescence spectrometry. *Appl Spectro* 53:338–342
299. Tertian R, Claisse F (1982) *Principles of Quantitative X-Ray Spectrometry*. Heyden, London
300. Rastegar B, Jundt F, Gallmann A, Rastegar F, Leroy MJF (1986) Sample homogeneity in energy-dispersive XRF trace-metal analysis. *X-Ray Spectrom* 15:83–86
301. Meltzer C, King BS (1991) Trace element analysis of solutions at the ppb level. *Adv X-ray Anal* 34:41–55
302. Fenkart K, Eng E, Frey U (1978) Determination of elements in waste-water by X-ray fluorescence analysis – sample preparation and matrix correction method. *Fresenius Z Anal Chem* 293:364–369

303. Gao N, Ponomarev IY, Xiao QF, Gibson WM, Carpenter DA (1997) Enhancement of microbeam X-ray fluorescence analysis using monolithic polycapillary focusing optics. *Appl Phys Lett* 71:3441–3443
304. Nielson AJ, Turner DC, Wilson AW, Wherry DC, Wong R (1995) An order of magnitude improvement in detection limits achieved by using a new sample support in small spot XRF analysis. *Adv X-Ray Anal* 39:799–804
305. Wilson AW, Turner DC, Robbins AA (1997) Improvements in sample support films for microsample X-ray analysis. *Adv X-ray Anal* 41:301–307
306. Hettipathirana TD (2001) Speciation of sub-parts per billion levels of Cr(III) in waters by solid-phase adsorption followed by thin-layer X-ray fluorescence spectrometry. *X-Ray Spectrom* 30:330–337
307. Edwards T, Ferrier B, Harriman R (1993) Preliminary investigation on the use of ion-exchange resins for monitoring river water composition. *Sci Total Environ* 135:27–36
308. Allen B, Sackett D, Parsons C, Shefsky S (1997) On-site analysis of metals in liquids using portable X-ray fluorescence. *Field Anal. Methods Hazard. Wastes Toxic Chem., Proc. Spec. Conf., Air and Waste Management Assoc.* Pittsburgh, PA, USA, pp. 838–841
309. Gharaibeh SH, Abu-El-Sha'r WY, Al-Kofahi MM (1998) Removal of selected heavy metals from aqueous solutions using processed solid residue of olive mill products. *Water Res* 32:498–502
310. Streli C, Aiginger H, Wobrauschek P (1993) Light-element analysis with a new spectrometer for total-reflection X-ray fluorescence. *Spectrochim Acta* 48B:163–170
311. Klockenkämper R (1997) *Total-Reflection X-ray Fluorescence Analysis*. Wiley, New York
312. Wegrzynek D, Holynska B, Ostachowicz B (1998) A comparison of the performance of a fundamental parameter method for analysis of total reflection X-ray fluorescence spectra and determination of trace elements, versus an empirical quantification procedure. *Spectrochim Acta* 53B:43–48
313. Yap CT (1988) X-ray total reflection fluorescence analysis of iron, copper, zinc, and bromine in human-serum. *Appl Spectrosc* 42:1250–1253
314. de Boer DKG (1991) X-ray standing waves and the critical sample thickness for total-reflection X-ray fluorescence analysis. *Spectrochim Acta* 46B:1433–1436
315. Klockenkämper R, von Bohlen A (1989) Determination of the critical thickness and the sensitivity for thin-film analysis by total reflection X-ray fluorescence spectrometry. *Spectrochim Acta* 44B:461–469
316. Knoth J, Schwenke H (1978) X-ray-fluorescence spectrometer with totally reflecting sample support for trace analysis at ppb level. *Fresenius Z Anal Chem* 291:200–204
317. Holyńska B, Olko M, Ostachowicz B, Ostachowicz J, Wegrzynek D, Claes M, Van Grieken R, de Bokx P, Kump P, Necemer M (1998) Performance of total reflection and grazing emission X-ray fluorescence spectrometry for the determination of trace metals in drinking water in relation to other analytical techniques. *Fresenius J Anal Chem* 362:294–298
318. Barreiros MA, Carvalho ML, Costa MM, Marques MI, Ramos MT (1997) Application of total reflection XRF to elemental studies of drinking water. *X-Ray Spectrom.* 26:165–168

319. Holyńska B, Ostachowicz B, Wegrzynek D (1996) Simple method of determination of copper, mercury and lead in potable water with preliminary pre-concentration by total reflection X-ray fluorescence spectrometry. *Spectrochim Acta* 51B:769–773
320. Kump P, Necemer M, Veber M (1997) Determination of trace elements in mineral water using total reflection X-ray fluorescence spectrometry after pre-concentration with ammonium pyrrolidinedithiocarbamate. *X-Ray Spectrom* 26:232–236
321. Prange A, Knöchel A, Michaelis W (1985) Multi-element determination of dissolved heavy metal traces in sea water by total-reflection x-ray fluorescence spectrometry. *Anal Chim Acta* 172:79–100
322. Prange A, Kremling K (1985) Distribution of dissolved molybdenum, uranium and vanadium in Baltic Sea waters. *Mar Chem* 16:259–274
323. Schmidt D, Gerwinski W, Radke I (1993) Trace metal determinations by total-reflection X-ray fluorescence analysis in the open Atlantic Ocean. *Spectrochim Acta* 48B:171–181
324. Menegario AA, Pellegrinotti DC, Gine MF, Filho VFN (2003) On-line preconcentration flow system for multi-elemental analysis by total-reflection X-ray fluorescence spectrometry. *Spectrochim Acta* 58B:543–549
325. Gerwinski W, Schmidt D (2001) Automated solid-phase extraction for trace metal analysis of sea water: sample preparation for total-reflection X-ray fluorescence measurements. *Spectrochim Acta* 53B:1355–1364
326. Griesel S, Reus U, Prange A (2001) Electro-deposition as a sample preparation technique for total-reflection X-ray fluorescence analysis. *Spectrochim Acta* 56B:2107–2115
327. Lofthouse SD, Greenway GM, Stephen SC (1998) Comparison of inductively coupled plasma mass spectrometry with a microconcentric nebuliser and total reflection X-ray spectrometry for the analysis of small liquid volume samples. *J Anal At Spectrom* 13:1333–1335
328. Aster B, von Bohlen A, Burba P (1997) Determination of metals and their species in aquatic humic substances by using total-reflection X-ray fluorescence spectrometry. *Spectrochim Acta* 52B:1009–1018
329. Figura P, McDuffie G (1980) Determination of labilities of soluble trace-metal species in aqueous environmental samples by anodic-stripping voltammetry and chelex column and batch methods. *Anal Chem* 52:1433–1439
330. Alvarez MB, Malla ME, Batistoni DA (2004) Performance evaluation of two chelating ion-exchange sorbents for the fractionation of labile and inert metal species from aquatic media. *Anal Bioanal Chem* 378:438–446
331. Görgl R, Wobrauschek P, Kregsamer P, Streli C, Haller M, Knöchel A, Radtke M (1997) Total reflection X-ray fluorescence analysis excited by synchrotron radiation (SR-TXRF): Variation of excitation conditions and sample geometries. *X-Ray Spectrom* 26:189–194
332. Streli C, Wobrauschek P, Kregsamer P, Pepponi G, Pianetta P, Pahlke S, Fabry L (2001) Synchrotron radiation induced total reflection X-ray fluorescence of low Z elements on Si wafer surfaces at SSRL - comparison of excitation geometries and conditions. *Spectrochim Acta* 56B:2085–2094
333. Pepponi G, Streli C, Wobrauschek P, Zamini S, Zoger N, Falkenberg G (2003) Comparison of synchrotron radiation total reflection X-ray fluorescence excitation-detection geometries for samples with differing matrices. *Spectrochim Acta B* 58:2139–2144

334. Strelcić C (1997) Total reflection X-ray fluorescence analysis of light elements. *Spectrochim Acta* 52B:281–293
335. Sakurai K, Eba H, Inoue K, Yagi N (2001) Downsizing of Johansson spectrometer for X-ray fluorescence trace analysis with brilliant undulator source. *Nucl Instrum Methods Phys Res* 467-468A:1549–1552
336. Sakurai K, Eba H, Inoue K, Yagi N (2002) Wavelength-dispersive total-reflection X-ray fluorescence with an efficient Johansson spectrometer and an undulator X-ray source: detection of 10-16g-level trace metals. *Anal Chem* 74:4532–4535
337. Kurunczi S, Sakurai K (2005) Natural Water Specimen Preparation for TXRF analysis, using a Johansson wavelength-dispersive spectrometer. *X-Ray Spectrom* 34:56–58
338. Angloher G, Beckhoff B, Bühler M, Feilitzsch Fv, Hertrich T, Hettl P, Höhne J, Huber M, Jochum J, Mößbauer RL, Schnagl J, Scholze F, Ulm G (2000) Development of superconducting tunnel junction detectors for high resolution X-ray spectroscopy. *Nucl Instrum Methods Phys Res* 444A:214–219
339. Veldkamp M, Beckhoff B, Fliegauf R, Ulm G, Frank M, Friedrich S, Labov SE (2002) Characterisation of superconducting tunnel junction X-ray detectors by means of monochromatized undulator radiation. *Nucl Instrum Methods Phys Res* 487A:450–456
340. Hopke PK (1988) Target transformation factor analysis as an aerosol mass apportionment method – a review and sensitivity study. *Atmos Environ* 22:1777–1792
341. Balásházy I, Heistracher T, Hofmann W (1996) Air flow and particle deposition patterns in bronchial airway bifurcations: The effect of different CFD models and bifurcation geometries. *J Aerosol Med* 9:287–301
342. Götz G, Mészáros E, Vali G (1991) *Atmospheric Particles and Nuclei*. Akadémiai Kiadó, Budapest
343. Directive (1999) Council Directive 1999/30/EC of 22 April 1999 relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air. *Official Journal of the European Communities* L163(29/06/1999):0041–0060
344. Howell S, Pszenny AAP, Quinn P, Huebert B (1998) A field intercomparison of three cascade impactors. *Aerosol Sci Technol* 29:475–492
345. Jenkins R, Gould RW, Gedcke D (1981) *Quantitative X-ray Spectrometry*. Marcel Dekker, New York
346. Samek L, Injuk J, Van Espen P, Van Grieken R (2002) Performance of a new compact EDXRF spectrometer for aerosol analysis. *X-Ray Spectrom* 31:84–86
347. Lodge JP, ed (1989) *Methods of air sampling and analysis*, 3rd Edn, Lewis Publishers, Chelsea, MI, USA
348. Holynska B, Ptasinski J, Maenhaut W, Annegarn HJ (1997) Energy-dispersive x-ray fluorescence spectrometer with capillary optics for the chemical analysis of atmospheric aerosols with high time resolution. *J Aerosol Sci* 28:1455–1463
349. Kucera J, Smodiš B, Burns K, De Regge P, Campbell M, Havránek V, Makarewicz M, Toerwenyi A, Zeiller E (2001) Preparation and characterization of a set of IAEA reference air filters for quality control in air-pollution studies. *Fresenius J Anal Chem* 370:229–233
350. Osán J, Alföldy B, Kurunczi S, Török S, Bozó L, Injuk J, Worobiec A, Van Grieken R (2001) Characterization of atmospheric aerosol particles over Lake Balaton, Hungary, using X-ray emission methods. *Időjárás* 105:145–156

351. Borbély-Kiss I, Koltay E, Szabó Gy, Bozó L, Tar K (1999) Composition and sources of urban and rural atmospheric aerosol in Eastern Hungary. *J Aerosol Sci* 30:369–391
352. Hlavay J, Polyák K, Weisz M (2001) Monitoring of the natural environment by chemical speciation of elements in aerosol and sediment samples. *J Environ Monit* 3:74–80
353. Klockenkämper R, Bayer H, von Bohlen A, Schmeling M, Klockow D (1995) Collection of airborne particulate matter for a subsequent analysis by total reflection X-ray fluorescence. *Anal Sci* 11:495–498
354. Salvà A, von Bohlen A, Klockenkämper R, Klockow D (1993) Multielement analysis of airborne particulate matter by total reflection X-ray fluorescence. *Quim Anal* 12:57–62
355. Schmeling M (2001) Total-reflection X-ray fluorescence – a tool to obtain information about different air masses and air pollution. *Spectrochim Acta* 56B:2127–2136
356. Schmeling M (2003) Seasonal variations in diurnal concentrations of trace elements in atmospheric aerosols in Chicago. *Anal Chim Acta* 496:315–323
357. Schneider B (1989) The determination of atmospheric trace metal concentrations by collection of aerosol particles on sample holders for total-reflection X-ray fluorescence. *Spectrochim Acta* 44B:519–523
358. Injuk J, Van Grieken R (1995) Optimisation of total-reflection X-ray fluorescence for aerosol analysis. *Spectrochim. Acta* 50B:1787–1803
359. Esaka F, Watanabe K, Onodera T, Taguchi T, Magara M, Usuda S (2003) The use of Si carriers for aerosol particle collection and subsequent elemental analysis by total-reflection X-ray fluorescence spectrometry. *Spectrochim Acta* 58B:2145–2155
360. Török S, Osán J, Beckhoff B, Ulm G (2004) Ultra-trace speciation of nitrogen compounds in aerosols collected on silicon wafer surfaces by means of TXRF-NEXAFS. *Powder Diffr* 19:81–86
361. Osán J, Szalóki I, Ro CU, Van Grieken R (2000) Light element analysis of individual microparticles using thin-window EPMA. *Mikrochim Acta* 132:349–355
362. Ro CU, Osán J, Szalóki I, de Hoog J, Worobiec A, Van Grieken R (2003) A Monte Carlo program for quantitative electron-induced X-ray analysis of individual particles. *Anal Chem* 75:851–859
363. Jones KW, Gordon BM (1989) Trace-element determinations with synchrotron-induced X-ray emission. *Anal Chem* 61:341A–358
364. Török S, Sándor S, Xhoffer C, Van Grieken R, Jones KW, Sutton SR, Rivers ML (1992) X-ray microprobe studies of Hungarian background and urban aerosols. *Adv X-ray Anal* 35:1183–1188
365. Van Malderen H, Hoornaert S, Injuk J, Przybylowicz WJ, Pineda CA, Prozesky VM, Van Grieken R (2001) Individual particle characterization of Siberian aerosols by micro-PIXE and backscattering spectrometry. *X-Ray Spectrom* 30:320–329
366. Markowicz AA, Van Grieken RE (2002) Quantification in XRF analysis of intermediate-thickness samples. In: Van Gieken RE, Markowicz AA (eds) *Handbook on X-ray spectrometry*. Marcel Dekker, New York, pp. 407–432
367. Armstrong JT, Buseck PR (1985) A general characteristic fluorescence correction for the quantitative electron microbeam analysis of thick specimens, thin films and particles. *X-Ray Spectrom* 14:172–182

368. Rindby A, Voglis P, Attaelmanan A (1996) Analysis of inhomogeneous and irregularly shaped samples by the use of XRF micro-beam correlation analysis. *X-Ray Spectrom* 25:39–50
369. Vincze L, Somogyi A, Osán J, Vekemans B, Török S, Janssens K, Adams F (2002) Quantitative trace-element analysis of individual fly-ash particles by means of micro-XRF. *Anal Chem* 74:1128–1135
370. Vincze L, Janssens K, Adams F (1993) A general Monte Carlo simulation of energy-dispersive X-ray fluorescence spectrometers 1. Unpolarized radiation, homogeneous samples. *Spectrochim Acta* 48B:553–573
371. Vincze L, Janssens K, Rivers ML, Jones KW, Adams F (1995) A general Monte Carlo simulation of ED-XRF spectrometers. II: Polarized monochromatic radiation, homogeneous samples. *Spectrochim Acta* 50B:127–147
372. Vincze L, Janssens K, Vekemans B, Adams F (1999b) Modeling of photon scattering at high X-ray energies: experiment versus simulation. *J Anal At Spectrom* 14:529–533.
373. Hovington P, Drouin D, Gauvin R (1997) CASINO: A new Monte Carlo code in C language for electron beam interaction – Part I: Description of the program. *Scanning* 19:1–14
374. Ro CU, Osán J, Van Grieken R (1999) Determination of low-Z elements in individual environmental particles using windowless EPMA. *Anal Chem* 71:1521–1528
375. Kirkpatrick P, Weidmann L (1945) Theoretical continuous X-ray energy and polarization. *Phys Rev* 67:321–339
376. Török S, Osán J, Vincze L, Alföldy B, Kerkápoly A, Vajda N, Pérez CA, Falkenberg G (2003) Comparison of nuclear and X-ray techniques for actinide analysis of environmental hot particles. *J Anal At Spectrom* 18:1202–1209
377. Vekemans B, Janssens K, Vincze L, Adams F, Van Espen P (1994) Analysis of X-ray spectra by iterative least squares (AXIL): New developments. *X-Ray Spectrom* 23:278–285
378. Vincze L, Janssens K, Vekemans B, Adams F (1999a) Monte Carlo simulation of X-ray fluorescence spectra: Part 4. Photon scattering at high X-ray energies. *Spectrochim Acta* 54B:1711–1722
379. Török S, Osán J, Vincze L, Kurunczi S, Tamborini G, Betti M (2004b) Characterization and speciation of depleted uranium in individual soil particles using microanalytical methods. *Spectrochim Acta Part B* 59:689–699
380. Osán J, Török S, Alföldy B, Falkenberg G (2004) Characterization of anthropogenic sediment particles after a transboundary water pollution of River Tisza using synchrotron radiation. *Spectrochim Acta* 59B:701–708
381. Danesi PR, Markowicz A, Chinea-Cano E, Burkart W, Salbu B, Donohue D, Ruedenauer F, Hedberg M, Vogt S, Zahradnik P, Ciurapinski A (2003) Depleted uranium particles in selected Kosovo samples. *J Environ Radioact* 64:143–154
382. Osán J, Kurunczi S, Török S, Van Grieken R (2002) X-ray analysis of river-bank sediment of the Tisza (Hungary): identification of particles from a mine pollution event. *Spectrochim Acta* 57B:413–422
383. Duff MC, Hunter DB, Tray IR, Bertsch PM, Reed DT, Sutton SR, Shea-McCarthy G, Kit-ten J, Eng P, Chipera SJ, Vaniman DT (1999) Mineral associations and average oxidation states of sorbed Pu on Tuff. *Environ Sci Technol* 33:2163–2169

384. Bertsch PM, Hunter DB, Sutton SR, Bajt S, Rivers ML (1994) In situ chemical speciation of uranium in soils and sediments by micro X-ray absorption spectroscopy. *Environ Sci Technol* 28:980–984
385. Tokunaga TK, Brown GE, Pickering IJ, Sutton SR, Bajt S (1997) Selenium redox reactions and transport between ponded waters and sediments. *Environ Sci Technol* 31:1419–1425
386. Schoonover JR, Havrilla GJ (1999) Combining X-ray fluorescence spectrometry and vibrational microscopy to assess highly heterogeneous actinide-contaminated materials. *Appl Spectrosc* 53:257–265
387. Ice GE (1997) Microbeam-forming methods for synchrotron radiation. *X-Ray Spectrom* 26:315–326
388. Pella PA, Lankosz M (1997) Highlights of X-ray spectrometry for microanalysis. *X-ray Spectrom* 26:327–332
389. Vekemans B, Janssens K, Vincze L, Aerts A, Adams F, Herogen J (1997) Automated segmentation of mu-XRF image sets. *X-Ray Spectrom* 26:333–346
390. Lankosz M, Pella PA (1997) A new approach to quantitative X-ray microfluorescence analysis of individual particles. *X-Ray Spectrom* 26:347–349
391. Jones KW, Berry WJ, Borsay DJ, Cline HT, Connor WC, Fullmer CS (1997) Applications of synchrotron radiation-induced X-ray emission (SRIXE). *X-Ray Spectrom* 26:350–358
392. Iida A (1997) X-ray spectrometric applications of a synchrotron X-ray microbeam. *X-Ray Spectrom* 26:359–363
393. Havrilla GJ (1997) Applications of X-ray microfluorescence to materials analysis. *X-Ray Spectrom* 26:364–373
394. Ding X, He Y, Yan Y (1997) X-ray source for x-ray microfluorescence using a monolithic X-ray focusing lens combined with aperture optics. *X-Ray Spectrom* 26:374–379
395. Hosokawa Y, Ozawa S, Nakazawa H, Nakayama Y (1997) An X-ray guide tube and a desk-top scanning X-ray analytical microscope. *X-Ray Spectrom* 26:380–387
396. Worley CG, Havrilla GJ, Dunn PS (2001) Quantification of large scale micro-X-ray fluorescence elemental images. *Appl Spectrosc* 55:1448–1454
397. Le Maitre RW (ed.), Streckeisen A, Zanettin B, Le Bas MJ, Bonin B, Bateman P, Bellieni G, Dudek A, Efremova S, Keller J, Lameyre J, Sabine PA, Schmid R, Sorensen H, Woolley AR (2002) *Igneous rocks; a classification and glossary of terms; recommendations of the International Union of Geological Sciences Subcommission on the Systematics of Igneous Rocks*. 2nd ed Cambridge University Press, Cambridge, United Kingdom, p 236
398. Pearce JA (1987) An expert system for the tectonic characterization of ancient volcanic rocks. *Journ Volc Geotherm Res*, 32, 51–65
399. Wells N, Smidt RE (1978) Methods for mineral and element analysis. New Zealand Soil Bureau, Sci Rep 10D, 12
400. Hutton JT, Elliott SM (1980) An accurate XRF method for the analysis of geochemical exploration samples for major and trace elements using one glass disc. *Chem Geol*. 29:1–11
401. Bertin (1975) *Principles and Practice of X-Ray Spectrometric Analysis*. 2nd edn Plenum Press, New York, London, pp 1079
402. Lachance GR (1993) X-Ray Fluorescence Spectrometry. In: Hyman M, Rowe MW (eds), *Adv Anal Geochem* 1:155–192

403. Hahn-Weinheimer P, Hirner A, Weber-Diefenbach K (1995) Röntgenfluoreszenzanalytische Methoden . Grundlagen und praktische Anwendung in den Geo-, Material- und Umweltwissenschaften. Analytische Chemie VIII, Vieweg, Braunschweig, pp 283
404. Weber-Diefenbach (2000) Physikalisch-chemische Untersuchungsmethoden in den Geowissenschaften. In: Pavievi MK Amthauer G (eds) Schweizerbart'sche Verlagsbuchhandlung, Nägele u. Obermiller, Stuttgart, pp.115–131
405. Brill M (1996) Energy-dispersive vs. wavelength-dispersive x-ray fluorescence spectrometry. Metall, Berlin 50:662–668
406. Kramar U (1997) Advances in energy-dispersive X-ray fluorescence. J Geochem Explor 58:73–80
407. Markham M, Floyd PA (1998) Geochemical fingerprinting of west Cornish greenstones as an aid to provenancing neolithic axes. Proc Ussher Society 9:218–223
408. Vaniman DT, Bish DL, Blake DF, Elliott ST, Sarrazin P, Collins SA, Chipera S (1998) Landed XRD/ XRF analysis of prime targets in the search for past or present Martian life. Journ Geophy Res E. 103:31,477–31,489
409. Vaniman DT, Bish DL, Blake DF, Chipera SJ (2000) CCD-based XRD/ XRF for determining environmental mineralogy on Mars. In: Hubbard S. (ed), Concepts and approaches for Mars exploration. LPI Contribution, 300–301
410. May MT, McCurdy MW, Clement EB (1997) XRF surveys for three mining waste sites. Proc of the 4th International Conference on Tailings and Mine Waste. A. A. Balkema. Rotterdam, Netherlands, 4:461–469
411. Martino L, Cho E, Wrobel J (1994) In situ analysis of soil at an open burning/ open detonation disposal facility. Argonne National Laboratory, Argonne, IL, United States, pp 30
412. Mirecki J, Dumars A, Laws B, Tucker J (1999) Comparison of Pb concentrations in contaminated residential soils using portable XRF (field) and ICP-AES (lab) methods. Geol Soc Am. 31:31
413. Jordan MD, Crawford A, Mirecki JE (2000) Analysis of lead-contaminated soil near a residence in Charleston, South Carolina by portable XRF and ICP-AES. Geol Soc Am. 32: 29
414. Bawden-Smith J (2001) Reducing contaminated soil rehabilitation costs; review of portable XRF performance on Australian soils. The Aus IMM Bulletin (1990) 6:17–19
415. McCain RG (1993) Qualitative evaluation of heavy metals in soils using portable XRF instruments. Westinghouse Hanford, Richland, United States, pp10
416. Zhou S, Sun C, He Z, Wu D (1997) The XRF mark of gold deposit in Beishan, Xinjiang. Chengdu Liguong Xueyuan Xuebao. Journ Chengdu Inst Technology 24: 24–28
417. Li G, Jia W, Zhou R, Tang H, Fang F, Ma Y (1998) Research on field, highly sensitive X-ray fluorescence system. Chengdu Liguong Xueyuan Xuebao. J Chengdu Inst Technology 25:13–20
418. Konstantinov MM, Strujkov SF (1995) Application of indicator halos (signs of ore remobilization) in exploration for blind gold and silver deposits. J Geochem Explor. 54:1–17
419. Tiwari MK, Singh AK, Sawhney KJS (2001) Analysis of stainless steel samples by energy dispersive X-ray fluorescence (EDXRF) Spectrometry. Bull Material Sci 24:633–638

420. Evans RD (1982) The Atomic Nucleus. Krieger Publ Comp reprint: pp 972
421. Streckeisen A (1980) Classification and Nomenclature of Volcanic Rocks, Lamprophyres, Carbonatites and Melilitic Rocks. IUGS Subcommittee on the Systematics of Igneous Rocks. *Geol Rundsch*, 69:194–207
422. Le Bas MJ, Le Maitre RW, Streckeisen A, Zanettin B (1986) A Chemical Classification of Volcanic Rocks Based on the Total Alkali - Silica Diagram. *J Petrol* 27:745–7750
423. Burri C (1959) Petrochemische Berechnungsmethoden auf äquivalenter Grundlage. Birkhäuser, Basel, pp 343
424. Müller P (1982) Von der CIPW-Norm ausgehende Berechnung von Mineralbeständen magmatischer Gesteine in Analogie zu der Modalzusammensetzung plutonischer und vulkanischer Gesteine. *Geol Jbh D* 55: p 41
425. Best MG (1982) Igneous and Metamorphic Petrology. Freeman, Appendix E: 616–619
426. Cohen D, Ward CR (1991) SEDNORM; a program to calculate a normative mineralogy for sedimentary rocks based on chemical analyses. *Comput Geosci* 17:1235–1253
427. Rosen OM, Abbyasov AA, Migdisov AA, Yaroshevskii AA (2000) MINLITH—a Program to Calculate the Normative Mineralogy of Sedimentary Rocks: the Reliability of Results Obtained for Deposits of Old Platforms. *Geochem Intern* 38: 388–400
428. Wager LR (1968) Rhythmic and cryptic layering in mafic and ultramafic plutons. In: Hess HH Poldervaart A (eds) Basalts - The Poldervaart treatise on rocks of basaltic composition, Interscience, New York 2:573–622
429. Wilson JR (1998) Magma chamber processes revealed by studies of layered intrusions. In: Wilson JR Michelsen O (eds) Geoscience in Aarhus. Aarhus University, Aarhus, Denmark, pp 13–16
430. Cheburkin AK, Frei R, Shotyk W (1997) An energy-dispersive miniprobe multi-element analyzer (EMMA) for direct analysis of trace elements and chemical age dating of single mineral grains. *Chem Geol* 135: 75–87
431. Harvey PK, Atkin BP (1987) Automated XRF spectrometric analysis; a rapid, cost-effective analytical technique for the mineral industry. *J Geochem Explor* 29:413–415
432. Bach H, Krause D (eds) (1999) Analysis of the Composition and Structure of Glass and Glass Ceramics. Schott Series on Glass and Class Ceramics, Springer, Berlin, Heidelberg, pp 528
433. Potts PJ, Ellis AT, Kregsamer P, Marshall J, Streli C, West M, Wobrauschek P (2003) Atomic spectrometry update. X-ray fluorescence spectrometry. *J Anal At Spectrometry* 18:1297–1316
434. Mzyk Z, Baranowska I, Mzyk J (2000) Research on grain size effect in XRF analysis of pelletized samples. *X-Ray Spectrom* 31:39–46
435. Darnley A, Björklund A, Bølviken B, Gustavsson N, Koval PV, Plant JA, Steenfelt A, Tauchid M, Xuejing X (1995) A global geochemical database for environmental and resource management. Recommendations for international geochemical mapping. Final report of IGCP-project 259, UNESCO Publishing, Paris, France, pp 122
436. Reimann C, Siewers U, Tarvainen T, Bitukova L, Eriksson J, Gilucis A, Gregorauskiene V, Lukashev V, Matinian NN, Pasieczna A (2000) Baltic soil survey: total concentrations of major and selected trace elements in arable soils from 10 countries around the Baltic Sea. *Sci Tot Envir* 257:155–170

437. Reimann C, Siewers U, Tarvainen T, Bitukova L, Eriksson J, Gilucis A, Gregorauskiene V, Lukashev V, Matinian NN, Pasieczna A (2003) Agricultural soils in Northern Europe: A Geochemical Atlas. *Geol Jb SD5*, p 279
438. Alexander PO (1999) Biogene indicators of kimberlites and lamproites. In: Science and technology of diamond. Bhatnagar GS (ed) Cambridge Intern Sci Publ. Cambridge, UK pp 15–37
439. Renault S; Sailerova E; Fedikow MAF (2001) Phytoremediation of mine tailings and bio-ore production; results from a study on plant survival at the central Manitoba (Au) minesite (NTS 52L/ 13). Report of Activities - Manitoba Energy and Mines, Minerals Division; Pages 138–149
440. Solodukhin VP (1998) Nuclear-physical methods of analysis in oil geology and industry of Kazakhstan. In: Proc 4th Intern. Conf. Methods and Applications of Radioanalytical Chemistry; Part 2. *Journ Radioanal Nucl Chem* 234:101–105
441. Parus J, Kierzek J, Malozewska-Bucko B (2000) Determination of the carbon content in coal and ash by XRF. *X-Ray Spectrom* 29: 192–195
442. Shao L, Jones T, Gayer R, Dai S, Li S, Jiang Y, Zhang P (2003) Petrology and geochemistry of the high-sulphur coals from the Upper Permian carbonate coal measures in the Heshan Coalfield, southern China. *Internat J Coal Geol* 55:1–26.
443. Dill HG, Poehlmann H (2002) Chemical composition and mineral matter of paralic and limnic coal types of lignite through anthracite rank (Germany). In: Hills LV, Henderson CM, Bamber EW (eds) Carboniferous and Permian of the world; XIV ICCP Proc Memoir - *Can Soc Petrol Geol* 19:851–867
444. Karayigit AI, Spears DA, Booth CA (2000) Antimony and arsenic anomalies in the coal seams from the Gokler Coalfield, Gediz, Turkey. *Internat J Coal Geol* 44: 1–17
445. Brown FV, Jones SA (1980) On-site determination of ash in coal utilizing a portable XRF analyzer. In: Rhodes J; Barrett CS; Leyden DE, Newkirk JB, Predecki PK, Ruud CO (eds) Twenty-eighth annual conference on applications of X-ray analysis. *Adv X-Ray Anal* 23:57–63
446. Schramm M, Bornemann O, Wilke F, Siemann M, Dijk HL (2002) Bromine Analysis - A Powerful Tool to solve Stratigraphical Problems in Exploration Boreholes for Salt Caverns.- SMRI, Technical Paper, Fall 2002 Meeting, Bad Ischl, Austria: pp. 12
447. Beckhoff B, Kanngießer B (1997) Improvement of the Detection sensitivity of EDXRF Trace Element Analysis by means of efficient x-ray focusing based on strongly curved HOPG crystals. *Adv X-Ray Anal* 39: 109–117
448. Zhdanov AY (2003) Catalogue of the manufacturers and suppliers of instrumentation equipment and laboratory equipment. <http://www.spectrometer.ru/manufacturers-suppliers/micro-xrf-spectrometers.htm>
449. Rammlmair D, Tacke KD, Jung H (2001) Application of new XRF-scanning techniques to monitor crust formation in column experiments. In: Securing the Future, Proc Intern Conf Mining Envir, Skellefteå, 2:683–692
450. Vekemans B, Janssens K, Vincze L, Aerts A, Adams F, Hertogen J (1997) Automated Segmentation of μ -XRF Image Sets. *X-Ray Spectrom* 26: 333–346
451. Price GJ, Fraser GW, Pearson JF, Hutchinson IB, Holland AD, Nussey J, Vernon D, Pullan D, Turner K (2003) Imaging x-ray fluorescence spectroscopy using microchannel plate x-ray optics. *Spectroscopy Europe* 15:8–13

452. Rammlmair D, Reinhardt L, Kleinmann A (2002) High resolution EDXRF-scanning deciphering seasonal variation in laminated marine and varved lacustrine sediments. Abstract EGS - AGU - EUG Joint Ass, Nice, France, EAE03-A-12865
453. von Rad U, Ali Khan A, Berger WH, Rammlmair D, Treppke U (2002) Varves, turbidites and cycles in upper Holocene sediments (Makran Slope, Northern Arabian Sea). In: Clift PD, Kroon D, Gaedicke C, Craig J (eds) The Tectonic and Climatic Evolution of the Arabian Sea Region. Geol. Soc. Spec. Publ. 195:387–406
454. Kleinmann A, Rammlmair D (2003) Hochauflösende EDXRF-Scans von mittelholozänen gewarvten Sedimenten aus dem Schleinsee und Belauer See. - Terra Nostra 6: 245–249
455. Rammlmair D, Wessels M (2003) Chemical characterization of Lake Constance sediments record by high resolution EDXRF, EGS - AGU - EUG Joint Ass, Nice, France, Abstract EAE03-A-11705
456. Oberthür T, Rammlmair D, Kojonen K, (2000) Comparison of automated particle search techniques for platinum group elements (PGE) and minerals (PGM): μ -XRF and electron-microprobe. In: Rammlmair D, Mederer J, Oberthür T, Heimann RB, Penttinghaus H (eds) Applied Mineralogy in Research, Economy, Technology, Ecology and Culture, A.A. Balkema, Rotterdam, Brookfield, 1, 375–378
457. Melcher F, Oberthür T, Rammlmair D (2002) - The carbonate-hosted, Ge- and Ag-rich Khusib Springs Cu-Zn-Pb sulphide deposit, Namibia: ore geochemistry and mineralogical variations. IAGOD/Geocongress 34–35
458. Gottlieb P, Butcher AR, Ho-Tun E, Sutherland DN (2000) Applications of automated process mineralogy. In: Rammlmair D, Mederer J, Oberthür T, Heimann RB, Penttinghaus H (eds) Applied Mineralogy in Research, Economy, Technology, Ecology and Culture, A.A. Balkema, Rotterdam, Brookfield, 1: 321–323
459. Butcher AR, Helms TA, Gottlieb P, Bateman R, Ellis S, Johnson NW (2000) Advances in the quantification of gold deportment by QemSCAN. In: 7th Mill Operators' Conference, Kalgoorlie, AusIMM. 267–271
460. Togami S, Takano M, Kumazawa M (2000) An Algorithm for the transformation of XRF images into mineral-distribution maps. Can Mineral 38:1283–1294
461. Michibayashi K, Togami S, Takano M, Kumazawa M, Kageyama T (1999) Application of scanning X-ray analytical microscope to the petrographic characterization of a ductile shear zone: an alternative method to image microstructure Tectonophysics, 310, 55–67
462. Schwarzer RA, Wehrhahn M (1997) X-ray scanning apparatus for mapping texture and element distributions. Textures and Microstructures 29:65–76
463. Schwarzer RA (1998) Crystallography and microstructure of thin films studied by X-ray and electron diffraction. Materials Science Forum vols. 287–288, 23–60
464. Wang PC, Cargill III GS, Noyan IC, Liniger EG, Hu CK, Lee KY (1997) Thermal and electromigration strain distributions in 10 μ m-wide aluminum conductor lines measured by X-ray diffraction. Mat Res Soc Symp Proc 473:273–278
465. Horowitz P, Howell JA (1972) A scanning X-ray microscope using synchrotron radiation. Science 178:608–611
466. Jones KW, Gordon BM (1989) Trace element determinations with synchrotron-induced X-ray emission. Anal Chem 61:341A-356A

467. Rindby A, Engström P, Larsson S, Stocklassa B (1989) Microbeam technique for energy-dispersive X-ray fluorescence. *X-Ray Spectrom* 18, 109–112
468. Carpenter DA (1989) Improved laboratory X-ray source for microfluorescence analysis. *X-Ray Spectrom* 18:253–257
469. Werry D, Cross B (1989) Applications of small-area X-ray fluorescence analysis using a microbeam X-ray source. *Spec Intern* 1:58–59
470. Klein H, Bunge HJ (1999) Location resolved texture analysis. *Z. Metallkunde* 90:103–110
471. Schwarzer RA (1989) Scanning X-ray microscopy for texture mapping by energy dispersive diffraction. *Proc 12th ICXOM, Cracow* 1:pp 205–208
472. Schwarzer RA (1993) Texture distributions imaged by energy dispersive X-ray diffraction. *Steel Research* 64:570–574
473. Fischer AH, Schwarzer RA, (1998a) X-ray pole figure measurement and texture mapping of selected areas using an X-ray scanning apparatus. *Materials Science Forum* 273-275: 255–262
474. Schäfer B (1998) ODF computer program for high-resolution texture analysis of low-symmetry materials. *Materials Science Forum* 273-275: 113–118
475. Fischer AH, Schwarzer RA, (1998b) Mapping of local residual strain with an X-ray scanning apparatus. *Materials Science Forum* 273-275: 673–677
476. Maslen EN (1958) An X-ray collimator for single-crystal goniometers. *Sci. Instruments* 35:110–111
477. Larsson S, Engström P (1992) X-ray microbeam spectroscopy with the use of capillary optics. *Adv X-Ray Anal* 35:1019–1025
478. Fischer AH, Weirauch D, Schwarzer RA (1998) Peltier-cooled solid state drift-chamber detector for energy-dispersive X-ray pole figure measurement and texture mapping. *Materials Science Forum* 273-275: 263–270
479. Boltwood BB (1907) On the ultimate disintegration products of the radioactive elements. Part II. The disintegration products of uranium. *Am Journ Sci* 23:77–88
480. Suzuki K, Adachi M (1991) The chemical Th-U-total Pb isochron ages of zircon and monazite from the Gray granite of the Hida terrane, Japan. *Journ Earth Sci* 38:11–37
481. Montel JM, Veschambre M, Nicollet C (1994) Datation de la monazite à la microsonde électronique. *Comptes Rendus de l'Academie des Sciences Paris, Serie II, Sci Terre Planet.* 318:1489–1495
482. Foster G, Kinny P, Vance D, Prince C, Harris N (2000) The significance of monazite U-Th-Pb age data in metamorphic assemblages; a combined study of monazite and garnet chronometry. *Earth Planet Sci Lett* 181:327–340
483. Pyle, J.M., Spear, F.S., Wark, D.A. (2002) Electron microprobe analysis of REE in Apatite, Monazite, and Xenotime: Protocols and Pitfalls. In *Phosphates*, Kohn MJ, Rakovan J, Hughes JM. (eds) *Rev Mineral* 48, 337–362
484. Rhede D, Wendt I, Förster HJ (1996) A three-dimensional method for calculating independent chemical U/Pb- and Th/Pb-ages of accessory minerals. *Chem Geol* 130:247–253
485. Montel JM, Foret S, Veschambre M, Nicollet C, Provost A (1996) Electron microprobe dating of monazite. *Chem Geol* 131:37–53
486. Montel JM, Kornprobst J, Vielzeuf D (2000) Preservation of old U-Th-Pb ages in shielded monazite: Example from the Beni Bousera Hercynian kinzigites (Marocco). *Journ metam Geol* 18:335–342

487. Cocherie A, Albarede F (2001) An improved U-Th-Pb age calculation for electron microprobe dating of monazite. *Geochim Cosmochim Acta* 65: 4509–4522
488. Bruhn F, Möller A, Sie SH, Hensen BJ (1999) U-Th-Pb Chemical dating of monazites using the proton microprobe. *Nucl Instrum Methods Phys Res, Sect B* 158:616–620
489. Frei R, Prozesky VM, Przybzlowski W (1997) Studies of progressive leaching in single mineral Pb/Pb dating. *Nucl Instrum Methods Phys Res, Sect B* 130:676–681
490. Scherrer NC, Engi M, Berger A, Parrish RR, Cheburkin A (2002) Nondestructive chemical dating of young monazite using XRF 2. Context sensitive microanalysis and comparison with Th-Pb laser-ablation mass spectrometric data. *Chem Geol* 191:243–255
491. Engi M, Cheburkin AK, Köppel V (2002) Nondestructive chemical dating of young monazite using XRF 1. Design of a mini-probe, age data for samples from the Central Alps, and comparison to U-Pb (TIMS) data. *Chem Geol* 191:225–241
492. John T (2001) Subduction and continental collision in the Lufilian Arc - Zambezi Belt orogen: A petrological, geochemical, and geochronological study of eclogites and whiteschists (Zambia). Unpubl. doctorate thesis, Universität Kiel, pp 75
493. Nakai I, Terada Y, Itou M, Sakurai Y (2001) Use of highly energetic (116 keV) synchrotron radiation for X-ray fluorescence analysis of trace rare-earth and heavy elements. *J Synchrotron Rad* 8:1078–1081
494. Schroer CG, Kuhlmann B, Hunger UT, Günzler TF, Kurapova O, Fest S, Frehse F, Lengeler B, Drakopoulos M, Somogyi A, Simionovici AS, Snigirev A, Snigireva I, Schug C, Schröder WH (2003) Nanofocusing parabolic refractive x-ray lenses. *Appl Phys Lett* 82:1485–1487
495. Vekemans B, Vincze L, Somogyi A, Drakopoulos M, Kempenaers L, Simionovici A, Adams F (2003) Quantitative X-ray fluorescence analysis at the ESRF ID18F microprobe. *Nucl Instrum Methods Phys Res, Sect B* 199:396–401
496. Jochum KP, Dingwell DB, Rocholl A, Stoll B, Hofmann AW, Becker S, Besmehn A, Bessette D, Dietze HJ, Dulski P, Erzinger J, Hellebrandt E, Hoppe P, Horn I, Janssens K, Jenner GA, Klein M, McDonough WF, Maetz M, Mezger K, Münker C, Nikogosian IK, Pickhard C, Raczek I, Rhede D, Seufert HM, Simakin SG, Sobolev AV, Spettel B, Straub S, Vincze L, Wallianos A, Weckwerth G, Weyer S, Wolf D, Zimmer M (2000) The preparation and preliminary characterization of eight geological MPI-DING reference glasses for in-situ microanalysis. *Geostandard Newsletter* 24:87–133
497. Koepke J, Behrens H (2001) Trace element diffusion in andesitic melts: an application of synchrotron X-ray fluorescence analysis. *Geochim Cosmochim Acta* 65:1481–1498
498. Koepke J, Falkenberg G, Rickers K, Diedrich O (2003) Trace element diffusion and element partitioning between garnet and andesite melt using synchrotron X-ray fluorescence microanalysis (μ -SRXRF). *Eur J Mineral* 15:883–892
499. Hlawatsch S, Garbe-Schönberg CD, Lechtenberg F, Manceau A, Tamura N, Kulik DA, Kersten M (2002) Trace metal fluxes to ferromanganese nodules from the western Baltic Sea as a record for long-term environmental changes, *Chem Geol* 182:697–709

500. Troll VR, Schmincke HU (2002) Magma mixing and crustal recycling recorded in ternary feldspar from compositionally zoned peralkaline ignimbrite 'A', Gran Canaria, Canary Islands, *Journ Petrol* 43:243–270
501. Troll VR, Sachs PM, Schmincke HU, Sumita M (2003) The REE-Ti mineral chevkinite in comenditic magmas from Gran Canaria, Spain: a SYXRF-probe study, *Contrib Mineral Petrol* 145:730–741
502. Sachs PM, Hansteen T (2000) Pleistocene underplating and metasomatism of the lower continental crust: a xenolith study. *Journ Petrol* 41:331–356
503. Harting M, Rickers K, Kramar U, Simon R, Staub S, Schulte P (2002) Multielement geochemical investigations by SRXRF microprobe studies on tectite material: evidence from the NE-Mexican Cretaceous/Tertiary record. *EOS Trans. AGU*, 83(47) Abstract P22B-0403
504. Rindby A, Engström P, Janssens K, Osán J (1997) Micro-distribution of heavy elements in highly inhomogeneous particles generated from μ -beam XRF/XRD analysis. *Nucl Instrum Methods Phys Res, Sect B* 124:591–604
505. Vincze L, Somogyi A, Osán J, Vekemans B, Török S, Janssens K, Adams F (2002a) Quantitative trace element analysis of individual fly ash particles by means of X-ray microfluorescence, *Anal Chem* 74:1128–1135
506. Salbu B, Kerkling T, Lind OC, Oughton DH, Drakopoulos M, Simionovici A, Snigireva I, Snigirev A, Weitkamp T, Adams F, Janssens K, Kashparov VA (2001) High energy X-ray microscopy for characterisation of fuel particles. *Nucl Instrum Methods Phys Res A* 467–468, 1249–1252
507. Osán, J., Török, S. Alföldy B. and Falkenberg G. (2004) Characterization of anthropogenic sediment particles after a transboundary water pollution of River Tisza using synchrotron radiation. Submitted to *Spectrochimica Acta Part B*, Manuscript# GL1317
508. Salbu B, Janssens K, Lind OC, Proost K, Danesi PR (2003) Oxidation states of uranium in DU particles from Kosovo. *J Envir Radioact*, 64: 167–173
509. Roedder, E. (1984): Fluid inclusions. *Rev Min* 12: p 644
510. Günther D, Audétat A, Frischknecht R, Heinrich CA (1998) Quantitative analysis of major, minor and trace elements in fluid inclusions using laser ablation-inductively coupled plasma mass spectrometry. *J Anal At Spectrometry* 13:263–270
511. Günther D, Hattendorf B, Audétat A (2001) Multi-element analysis of melt and fluid inclusions with improved detection capabilities for Ca and Fe using laser ablation with a dynamic reaction cell ICP-MS. *J Anal At Spectrometry* 16:1085–1090
512. Audétat A, Günther D, Heinrich CA (1998) Formation of a magmatic-hydrothermal ore deposit: Insights with LA-ICP-MS analysis of fluid inclusions. *Science* 279:2091–2094
513. Heinrich CA, Günther D, Audétat A, Ulrich T, Frischknecht R (1999) Metal fractionation between magmatic brine and vapor, determined by microanalysis of fluid inclusions. *Geology* 27:755–758
514. Ménez B (1999): Les microsondes photon et proton appliquées à l'analyse ponctuelle d'inclusions fluides: Un outil pour reconstituer l'évolution des paléosystèmes hydrothermaux [Individual fluid inclusion microanalysis combining photon and proton microprobes: a tool for reconstructing paleohydrothermal processes]. Ph. D. thesis, Paris VII University

515. Ménez B, Philippot P, Bonnin-Mosbah M, Simionovici A, Gibert F (2002) Analysis of individual fluid inclusions using synchrotron X-ray fluorescence microprobe: progress toward calibration for trace elements. *Geochim Cosmochim Acta* 66:561–576
516. Kamenetsky VS, van Achterberg E, Ryan CG, Naumov VB, Mernagh TP, Davidson P (2002) Extreme chemical heterogeneity of granite-derived hydrothermal fluids: An example from inclusions in a single crystal of miarolitic quartz. *Geology* 30:459–462
517. Ryan CG, McInnes BJA, Williams PJ, Dong G, Win TT, Yeats CJ (2001) Imaging fluid inclusion content using the new CSIRO-GEMOC nuclear microprobe. *Nucl Instrum Methods Phys Res, Sect B* 181:570–577
518. Ryan CG, Van Achterberg E, Yeats CJ, Driberg SL, Mark G, McInnes BM, Win TT, Cripps G, Suter GF (2002) Quantitative, high sensitivity, high resolution, nuclear microprobe imaging of fluids, melts and minerals. *Nucl Instrum Methods Phys Res, Sect B* 188:18–27
519. Bühn B, Rankin AH, Radtke M, Haller M, Knöchel A (1999) Burbankite, a (Sr, REE, Na, Ca)-carbonate in fluid inclusions from carbonatite-derived fluids; identification and characterization using laser Raman spectroscopy, SEM-EDX, and synchrotron micro-XRF analysis. *Am Min*, 84, 1117–1125
520. Philippot P, Ménez B, Simionovici A, Chabiron A, Cuney M, Snigirev A, Snigireva I (2000) X-ray imaging of uranium in individual fluid inclusions. *Terra Nova* 12:77–83
521. Ryan CG, Heinrich CA, Mernagh TP (1993) PIXE microanalysis of fluid inclusions and its application to study ore metal segregation between magmatic brine and vapor. *Nucl Instrum Methods Phys Res, Sect B* 77:463–471
522. Damman AH, Kars SM, Touret JLR, Rieffe EC, Kramer JALM, Vis RD, Pintea I (1996) PIXE and SEM analysis of fluid inclusions in quartz crystals from the K-alteration zone of the Rosia Poieni porphyry-Cu deposit, Apuseni Mountains, Rumania. *Eur J Mineral* 8:1081–1096
523. Kanngießer B, Malzer W, Reiche I (2003) A new 3D micro X-ray fluorescence analysis set up – First archeometric applications. *Nucl Instrum Methods Phys Res, Sect B* 211:259–264
524. Vanko DA, Bonnin-Mosbah M, Philippot P, Roedder E, Sutton S (2001) Fluid inclusions in quartz from oceanic hydrothermal specimens and the Bingham, Utah porphyry-Cu deposit: a study with PIXE and SXRF. *Chem Geol*, 173:227–238
525. Vanko DA, Mavrogenes JA (1998) Synchrotron-source X-ray fluorescence microprobe: analysis of fluid inclusions. In: McKibben MA, Shanks WC, Ridley WI (eds.) *Applications of Microanalytical Techniques to Understanding Mineralizing Processes*. *Rev. Econ. Geol.* 7:251–263
526. Rickers K., Thomas, R. and Heinrich W., ‘Trace-element analysis of individual synthetic and natural fluid inclusions with synchrotron radiation XRF using Monte Carlo simulations for quantification.’ *European Journal of Mineralogy* 16 (2004) 23–35
527. Vincze L, Janssens K, Adams F (1993) A general Monte Carlo simulation of energy-dispersive X-Ray fluorescence spectrometers – Part I. *Spectr. Acta* 48B:553–573
528. Vincze L, Janssens K, Adams F, Rindby A (1995a) A detailed ray-tracing code for capillary X-ray optics. *X-ray Spectrom* 24:27–37

529. Vincze L, Janssens K, Adams F, Rivers ML, Jones KW (1995b) A general Monte Carlo simulation of energy-dispersive X-Ray fluorescence spectrometers – Part II. *Spectr. Acta* 50B:127–148
530. Vincze L, Janssens K, Adams F, Jones KW (1995c) A general Monte-Carlo simulation of energy dispersive X-ray fluorescence spectrometers: Part III. *Spectr. Acta* 50B:1481–1500
531. Schmidt C, Rickers K (2003) In-situ determination of mineral solubilities in fluids using a hydrothermal diamond-anvil cell and SR-XRF: Solubility of AgCl in water as an example. *Am Min* 88:288–292
532. Bassett WA, Shen AH, Bucknum M, Chou IM (1993) A new diamond anvil cell for hydrothermal studies to 2.5 GPa and from –190 to 1200 ° C. *Rev Sci Instr* 64:2340–2345
533. Rickers K, Schmidt C (2002) In situ determination of monazite solubility and dissolution kinetics using a diamond-anvil cell and SR-XRF. *Hasylab annual report*:937–938
534. Sanchez-Valle C, Martinez I, Daniel I, Philippot P, Bohic S, Simionovici A (2003) Dissolution of strontianite at high P-T conditions: An in-situ synchrotron X-ray fluorescence study. *Am Min* 88:978–985
535. Brown GE Jr., Calas G, Waychunas GA, Petiau J (1988) X-ray absorption spectroscopy: Applications in mineralogy and geochemistry. *Rev Min* 18:431–512
536. Brown GE Jr., Farges F, Calas G (1995) X-ray scattering and X-ray spectroscopy studies of silicate melts. *Rev Min* 32:317–410
537. Schulze DG, Stucki JW, Bertsch PM (eds) (1999) Synchrotron X-ray methods in clay science. *CMS Workshop Lectures* 9: pp 244
538. Fenter PA, Rivers ML, Sturchio NC, Sutton SR (eds) (2002) Applications of synchrotron radiation in low-temperature geochemistry and environmental science. *Rev Min* 49:pp 579
539. Henderson GS, Baker DR (eds.) (2002) Synchrotron Radiation: Earth, Environmental, and material sciences applications. *Min Assoc Can, Short Course*, SC 30: pp. 178
540. Tröger L, Arvanitis D, Baberschke K, Michaelis, H, Grimm U, Zschech E (1992) Full correction of the self-absorption in soft-fluorescence extended X-ray absorption fine structure. *Phys Rev B* 46:3283–3289
541. Manceau A, Marcus MA, Nobumichi T (2002) Quantitative speciation of heavy metals in soils and sediments by synchrotron X-ray techniques. *Rev Min* 49:341–428
542. Lytle FW, Greegor RB, Sandstrom DR, Marques DR, Wong J, Spiro CL, Huffman GP, Huggins FE. (1984) Measurement of soft X-ray absorption spectra with a fluorescence ion chamber detector. *Nucl Instrum Methods Phys Res A* 226:542–548
543. Gauthier C, Solé VA, Signorato R, Goulon J, Moguiline E (1999) The ESRF beamline ID26: X-ray absorption on ultra dilute samples. *J Synchrotron Rad* 6:164–166
544. Brüggmann U, Haack N, Hermann M, Johnas SKJ, Kappen P, Klementiev K, Welter E (2002) Improvements for absorption spectroscopy at beamlines A1, E4, X1. *Hasylab annual report 2002*: 83–87
545. Dyar MD, Lowe EW, Guidotti CV, Delaney JS (2002a) Fe³⁺ and Fe²⁺ partitioning in metapelites: A synchrotron micro-XANES study. *Am Min* 87:514–522

546. Schmid R, Wilke M, Oberhänsli R, Janssens K, Falkenberg G, Franz L, Gaab A (2003). Micro-XANES Determination of Ferric Iron and its Application in Thermobarometry. *Lithos*, 70 381–392
547. Sutton SR, Bertsch PM, Newville M, Rivers ML, Lanzirrotti A, Eng P (2002) Microfluorescence and Microtomography. Analyses of heterogeneous earth and environmental materials. *Rev Min* 49:429–484
548. Garvie LAJ, Buseck PR (1998) Ratios of ferrous to ferric iron from nanometre-sized areas in minerals. *Nature* 396:667–670
549. Welter E, Calmano W, Mangold S, Tröger L. (1999) Chemical speciation of heavy metals in soils by use of XAFS spectroscopy and electron microscopical techniques. *Fresenius' J. Anal. Chem.* 364, 238–244
550. Calmano W, Mangold S, Welter E (2001) An XAFS investigation of the artefacts caused by sequential extraction analyses of Pb-contaminated soils. *Fresenius' J. Anal. Chem.* 371, 823–830
551. Vincze L, Wei F, Proost K, Vekemans B, Janssens K, He Y, Yan Y, Falkenberg G (2002b) Suitability of polycapillary optics for focusing of monochromatic synchrotron radiation as used in trace level micro-XANES measurements. *J Anal At Spectrometry* 17:177–182
552. Wilke M, Farges F, Petit PE, Brown Jr. GE, Martin F (2001) Oxidation state and coordination of Fe in minerals: an Fe K XANES spectroscopic study. *Am Min* 86, 714–730
553. Bajt S, Sutton SR, Delaney JS (1995) X-ray microprobe analysis of iron oxidation-states in silicates and oxides using x-ray absorption near-edge structure (XANES). *Geochim Cosmochim Acta* 58:5209–5214
554. Dyar MD, Gunter ME, Delaney JS, Lanzirrotti, Sutton SR (2002b) Use of the spindle stage for orientation of single crystals for microXAS: Isotropy and anisotropy in Fe-XANES spectra. *Am Min* 87:1500–1504
555. Jackson WE, Mustre de Leon J, Brown GE Jr, Waychunas GA, Conradson SD, Combes J-M (1993) High-temperature XAS study of Fe_2SiO_4 liquid: Reduced coordination of ferrous iron. *Science* 262, 229–233
556. Farges F, Waychunas GA, Brown GE Jr, Calas G, Galois L (1994) Structural transformation in Ni-bearing $\text{Na}_2\text{Si}_2\text{O}_5$ glass and melt. *Geophys Res Lett* 21:1931–1934
557. Farges F, Hao Gan, Rehr JR, Brown GE Jr, Navrotsky A (1996) A Coordination chemistry of Ti(IV) in silicate glasses and melts: III. Glasses and melts from ambient to high temperatures *Geochim Cosmochim Acta* 60:3055–3065
558. Bassett WA, Anderson AJ, Mayanovic RA, Chou IM (2000) Hydrothermal diamond anvil cell XAFS studies of first row transition elements in aqueous solutions up to supercritical conditions. *Chem Geol* 167:3–10
559. Anderson AJ, Jayanetti S, Mayanovic RA, Bassett WA, Chou IM (2002) X-ray spectroscopic investigations of fluids in the hydrothermal diamond anvil cell: The hydration structure of aqueous La^{3+} up to 300°C and 1600°C. *Am Min* 87:262–268
560. Seward TM, Henderson CMB, Charnock JM, Driesner T (1999) An EXAFS study of solvation and ion pairing in aqueous strontium solutions to 300°C. *Geochim Cosmochim Acta* 63:2409–2418
561. Bargar JR, Tebo BM, Villinski JE (2000) In situ characterization of Mn(II) oxidation by spores of the marine *Bacillus* sp. Strain SG-1. *Geochim Cosmochim Acta* 64:2775–2778

562. Frahm R (1989) New method for time-dependent X-ray absorption studies. *Journ Sci Instr* 60:2515–2518
563. Lützenkirchen-Hecht D, Grundmann S, Frahm R (2001) Piezo-QEXAFS with fluorescence detection: fast time-resolved investigations of dilute specimens. *J Synchrotron Rad* 8:6–9
564. Janssens K., Vittiglio G., Dereadt I., Aerts A., Vekemans B., Vincze L., Wei F., Deryck, Schalm O., Adams F., Rindby A., Knöchel A., Simionovici A., Snigirev A. (2000) Use of microscopic XRF for non-destructive analysis in art and archeometry. *X-Ray Spectrom.* 29(1): 73–91
565. Lahanier Ch., Preusser F.D., Van Zelst. (1986) Study and conservation of museum objects: Use of classical analytical techniques. *Nuclear Instrum. Methods Phys. B* 14: 1–9
566. Mantler M., Schreiner M. (2000) X-Ray fluorescence spectrometry in art and archaeology. *X-Ray Spectrom.* 29(1): 3–17
567. Klockenkämper R. (1997) *Total-Reflection X-Ray Fluorescence Analysis*. Wiley, New York 208–214
568. Vandenabeele P., van Bohlen A., Moens L., Klockenkämper R., Joukes F., Dewispelaere G. (2000) Spectroscopic examination of two Egyptian masks—a combined method approach. *Anal. Lett.* 33(15): 3315–3332
569. Mommsen H., Beier Th., Dittmann H., Heimermann D., Hein A., Rosenberg A., Boghardt M. (1996) X-Ray fluorescence analysis with synchrotron radiation on the inks and papers of incunabula. *Archaeometry* 38: 347–357
570. Schreiner M., Mantler M. (1994) *Proceedings of the 4th International Conference on Non-destructive Testing of Museum Objects*, Berlin: 221–230
571. Fiorini C., Longoni A. (1998) Application of a new noncryogenic X-ray detector in portable instruments for archaeometric analyses. *Rev. Sci. Instrum.* 69(3): 1523–1528
572. Vittiglio G., Janssens K., Vekemans B., Adams F., Oost A. (1999) A compact small-beam XRF instrument for in-situ analysis of objects of historical and/or artistic value. *Spectrochim. Acta Part B* 54: 1697–1710
573. Bichlmeier S., Janssens K., Heckel J., Gibson D., Hoffmann P., Ortner H.M. (2001) Component selection for a compact micro-XRF spectrometer. *X-Ray Spectrom.* 30: 8–14
574. Bronk H., Röhrs S., Bjeoumikhov A., Langhoff N., Schmalz, Wedell R., Gorny H.E., Herold A., Waldschläger U. (2001) ArtTAX®: A new mobile spectrometer for energy dispersive micro X-Ray fluorescence spectrometry on art and archaeological objects. *Fresenius' J. Anal. Chem.* 371: 307–316
575. Kanngießer B., Malzer W., Reiche I. (2003) A new 3D micro X-ray fluorescence analysis set-up – First archaeometric applications. *Nucl. Instrum. Methods Phys. B* 211(2): 259–264
576. Schramm HP., Hering B., (1995) *Historische Malmaterialien und ihre Identifizierung*. Enke Verlag Stuttgart: 19–78
577. Harley R., (1982) *Artists' Pigments, c. 1600–1835*. 2nd ed., Butterworths London
578. Hahn O., Oltrogge D., Bevers H. (2004) Coloured prints of the 16th century – non-destructive analyses on coloured engravings from Albrecht Dürer and contemporary artists. *Archaeometry* 46(1): 273–282
579. Klockenkämper R., von Bohlen A., Moens L. (2000) Analysis of pigments and inks on oil paintings and historical manuscripts using total reflection X-Ray fluorescence spectrometry. *X-Ray Spectrom.* 29(1): 119–129

580. Neelmeijer C., Brissaud I., Calligaro T., Demortier G., Hautojärvi A., Mäder M., Martinot L., Schreiner M., Tuurnala T., Weber G. (2000) Paintings – a challenge for XRF and PIXE analysis. *X-Ray Spectrom.* 29(1): 101–110
581. Wehling B., Vandenabeele P., Moens L., Klockenkämper R., von Bohlen A., Van Hooydonk G., de Reu M. (1999) Investigation of pigments in medieval manuscripts by micro Raman spectroscopy and total reflection X-Ray fluorescence spectrometry. *Mikrochim. Acta* 130: 253–260
582. Hahn O., Gorny H.E. (2000) Zerstörungsfreie Charakterisierung historischer Eisengallustinten mittels Röntgenfluoreszenzanalyse. *Zeitschrift für Kunsttechnologie und Konservierung*, 14(2): 384–390
583. Malzer W., Hahn O., Kanngießer B. (2004) A fingerprint model for inhomogeneous ink paper layer systems measured with micro X-ray fluorescence analysis. *X-Ray Spectrom.* 33: 229–233
584. Lutz J., Pernicka E. (1996) Energy dispersive X-ray fluorescence analysis of ancient copper alloys: Empirical values for precision and accuracy. *Archaeometry* 38(2): 313–323
585. Wadsak M., Constantinides I., Vittiglio G., Adriaens A., Janssens K., Schreiner M., Adams F.C., Brunella P., Wuttmann M. (2000) Multianalytical study of patina formed on archaeological metal objects from Bliesbruck-Reinheim. *Mikrochim. Acta* 133: 159–164
586. Klockenkämper R., Bubert H., Hasler K. (1999) Detection of near-surface silver enrichment on Roman imperial silver coins by X-ray spectral analysis. *Archaeometry* 41(2): 311–320
587. Linke R., Schreiner M., Demortier G., Alram M. (2003) Determination of the provenance of medieval silver coins: potential and limitations of X-ray analysis using photons, electrons or protons. *X-Ray Spectrom.* 32: 373–380
588. Reiche I., Berger A., Görner W., Merchel S., Radtke M., Riederer J., Riesemeier H., Roth M. (2004) Following the traces of Albrecht Dürer: analysis of silver-point drawings by spatially resolved synchrotron-induced X-ray fluorescence analysis. *Nucl. Instrum. Methods Phys. B* 226: 83–91
589. Milazzo M., Cicardi C. (1998) X-ray fluorescence characterization of the Corona Ferrea. *Archaeometry* 40(2): 351–360
590. Pernicka E., Radtke M., Riesemeier H., Wunderlich C.H. (2004) European network of competence at 1600 BC. Highlights of the BESSY annual report 2003: 8–9
591. Adriaens A., Veny P., Adams F., Sporken R., Louette P., Earl B., Özbal H., Yener K.A. (1999) Analytical investigation of archaeological powders from Göltepe (Turkey). *Archaeometry* 41(1): 81–89
592. Dillman P., Balasubramaniam R. (2001) Characterization of ancient Indian iron and entrapped slag inclusions using electron, photon and nuclear microprobes. *Bull. Mater. Sci.* 24(3): 317–322
593. Crocetti G., Mattias P., Barrese E., Veggiani A. (1997) Mineralogic-petrographic observations and determinations of archaeological and ceramic fragments of Perticara Mountain, Marecchia Valley, Marche [Italy]. *Mineral. Petrogr. Acta* 39: 351–373
594. Morandi N., Nannetti M.C., Minguzzi V., Monti S., Marchesi M., Mattioli C., Desalvo F. (1997) Ceramics from the Etruscan city of Marzabotto: geochemical-mineralogical approach and connections with raw materials. *Mineral. Petrogr. Acta* 39: 341–350

595. Pillay A.E., Punyadeera C., Jacobson L., Eriksen J. (2000) Analysis of ancient pottery and ceramic objects using X-Ray fluorescence spectrometry. *X-Ray Spectrom.* 29: 53–62
596. Bakraji E.H., Othman I., Karajou J. (2001) Provenance studies of archaeological ceramics from Mar-Takla (Ain-Minin, Syria) using radioisotope X-ray fluorescence method. *Nucl. Sci. Tech.* 12(2): 149–153
597. Mandal S. (1997) Striking the balance: the roles of petrography and geochemistry in stone axe studies in Ireland. *Archaeometry* 39(2): 289–308
598. Franzini M., Leoni L., Lezzerini M., Sartori F. (1999) On the binder of some ancient mortars. *Mineralogy and Petrology* 67(1–2): 59–69
599. Röhrs S. (1999) Materialanalyse und Provenienzuntersuchung an Ziegelsteinen des 19. Jahrhunderts aus dem Berliner Umland. *Berliner Beiträge zur Archäometrie* 16: 43–89
600. Torfs K., Van Grieken R., Zezza F., Garcia N., Macri F. (1997) The cathedral of Bari, Italy: evaluation of environmental effects on stone decay phenomena. *Stud. Conserv.* 42(4): 193–206
601. Leung P.L., Stokes M.J., Chen Tiemei, Quin Dashu (2000) A study of ancient Chinese porcelain wares of the Song-Yuan dynasties from Cizhou and Ding kilns with energy dispersive X-ray fluorescence. *Archaeometry* 42(1): 129–140
602. Yu K., Miao J.M. (1999) Characterization of blue and white porcelains using the Mn/Fe ratio from EDXRF, with particular reference to porcelains of the Xuande period (1426 to 1435 A.D.). *Appl. Radiat. Isot.* 51(3): 279–283
603. Hein A., Tsolakidou A., Iliopoulos I., Mommsen H., Buxeda i Garrigos J., Montana G., Kilikoglou V (2002) Standardisation of elemental analytical techniques applied to provenance studies of archaeological ceramics: an inter laboratory study. *Analyst* 127(4): 542–553
604. Adan-Bayewitz D., Asaro F., Giauque R.D. (2001) Determining pottery provenance: Application of a new high-precision X-ray fluorescence method and comparison with instrumental neutron activation analysis. *Archaeometry* 41(1): 1–24
605. Garcia-Heras M., Blackman M.J., Fernandez-Ruiz R., Bishop R.L. (2001) Assessing ceramic compositional data: a comparison of total reflection X-ray fluorescence and instrumental neutron activation analysis on late Iron Age Spanish Celtiberian ceramics. *Archaeometry* 43(3): 325–347
606. Seelenfreund A., Miranda J., Dinator M.I., Morales J.R. (2002) The provenance of archaeological obsidian artifacts from Northern Chile determined by source-induced X-ray fluorescence. *J. Radioanal. Nucl. Chem.* 251(1): 15–19
607. Wobrauschek P., Halmetschlager G., Zamini S., Jokubonis C., Trnka G., Karwoski M. (2000) Energy-dispersive X-Ray fluorescence analysis of celtic glasses. *X-Ray Spectrom.* 29(1): 25–33
608. Kunicki-Goldfinger J., Kierzek J., Kasprzak A., Malozewska-Buko B. (2000) A study of eighteenth century glass vessels from Central Europe by X-ray fluorescence analysis. *X-Ray Spectrom.* 29: 310–316
609. Heck M., Hoffmann P. (2000) Coloured opaque glass beads of the Merovingians. *Archaeometry* 42(2): 341–357
610. Jembrih D., Schreiner M., Peev M., Krejsa P., Clausen C. (2000) Identification and classification of iridescent glass artefacts with XRF and SEM/EDX. *Mikrochim. Acta* 133(1–4): 151–157

611. Jembrih-Simbürger D., Neelmeijer C., Schalm O., Frederickx P., Schreiner M., De Vis K., Mäder M., Schryvers D., Caen J. (2002) The colour of silver stained glass—analytical investigations carried out with XRF, SEM/EDX, TEM and IBA. *J. Anal. Atom Spectrom.* 4: 321–328
612. Bonizzoni L., Galli A., Milazzo M. (2002) Analyses of the stained glasses of Certosa di Pavia. *X-Ray Spectrom.* 31(1): 35–38
613. Janssens K., Vittiglio G., Dereadt I., Aerts A., Vekemans B., Vincze L., Wei F., Deryck, Schalm O., Adams F., Rindby A., Knöchel A., Simionovici A., Snigirev A. (2000) Use of microscopic XRF for non-destructive analysis in art and archeometry. *X-Ray Spectrom.* 29(1): 73–91
614. Wegstein M., Urban H., Rostam-Khani P., Wittershagen A., Kolbesen B.O. (1997) Total-reflection X-ray fluorescence spectrometry, a powerful tool for semi-quantitative analysis of archaeological glass samples. *Spectrochim. Acta Part B* 52: 1057–1061
615. Röhrs S., Stege H. (2004) Analysis of Limoges painted enamels from the 16th to 19th centuries by using a portable micro X-ray fluorescence spectrometer. *X-Ray Spectrom.* 33: 396–401
616. Douglas J.G., Chase W.T. (2001) Examination of two Eastern Zhou Jade and Gold Assemblages from Jincun, Near Luoyang, Henan Province, China, and implications for the original configuration of the Freer Pectoral. *Stud. Conserv.* 46: 35–48
617. Joseph D., Lal M., Shinde P.S., Padalia B.D. (2000) Characterization of gem stones (rubies and sapphires) by energy-dispersive X-ray fluorescence spectrometry. *X-ray spectrom.* 29: 147–150
618. Elen S., Fritsch E. (1999) The separation of natural from synthetic colourless sapphire. *Gems & Gemology* 35(1): 30–41
619. Adams F., Adriaens A., Aerts A., De Raedt I., Janssens K., Schalm O. (1997) Micro and surface analysis in art and archaeometry. *J. Anal. Atom Spect.* 12: 257–265
620. Potts P.J., Webb P.C., Williams-Thorpe O. (1997) Investigation of a correction procedure for surface irregularity effects based on scatter peak intensities in the field analysis of geological and archaeological rock samples by portable X-ray fluorescence spectrometry. *J. Anal. Atom Spect.* 12: 769–776
621. Van Bohlen A., Meyer F. (1997) Microanalysis of old violin varnishes by total-reflection X-ray fluorescence. *Spectrochim. Acta Part B* 52: 1053–1056
622. Janssens K., Vincze L., Vekemans B., Williams C.T., Radtke M., Haller M., Knöchel A. (1999) The non-destructive determination of REE in fossilized bone using synchrotron radiation induced K-line X-ray microfluorescence analysis. *Fresenius' J. Anal. Chem.* 363: 413–420
623. Kuszumow A., Vekemans B., Schalm O., Dorriné W., Chevallier P., Dillmann P., Chul-Un Ro, Janssens K., van Grieken R. (1998) Analyses of petrified wood by electron, X-ray and optical microprobes. *J. Anal. Atom Spect.* 13: 319–333
624. Bartoll J., Unger A., Püschner K., Stege H. (2003) Micro-XRF investigations of chlorine-containing wood preservatives in art objects. *Stud. Conserv.* 48(3): 195–202
625. Schweizer, F.; Friedman; A.M.: *Archaeometry* **14** (1972) 103–107
626. (a) Merrick, J.M.; Metcalf, D.M.: *Archaeometry* **11** (1969) 61–65 (b) Howkes, S.C.; Merrick, J.M.; Metcalf, D.M.: *Archaeometry* **9** (1966) 98–138
627. Klockenkämper, R.; Hasler, K.: *Fresenius Z. Anal. Chem.* **289** (1978) 346–352

628. Uzonyi, I.; Bugoi, R.; Sasanu, A.; Kiss, A.Z.; Constantinescu, B.; Torbagyi, M.: Nucl. Instr. And Meth. In Phys. Res. **B 161–163** (2000) 748–752
629. Archibald, M.M.; Cowell, M.R.: “The fineness of Northumbria sceattas” in Metallurgy in Numismatics **2**(Ed. by Oddy), The Royal Numismatic Society Special Publication No. 19 (1988), London, pp. 55–64
630. (a) Emeleus, V.M.: Archaeometry **1** (1958) 6–15 (b) Ravetz, A.: Archaeometry **6** (1963) 46–55 (c) Blykssen, H.; Smith, Ph. B.: Archaeometry **5** (1962) 113–118 (d) Thiele, R.W.; Aung Khin, U.; Kyaw, U.: Archaeometry **14** (1972) 199–219 (e) Barrandon, J.N.; Callu, J.P.; Brenot, C.: Archaeometry **19** (1977) 173–186
631. (a) Reimers, P.; Lutz, G.J.; Segebade, C.: Archaeometry **19** (1977) 167–172 (b) Weise, H.P.; Segebade, C.: J. Radioanal. Chem. **49** (1979) 95–102 (c) Morrisson, C.; Barrandon, J.N.; Bendall, S.: in Metallurgy in Numismatics **2**(Ed. by Oddy), The Royal Numismatic Society Special Publication No. 19 (1988) London, pp. 23–40
632. Carter, G.F.; Caley, E.R.; Carlson, J.H.; Carriveau, G.W.; Hughes, M.J.; Rengan, K.; Segebade, C.: Archaeometry **25** (1983) 201–213
633. “Code of practice for the technical examination of numismatic material” in Metallurgy in Numismatics **2**(Ed. by Oddy), The Royal Numismatic Society Special Publication No. 19 (1988), London, pp.129–132
634. Hall, E.T.: Archaeometry **3** (1960) 29–35
635. Ferreira, G.P.; Gil, F.B.: Archaeometry **23** (1981) 189–197
636. Mommsen, H.; Schmittinger, T.: Archaeometry **23** (1981) 71–76
637. Janssens, K.; Vittiglio, G.; Deraedt, I.; Aerts, A.; Vekemans, B.; Vincze, L.; Wie, F.; Deryck, I.; Schalm, O.; Adams, F.; Rindby, A.; Knöchel, A.; Simionovici, A.; Snigirev, A.: X-Ray Spectrom. **29** (2000) 73–91
638. Hall, E.T.: Archaeometry **4** (1961) 62–66
639. Mantler, M.; Schreiner, M.: X-Ray Spectrom. **29** (2000) 3–17
640. (a) Condamin, J.; Picon, M.: Archaeometry **7** (1964) 98–105 (b) Condamin, J.; Picon, M.: “Changes suffered by coins in the course of time and the influence of these on the results of different methods of analysis” in Methods of chemical and Metallurgical Investigation of ancient coins, Royal Numismatic Society (1972) London
641. Delamare, F.; Montmitonnet, P.; Morrisson, C.: in Metallurgy in Numismatics **2**(Ed. by Oddy), The Royal Numismatic Society Special Publication No. 19 (1988), London, pp. 41–53
642. Calliari, I.; Magrini, M.; Zambon, A.; Guerrieco, P.; Martini, R.: X-Ray Spectrochim. **28** (1999) 86–90
643. Platzbarzdis, A.: “Die königlich schwedische Münze in Livland”, Almquist & Wiksell, Stockholm 1968, S. 122
644. Beauchesne, F.; Barrandon, J.N.; Alves, L.; Gil, F.B.; Guerra, M.F.: Archaeometry **30** (1988) 187–197
645. Linke, R.; Schreiner, M.: Microchim Acta **133** (2000) 165–170
646. Cronyn, J.; Foley, K.: “Numismatik and Conservation: The Conservator’s view” in Museums Journal **79** (1979), Nr. 1 to 3; Pirie, E.: “Numismatik and Conservation: A Numismatic View” in Museums Journal **79** (1979) Nr. 1
647. Florkowski, T.; Sto’s, Z.: Archaeometry **17** (1975) 165–175
648. Zwicky-Sobczyk, C.N.; Stern, W.B.: Archaeometry **39** (1997) 393–405
649. Carter, G.F.: Archaeometry **7** (1965) 106–113
650. Carter, F.: Anal. Chem. **36** (1964) 1264–1268

651. Winkowsky, H.: "Münzen pflegen", Kleine numismatische Bibliothek 3 (1974) Battenberg Verlag, München
652. Al-Kofahi, M.M.; Al-Tarawneh, K.F.: X-Ray Spectrom. **29** (2000) 39–47
653. Mandal, A.C.; Sarkar, M.; Bhattacharya, D.: Eur. Phys. J. AP **17** (2002) 81–84
654. Al-Kofahi, M.M.; Al-Tarawneh, K.F.; Shobaki, J.M.: X-Ray Spectrom. **26** (1997) 10–14
655. Stahl, A.M.; Gaspar, P.P.; Striegel, M.F.: in Metallurgy in Numismatics **2** (Ed. by Oddy), The Royal Numismatic Society Special Publication No. 19 (1988), London, pp. 87–93
656. Lutz, J.; Pernicka, E.: Archaeometry **38** (1996) 313–323
657. Cowell, M.: in X-ray microfluorescence analysis applied to archaeology (ed. T. Hackens et al.), PACT 1 Strasbourg (1977) 76–85
658. Stankiewicz, W.; Fudal, A.; Wojtowicz, M.: X-ray Spectrom. **12** (1983) 92–96
659. Klockenkämper, R.; Becker, M.; Otto, H.: Spectrochim. Acta **45B** (1990) 1043–1051
660. Auer, E.; Rehren, T.; von Bohlen, A.; Kirchner, D.; Klockenkämper, R.: Metalla **5** (1998) 71
661. Reiff, F.; Bartels, M.; Ortner, H.M.: Fresenius J. Anal Chem **371** (2001) 1146–1153
662. (a) Klockenkämper, R.; Hasler, K.: Fresenius Z. Anal. Chem. **290** (1978) 212–216 (b) Klockenkämper, R.; Bubert, H.; Hasler, K.: Archaeometry **41** (1999) 311–320
663. Butcher, K.: The American Journal of Numismatics **9** (1997) 17–35
664. Carter, G.F.; Carter, W.H.: Archaeometry **16** (1974) 201–209
665. Gale, N.H.; Gentner, W.; Wagner, G.A.: "Mineralogical and geographical Silver sources of archaic Greek coinage" in Metallurgy in Numismatics **1** (Ed. by Metcalf and Oddy), The Royal Numismatic Society Special Publication No. 13 (1980), London, pp. 3–49
666. Metcalf, D.M.; Schweizer, F.: Archaeometry **13** (1971) 177–190
667. Hrabanek, J.: Jb. Nass. Ver. Naturkde **123** (2002) 105–124
668. Cowell, M.R.; Lowick, N.M.: in Metallurgy in Numismatics **2** (Ed. by Oddy), The Royal Numismatic Society Special Publication No. 19 (1988), London, pp. 65–74
669. Constantinescu, B.; Cojocaru, V.; Bugoi, R.; Sasianu, A.: Proceeding of EPAC 2000, Vienna, Austria
670. Bowman, R.; Friedmann, A.M.; Learner, J.; Milsted, J.: Archaeometry **17** (1975) 157–163
671. Brissaud, I.; Wang, J.X.; Chevalier, P.: Nucl. Inst. Meth. **B49** (1990) 305
672. (a) Das, H.A.; Zonderhuis, J.: Archaeometry **7** (1964) 90–94 (b) Oddy, W.A.: Archaeometry **14** (1972) 109–117
673. Bayard A.M., Stoney A.D., The PLM/Microscope: An electron microscope for use on a light microscope stage designed for trace evidence analysis, Microscope, 1999, 47, 209–228
674. Christensen L.H., Drabaek I., Energy-dispersive X-ray fluorescence spectrometry of industrial paint samples, Anal. Chimica. Acta, 1986, 188, 15–24
675. Cousins D., Rendle D., Nolan P., The application of microspectrophotometry, X-ray diffraction and electron probe microanalysis to the analysis pigments in paints, J. Forens. Sci. Soc., 1984, 24, 348

676. Fischer R., Hellmiss G., Principles and forensic applications of X-ray diffraction and X-ray fluorescence, *Advances in Forensic Science*, Vol. 2, Medical Publishers, Inc., Chicago, IL, 1989, 129–158
677. Henson M.L., Jergovich T.A., Scanning electron microscopy and energy dispersive X-ray spectrometry (SEM/EDX) for the forensic examination of paints and coatings, in *Forensic Examination of Glass and Paint* (ed. B. Caddy) Taylor & Francis, London, 2001, 243–270
678. Mantler M., Schreiner M., X-ray fluorescence spectrometry in art and archeology, *X-ray spectrom.*, 2000, 29, 3–17
679. Massonnet G., Comparison of X-ray fluorescence and X-ray diffraction techniques for the forensic analysis of automotive paint, *Crime Lab. Dig.*, 1995, 22, 321–326
680. Stoecklein W., Becker S., Paint and Glass—A review, report to 13th INTERPOL Forensic Science Symposium, Lyon, October 16–19 2001
681. Suzuki E.M., Infrared spectra of U.S. automobile original topcoats (1974–1989): III in situ identification of some organic pigments used in yellow, orange and brown non-metallic and brown metallic finishes-benzimidazolones, *J. Forens. Sci.*, 1997, 42, 619–648
682. Thronton J.I., Forensic paint examinations, in *Forensic Science Handbook* (ed. R. Saferstein) Prentice Hall, New Jersey, 1982, 529–571
683. Zeichner A., Levin N., Landau E., A study of paint coat characteristics produced by spray paints from shaken and nonshaken spray cans, *J. Forens. Sci.*, 1992, 37(2), 542–555
684. Zięba-Palus J. Selected cases of forensic paint analysis, *Science and Justice*, 1999, 39(2), 123–127
685. Zięba-Palus J. Application of micro-Fourier transform infrared spectroscopy to the examination of paint samples, *J. Mol. Struct.*, 1999, 511–512, 327–335
686. Barbooti M.M., Zaki N.S., Baha-Udolin S.S., Hassan E.B., Use of silica gel in the preparation of used lubricating oil samples for the determination of wear metals by flame AAS, *Analyst*, 1990, 115, 1059–1061
687. Espinoza E.O., Mann M.J., Leonardo L., Copeland A., Differentiation of automotive and locomotive lubricant oil, *J. Forens. Sci.*, 1994, 39(3), 839–83
688. Freitag K., Reus U., Fleischhauer J., The application of TXRF spectrometry for determination of trace metals in lubricating oils, *Fresenius Z. Anal. Chem.*, 1989, 334, 675
689. Liu Y.W., Harding A.R., Leyden D.E., Determination of wear metals in oil using energy dispersive X-ray spectrometry, *Anal. Chim. Acta*, 1986, 180, 349–355
690. Lloyd J.B.F., Evett I.W., Dubery J.M., Examination of petroleum products of high relative molecular mass for forensic science purposes by synchronous fluorescence spectroscopy, *J. Forens. Sci.*, 1980, 25(3), 589–602
691. Schäfer H.P., Meduna U., Element analyse in Frisch- und Altölen, *Fresenius Z. Anal. Chem.*, 1989, 334, 359–360
692. Siegel J.A., Fisher J., Gilna C., *J. Forens. Sci.*, 1985, 30, s. 741–759
693. Vigler M.S., Gaylor V.F., Trace metals analysis in petroleum products by ASS, *Appl. Spectroscopy* 1974, 28(4), 342–344
694. Zięba-Palus J., Examination of used motor oils by flame AAS for criminalistic purposes. A diagnostic study, *Forens. Sci.*, 1998, 91, 171–179

695. Zięba-Palus J., Kościelniak P., Differentiation of motor oils by infrared spectroscopy and elemental analysis for criminalistic purposes, *J. Mol. Struct.*, 1999, Vol. 482–483, 531–536
696. Almirall J.R., *Elemental analysis of glass fragments in Forensic Examination of Glass and Paint* (ed. B. Caddy) Taylor & Francis, 2001
697. Almirall J.R., Cole M.D., Gettinby G., Furton. K.G., Discrimination of glass sources using elemental composition and refractive index: development of predictive models, *Science & Justice*, 1998, 38(2), 93–100
698. Becker S., Gunaratnam L., Hicks T., Stoecklein W., Warman G., The differentiation in the float glass using refractive index and elemental analysis: Comparisons of techniques, *Prob. Forens. Sci.*, 2001, XLVI, 80–92
699. Brożek-Mucha Z., Zadora G., Differentiating between various types of glass using SEM-EDX elemental analysis. A preliminary study, *Problems of Forensic Sciences*, 1998, Vol. XXXVII, 68–89
700. Buscalia J.A., Elemental analysis of small glass fragments in forensic sciences, *Anal. Chimica Acta*, 1994, 228, 17–24
701. Curran J.M., Triggs C.M., Almirall J.R., Buckleton. J.S., Walsh. K.A.J., The interpretation of elemental composition measurements from forensic glass evidence, *Science & Justice*, 1997, 37(4), 241–249
702. Engstrom P., Laesson S., Rindby A., Stocklassa B., Nuclear instrumentation and methodology : B36 1998, 222
703. KlockenKamper R., Knoth J., Prange A., Schwenke H., Total reflection X-ray fluorescence spectroscopy, *Anal. Chem.*, 1992, 64, 1115A–1121A
704. Koons R., Rebbert P., Comparison of refractive index, energy dispersive X-ray fluorescence and inductively coupled plasma atomic emission spectrometry for forensic characterisation of sheet glass fragments, *J. Anal. Atomic Spectrom.*, 1991, 6, 451–456
705. Kubic T., Buscalia J., Total reflection X-ray fluorescence spectrometry- further application to elemental profiles on trace evidence, *Proceedings of The American ACADEMY OF Forensic Science Meeting*, Nashville, TN, February, 1996, 19–24, 2:50
706. Kuisma-Kursula P., Accuracy, precision and detection limits of SEM/WDS, SEM/EDS and PIXE in the multielemental analysis of medieval glass, *X-ray spectrom.*, 2000, 29, 111–118
707. Rindby A., Engstrom P., Larsson S., Stocklassa B., *X-ray spectrom.*, 1989, 18, 109
708. Ryland S., Sheet or container? Forensic glass comparisons with an emphasis on source classification, *J. Forens. Sci.*, 1986, 31, 1314–1329
709. Terry C.M., van Reiscen A., Lynch B.F., Quantitative analysis of glasses used within Australia, *Forensic Sci. Int.* 1985, 27, 247–260
710. Zadora G., Brożek-Mucha Z., The use of chosen methods of statistical and chemometric analysis in forensic examinations of glasses, *Problems of Forensic Sciences*, Vol. XL, 1999, 33–71
711. Brożek-Mucha Z., SEM-EDX study of inorganic gunshot residues from Makarov 9 mm ammunition, *Problems of Forensic Sciences*, Vol. XLI, 2000, 62–89
712. Brożek-Mucha Z., Zadora G., Grouping of ammunition types by means of frequency of occurrence of GSR, *Forensic Science International*, 2003, 135(2), 97–104

713. Charpentier B., Desrochers C., Analysis of primer residue from lead free ammunition by X-ray microfluorescence, *J. Forens. Sci.*, 2000, 45(2), 447–452
714. DeGaetano D., Siegel J.A., Klomparens K.L., A comparison of three techniques developed for the sampling and analysis of gunshot residue by SEM/EDX, *J. Forens. Sci.*, 1992, 37, 281–300
715. Keeley R.H., Nolan P.J., Automatic Particle analysis, Metropolitan Police Lab. Rep. and Rep. To Interpol Meet., Paris, London Metropolitan Police. London, U.K. 1986
716. Mosher P.V., McVicar M.J., Randall E.D., Sild E.H., Gunshot residue-similar particles produced by fireworks, *Can. Soc. Forens. Sci. J.*, 1998, 31(2), 157–168
717. Niewoehner L., Wenz W., Application of focused ion beam systems in gunshot residue investigations, *J. Forens. Sci.*, 1999, 44, 105–109
718. Phillips S.A., Pyrotechnic residues analysis-detection and analysis of characteristic particles by scanning electron microscopy/energy dispersive spectroscopy, *Science & Justice*, 2001, 41, 73–80
719. Romolo F.S., Margot P., Identification of gunshot residue: a critical review, *Forens. Sci.*, 2001, 119, 195–211
720. White R.S., Owens A.D., Automation of gunshot residue detection and analysis by scanning electron microscopy/energy dispersive X-ray analysis, *J. Forens. Sci.*, 1987, 32, 321–330
721. Wolten G.M., Nesbitt R.S., Calloway A.R., Loper G.L., Jones P.E., Particle analysis for the detection of gun shot residue: Scanning electron microscopy/energy dispersive X-ray characterisation on hand deposits, *J. Forens. Sci.*, 1979, 24(2), 409–422
722. Zeichner A., Foner H.A., Dvorachek M., Bergman P., Levin N., Concentration techniques for the detection of GSR by SEM/EDX, *J. Forens. Sci.*, 1989, 34(2), 312–320
723. Zeichner A., Levin N., Dvorachek M., Gunshot residues formed by using ammunitions that have mercury fulminate based primers, *J. Forens. Sci.*, 1992, 37, 1567–1573
724. Zeichner A., Levin N., More on the uniqueness of gunshot residues (GSR) particles, *J. Forens. Sci.*, 1997, 41, 1027–1028
725. M.L. Carvalho, J. Brito, M.A. Barreiros, Study of trace element concentration in human tissues by EDXRF spectrometry. *X-Ray Spectrometry* **27**(3) (1998), 198204
726. K. Geraki, M.J. Farquharson, *An x-ray fluorescence system for measuring trace element concentrations in breast tissue*. *Radiat. Phys. Chem.* **61**(1–6) (2001), 603–605
727. H. Feldstein, Y. Cohen, C. Shenberg, A. Klein, M. Kojller, W. Maenhaut, J. Cafmeyer, R. Cornelis, *Comparison between levels of trace elements in normal and inoculated mice by XRF and PIXE*. *Biol. Trace Elem. Res.* **61**(2) (1998), 169–180
728. M.L. Carvalho, A.F. Marques, *X-ray fluorescence spectrometry: applications in trace elements studies in human tissues from patients with cirrhosis*. *X-Ray Spectrometry* **30**(6) (2001), 397–402
729. M.L. Carvalho, R.A. Pereira, J. Brito, *Heavy metals in soft tissues of *Tursiops truncatus* and *Delphinus delphis* from west Atlantic Ocean by X-ray spectrometry*. *Sci. Tot. Environ.* **292**(3) (2002), 247–254

730. H.J. Sanchez, C. Perez, R.D. Perez, *XRF analysis of arsenic uptaking in mice organs and tissues*. Nucl. Instrum. Methods Phys. Res., Sect. B **124**(1) (1997), 140–142
731. J. Boman, A. Wagner, H. Brauer, D.V. Binh, *Trace elements in tissues from Vietnamese animals*. X-Ray Spectrometry **30**(6) (2001), 388–392
732. D. Dhawan, A. Singh, B. Singh, H.K. Bandhu, B. Chand, N. Singh, *Effect of lithium augmentation on the trace elemental profile in diabetic rats*. Biometals **12**(4) (1999), 375–382
733. J. Senda, N. Hashiguchi, Y. Tanaka, S. Komiyama, M. Shimahara, K. Kono, T. Watanabe, T. Dote, K. Usuda, *Determination of bone calcium and phosphorus in osteoporosis model rats by X-ray fluorescence analysis*. Trace Elem. Electrolytes **18**(2) (2001), 55–58
734. A. Ates, M. Ertugrul, *Determination of trace elements of emboli (clots) in the cardiovascular systems of patients by dispersive x-ray fluorescence analysis*. Instrum. Sci. Technol. **30**(4) (2002), 449–454
735. B. Alföldy, S. Torok, I. Balashazy, W. Hofmann, R. Winkler-Heil, EPMA and XRF characterization of therapeutic cave aerosol particles and their deposition in the respiratory system. X-Ray Spectrometry **31**(5) (2002), 363–367
736. A. Goel, D.P. Chauhan, D.K. Dhawan, *Protective effects of zinc in chlorpyrifos induced hepatotoxic biochemical and trace elemental study*. Biol. Trace Elem. Res. **74**(2) (2000), 171–183
737. N.Q. Liu, Q. Xu, X.L. Hou, P.S. Liu, Z.F. Chai, L. Zhu, Z.Y. Zhao, Z.H. Wang, Y.F. Li, *The distribution patterns of trace elements in the brain and erythrocytes in a rat experimental model of iodine deficiency*. Brain Res. Bull. **55**(2) (2001), 309–312
738. R. Schindler, C. Stahl, S. Venz, K. Ludat, W. Krause, U. Frei, *Removal of contrast media by different extracorporeal treatments*. Nephrol. Dial. Transplant. **16**(7) (2001), 1471–1474
739. Y. Dede, H.N. Erten, A. Zararsiz, N. Efe, *Determination of trace element levels in human scalp hair in occupationally exposed subjects by XRF*. J. Radioanal. Nucl. Chem. **247**(2) (2001), 393–397
740. A. MacPherson, J. Bacso, *Relationship of hair calcium concentration to incidence of coronary heart disease*. Sci. Tot. Environ. **255**(1–3) (2000), 11–19
741. J.J. Meitin, F. De La Fuente, A. Mendoza, *Some achievements on EDXRF analysis in Cuba. Applications in industry, medicine and environment*. [Nat. Cent. Scient. Res. (CNIC), Havana, Cuba]. Proceedings of the European Conference on Energy Dispersive X-Ray Spectrometry (EDXRS-98), Bologna, Italy, June 7–12, 1998 (1999), 351–355
742. T.Y. Toribara, *Analysis of single hair by XRF discloses mercury intake*. Hum. Exp. Toxicol. **20**(4) (2001), 185–188
743. M.L. Carvalho, F.E. Rodrigues Ferreira, M.C.M. Neves, C. Casaca, A.S. Cunha, J.P. Marques, P. Amorim, A.F. Marques, M.I. Marques, *Arsenic detection in nineteenth century Portuguese King post mortem tissues by energy-dispersive x-ray fluorescence spectrometry*. X-Ray Spectrometry **31**(4) (2002), 305–309
744. A.C. Todd, *L-shell x-ray fluorescence measurements of lead in bone: system development*. Phys. Med. Biol. **47**(3) (2002), 507–522
745. A.C. Todd, *L-shell x-ray fluorescence measurements of lead in bone: theoretical considerations*. Phys. Med. Biol. **47**(3) (2002), 491–505

746. V.S. Kondrashov, S.J. Rothenberg, *How to calculate lead concentration and concentration uncertainty in XRF in vivo bone lead analysis*. Appl. Radiat. Isot. **55**(6) (2001), 799–803
747. A.C. Todd, S. Carroll, C. Geraghty, F.A. Khan, E.L. Moshier, S. Tang, P.J. Parsons, *L-shell x-ray fluorescence measurements of lead in bone: accuracy and precision*. Phys. Med. Biol. **47**(8) (2002), 1399–1419
748. J.A.A. Brito, F.E. McNeill, D.R. Chettle, C.E. Webber, C. Vaillancourt, *Study of the relationships between bone lead levels and its variation with time and the cumulative blood lead index, in a repeated bone lead survey*. J. Environ. Monit. **2**(3) (2000), 271
749. Y.W. Cheng, J. Schwartz, D. Sparrow, A. Aro, S.T. Weiss, H. Hu, *Bone lead and blood lead levels in relation to baseline blood pressure and the prospective development of hypertension. (The Normative Aging Study)*. Am. J. Epidemiol. **153**(2) (2001), 164–171
750. L. Gerhardsson, J. Borjesson, S. Mattsson, A. Schutz, S. Skerfving, *Chelated lead in relation to lead in bone and ALAD genotype1*. Environ. Res. Sect. A **80**(4) (1999), 389–398
751. Y. Cheng, J. Schwartz, P.S. Vokonas, S.T. Weiss, A. Aro, H. Hu, *Electrocardiographic conduction disturbances in association with low-level lead exposure (The Normative Aging Study)*. Am. J. Cardiol. **82**(5) (1998), 594–599
752. J. Borjesson, S. Mattsson, M. Alpstein, *Trace element concentrations studied in vivo using X-ray fluorescence analysis*. Appl. Radiat. Isot. **49**(5–6) (1998), 437–445
753. R. Kadhim, A. Al-Hussany, P.A. Ali, D.A. Hancock, A.M. El-Sharkawi, *In vivo measurement of platinum in the kidneys using X-ray fluorescence*. In Vivo Body Compos. Stud. **904** (2000), 263–266
754. D.S. MacLean, J.D. Robertson, M. Jay, *Monitoring the retention of a protein antigen in complete Freund's adjuvant, alum, and pluronic F-127 gel formulations by X-ray fluorescence*. Pharm. Dev. Technol. **6**(2) (2001), 241–246
755. A.P. Bagshaw, M.F. Farquharson, *Simultaneous determination of iron, copper and zinc concentrations in skin phantoms using XRF spectrometry*. X-Ray Spectrometry **31** (2002), 47–52
756. M.J. Farquharson, D.A. Bradley, *The feasibility of a sensitive low-dose method for the in vivo evaluation of Fe in skin using K-shell x-ray fluorescence (XRF)*. Phys. Med. Biol. **44**(4) (1999), 955–965
757. M.J. Farquharson, A.P. Bagshaw, J.B. Porter, R.D. Abeysinghe, *The use of skin Fe levels as a surrogate marker for organ Fe levels, to monitor treatment in cases of iron overload*. Phys. Med. Biol. **45**(2) (2000), 1387–1396
758. V. Zaichick, N. Ovchjarenko, S. Zaichick, *In vivo energy dispersive x-ray fluorescence for measuring the content of essential and toxic trace elements in teeth*. Appl. Radiat. Isot. **50**(2) (1999), 283–293
759. P. Bloch, I.M. Shapiro, L. Soule, A. Close, B. Revich, *Assessment of lead exposure of children from K-XRF measurements of shed teeth*. Appl. Radiat. Isot. **49**(5–6) (1998), 703–705
760. S.S. Ranaweera, P.M.D.W. Sudarshanie, R. Hewamanna, *X-ray fluorescence technique for the assessment of pollution by heavy metals and their uptake by some inhabitant Flora of Lunawa Lagoon, Sri Lanka*. Harmonization Health Relat. Environ. Meas. Using Nucl. Isot. Tech., Proc. Int. Symp. 1996, International Atomic Energy Agency, Vienna, Austria (1997), 451–456

761. A. Mendoza, R. Cesareo, M. Valdes, J.J. Meitin, R. Perez, Y. Lorente, *Energy dispersive x-ray fluorescence analysis of marine pollution indicators*. J. Radioanal. Nucl. Chem. **240**(2) (1999), 459–465
762. M.F. Araujo, A. Cruz, M. Humanes, M.T. Lopes, J.A.L. Da Silva, J.J.R.F. Da Silva, *Elemental composition of demospongiae from the eastern Atlantic coastal waters*. Chem. Speciation Bioavailability **11**(1) (1999), 25–36
763. T. Akyuz, A. Bassari, C. Bolcal, E. Sener, M. Yildiz, R. Kucer, Z. Kaplan, G. Dogan, S. Akyuz, *Radioisotope X-ray fluorescence and neutron activation analyses of the trace element concentrations of the rainbow trout*. Czech. J. Phys. **49**(Suppl. 1, Pt. 1, 13th Radiochemical Conference 1998) (1999), 389–393
764. A. Senhou, A. Chouak, R. Cherkaoui, Z. Moutia, M. Lferde, A. Elyahyaoui, T. El Khoukhi, M. Bounakhla, K. Embarche, A. Gaudry, S. Ayrault, M. Moskura, *Sensitivity of biomonitors and local variations of element concentrations in air pollution biomonitoring*. J. Radioanal. Nucl. Chem. **254**(2) (2002), 343–349
765. A. Senhou, A. Chouak, R. Cherkaoui, M. Lferde, A. Elyahyaoui, T. El Khoukhi, M. Bounakhla, K. Embarche, X. Bertho, A. Gaudry, S. Ayrault, D. Piccot, *Comparison of 14 MeV-NAA, K₀-NAA and ED-XRF for air pollution biomonitoring*. J. Radioanal. Nucl. Chem. **253**(2) (2002), 247–252
766. C. Larsson, H.S. Helmissaari, *Accumulation of elements in the annual rings of Scots pine trees in the vicinity of a copper-nickel smelter measured by scanning EDXRF*. X-Ray Spectrometry **27**(2) (1998), 133–139
767. A. Viksna, E. Selin Lindgren, P. Standzenieks, *Analysis of pine needles by XRF scanning techniques*. X-Ray Spectrometry **30**(4) (2001), 260–266
768. M.J. Anjos, R.T. Lopes, E.F.O. Jesus, S.M. Simabuco, R. Cesareo, *Quantitative determination of metals in radish using x-ray fluorescence spectrometry*. X-Ray Spectrometry **31**(2) (2002), 120–123
769. P.H. Aragao, R. Cesareo, E.A.D. Fernandes, F. Balogun, U. Prota, M. Fiori, *Iron in olive tree leaves in the Mediterranean area*. J. Radioanal. Nucl. Chem. **249**(2) (2001), 509–512
770. M.J. Salvador, G.N. Lopes, V.F. Nascimento, O. Zucchi, *Quality control of commercial tea by x-ray fluorescence*. X-Ray Spectrometry **31**(2) (2002), 141–144
771. E.I. Obiajunwa, A.C. Adebajo, O.R. Omobuwajo, *Essential and trace element contents of some Nigerian medicinal plants*. J. Radioanal. Nucl. Chem. **252**(3) (2002), 473–476
772. L. Racz, A. Bumbalova, M. Harangozo, J. Tolgyessy, O. Tomecek, *Determination of cesium and selenium in cultivated mushrooms using radionuclide x-ray fluorescence technique*. J. Radioanal. Nucl. Chem. **245**(3) (2000), 611–614
773. U. Cevik, E. Ergen, G. Budak, A. Karabulut, E. Tirasoglu, G. Apaydin, A.I. Kopya, *Elemental analysis of Akcaabat tobacco and its ash by EDXRF spectrometry*. J. Quant. Spectrosc. Radiat. Transf. **78**(3–4) (2003), 409–415
774. D. Joseph, M. Lal, H.N. Bajpai, P.K. Mathur, *Levels of trace elements of few Indian spices by energy dispersive x-ray fluorescence (EDXRF) method*. J. Food Sci. Technol. **36**(3) (1999), 264–265
775. E. Almeida, V.F. Nascimento, E.P.E. Valencia, R. Silva, *Concentrations of Fe, Cu and Zn in rum by EDXRF using APDC preconcentration*. J. Radioanal. Nucl. Chem. **252**(3) (2002), 541–544

776. V. Rewatkar, A.A. Saoji, K.G. Rewatkar, *Studies of trace elements in some varieties of rice (Oryza sativa) by Energy Dispersive X-ray Fluorescence technique*. Asian J. Chem. **13**(1) (2001), 206–210
777. M.Y. Miah, M.K. Wang, M. Chino, *Energy dispersive x-ray fluorescence for rapid potassium, calcium, and chloride diagnosis in barley*. J. Plant Nutr. **22**(2) (1999), 229–235
778. R.E. Lopez de Ruiz, R.A. Olsina, A.N. Masi, *Different analytical methodologies for the preconcentration and determination of trace chromium by XRF in medicinal herbs with effects on metabolism*. X-Ray Spectrometry **31**(2) (2002), 150–153
779. A.V. Pukhovskij, N.V. Kovalev [Central Res. Inst. Agrochem. Service Agric. (CINAO), Moscow, Russia], Presented at International Congress on Analytical Chemistry, Moscow, Russia, June 15–21, 1997
780. J.P. Wheeler, N.D. Warren, *A dirichlet tessellation-based sampling scheme for measuring whole-body exposure*. Ann. Occup. Hyg. **46**(2) (2002), 209–217
781. N. Fukumoto, Y. Kobayashi, M. Kurahashi, I. Kojima, *X-ray fluorescent spectroscopy with a focused X-ray beam collimated by a glass capillary guide tube and element mapping of biological samples*. Spectrochim. Acta, Part B **54**(1) (1999), 91–98
782. J. Brazeau, R.K. Wong, *Analysis of gunshot residues on human tissues and clothing by x-ray microfluorescence*. J. Forensic Sci. **42**(3) (1997), 424–428
783. P. Wobrauschek, *Use of total reflection X-ray fluorescence analysis in the life sciences*. Biol. Trace Element Res. **43–45** (1994), 65–71
784. R. Klockenkämper, *Total reflection x-ray fluorescence analysis*. Wiley, New York (1997)
785. F. Adams, K. Janssens, A. Snigirev, *Microscopic x-ray fluorescence analysis and related methods with laboratory and synchrotron radiation sources*, J. Anal. At. Spectrom. **13** (1998), 319–331
786. R. Klockenkämper, A. von Bohlen, *Total reflection x-ray fluorescence moving towards nanoanalysis: a survey*. Spectrochim. Acta B **56** (2001), 2005–2018
787. P. Wobrauschek, *Total reflection x-ray fluorescence spectrometric determination of trace elements in the femtogram region: a survey*. J. Anal. At. Spectrom. **13** (1998), 333–337
788. G. Wiener, R. Günther, C. Michaelsen, J. Knoth, H. Schwenke, R. Borman, *Ion beam sputtering techniques for high-resolution concentration depth profiling with glancing-incidence x-ray fluorescence spectrometry*. Spectrochim. Acta B **52** (1997), 813–821
789. A. Prange, U. Reus, H. Schwenke, J. Knoth, *Optimization of TXRF measurements by variable incident angles*. Spectrochim. Acta B **54** (1999), 1505–1511
790. P. Wobrauschek, H. Aiginger, *X-ray fluorescence analysis in the ng region using total reflection of the primary beam*. Spectrochim. Acta B **35** (1980), 607–614
791. A. Prange, K. Kramer, U. Reus, *Boron nitride sample-carriers for total reflection X-ray fluorescence*. Spectrochim. Acta B **48** (2) (1993), 153–161
792. P. Hoffmann, K.H. Lieser, M. Hein, M. Flakowski, *Analysis of thin layers by total reflection x-ray fluorescence spectrometry*. Spectrochim. Acta B **44** (5) (1989), 471–476
793. P. Wobrauschek, H. Aiginger, *Analytical application of total reflection and polarized x-rays*. Fresenius Z. Anal. Chem. **324** (1986), 865–874

794. H. Yamaguchi, S. Itoh, S. Igarashi, K. Naitoh, R. Hasegawa, *TXRF analysis of solution samples using polyester film as a disposable sample-carrier cover*. Anal. Sci. **14** (1998), 909–912
795. M. Schmitt, P. Hoffmann, K.H. Lieser, *Perspex as sample-carrier in TXRF*. Fresenius Z. Anal. Chem. **328** (1987), 594–595
796. R. Klockenkämper, A. von Bohlen, *Elemental analysis of environmental samples by total reflection X-ray fluorescence: a review*. X-Ray Spectrometry **25** (1996), 156–162
797. A. Prange, H. Böttdeker, W. Michaelis, *Multi-element determination of trace elements in whole blood and blood serum by TXRF*. Fresenius Z. Anal. Chem. **335** (1989), 914–918
798. R. Klockenkämper, A. von Bohlen, B. Wiecken *Quantification in total reflection X-ray fluorescence analysis of microtome sections*. Spectrochim. Acta B **44** (5) (1989), 511–517
799. E.D. Greaves, G. Bernasconi, P. Wobrauschek, C. Streli: *Direct total reflection X-ray fluorescence trace element analysis of organic matrix materials with a semiempirical standard*. Spectrochim. Acta B **52** (1997), 923–933
800. M. Schmeling, F. Alt, R. Klockenkämper, D. Klockow: *Multi-element analysis by total reflection X-ray fluorescence spectrometry for the certification of lichen research material*. Fresenius J. Anal. Chem. **357** (1997), 1042–1044
801. C. Zarkadas, A.G. Karydas, T. Paradellis: *Applicability of direct total reflection X-ray fluorescence analysis in the case of human blood serum samples*. Spectrochim. Acta B **56** (2001), 2219–2228
802. M.L. Carvalho, P.J. Custódio, U. Reus, A. Prange: *Elemental analysis of human amniotic fluid and placenta by total reflection X-ray fluorescence and energy-dispersive X-ray fluorescence: child weight and maternal age dependence*. Spectrochim. Acta B **56** (2001), 2175–2180
803. A. Prange, *Total reflection x-ray spectrometry: method and applications*. Spectrochim. Acta B **44** (5) (1989), 437–452
804. L.M. Marcó P., E. Jiménez, E.A. Hernández C., A. Rojas, E.D. Greaves: *Determination of Zn/Cu ratio and oligoelements in serum samples by total reflection X-ray fluorescence spectrometry for cancer diagnosis*. Spectrochim. Acta B **56** (2001), 2195–2201
805. Á. Kelkó-Lévai, I. Varga, K. Zih-Perényi, A. Lásztity: *Determination of trace elements in pharmaceutical substances by graphite furnace atomic absorption spectrometry and total reflection X-ray fluorescence after flow injection ion-exchange preconcentration*. Spectrochim. Acta B **54** (1999), 827–833
806. M. Olsson, A. Viksna, H.-S. Helmisari: *Multi-element analysis of fine roots of Scots pine by total reflection X-ray fluorescence spectrometry*. X-Ray Spectrometry **28** (1999), 335–338
807. G. Tölg, R. Klockenkämper, *The role of total reflection x-ray fluorescence in atomic spectroscopy*. Spectrochim. Acta B **48** (2) (1993), 111–127
808. M. Dargie, A. Markowicz, A. Tajani, V. Valkovic: *Optimized sample preparation procedures for the analysis of solid materials by total reflection XRF*. Fresenius J. Anal. Chem. **357** (1997), 589–593
809. M. Wagner, P. Rostam-Khani, A. Wittershagen, C. Rittmeyer, B.O. Kolbesen, H. Hoffmann, *Trace element determination in drugs by total reflection x-ray fluorescence spectrometry*. Spectrochim. Acta B **52** (1997), 961–965

810. R.F. Burk, K.E. Hill, R. Read, T. Bellew, *Response of rat selenoprotein P to selenium administration and fate of its selenium*. Am. J. Physiol. **261** (1991), E26–E40
811. E.D. Greaves, L.M. Marcó Parra, A. Rojas, L. Sajo-Bohus, *Determination of platinum levels in serum and urine samples from pediatric cancer patients by TXRF*. X-Ray Spectrometry **29** (2000), 349–353
812. L.M. Marcó, E.D. Greaves, J. Alvarado: *Analysis of human blood serum and human brain samples by total reflection X-ray fluorescence spectrometry applying Compton peak standardization*. Spectrochim. Acta B **54** (1999), 1469–1480
813. R.F. Ruiz, J.D. Tornero, V.M. González, C. Alonso: *Quantification of Pt bound to DNA using total reflection X-ray fluorescence (TXRF)*. Analyst **124** (1999), 583–585
814. L. Benninghoff, D. von Czarnowski, E. Denkhau, K. Lemke: *Analysis of human tissues by total reflection X-ray fluorescence. Application of chemometrics for diagnostic cancer recognition*. Spectrochim. Acta B **52** (1997), 1039–1046
815. P. Wobrauschek, C. Streli, P. Kregsamer, W. Ladisich, R. Riederer: *Recent developments in TXRF with various excitation source*. J. Trace Microprobe Technol. **14** (1996), 103–117
816. A. Knöchel, F. Lechtenberg, M. Paulsen, A. Ranck, S. Staub, G. Weseloh: *Ortsabhängige Multielementanalysen in schadstoffbelasteten Lungengewebe von Arbeitern aus dem Uranbergbau*. ISBN: 3-924330-41-7, Hamburg (2001), 1–126
817. D. von Czarnowski, E. Denkaus, H. Lemke: *Determination of trace element distribution in cancerous and normal human tissues by total reflection X-ray fluorescence analysis*. Spectrochim. Acta B **52** (1997), 1047–1052
818. A. Kubala-Kuku, J. Braziewicz, D. Bana, U. Majewska, S. Gód, A. Urbaniak: *Trace element load in cancer and normal lung tissue*. Nucl. Instr. Meth. Phys. Res. B **150** (1999), 193–199
819. U. Majewska, J. Braziewicz, D. Bana, A. Kubala-Kuku, S. Gód, M. Pajek, M. Zadrozna, M. Jaskóla, T. Czyzewski, *Some aspects of statistical distribution of trace element concentrations in biomedical samples*. Nucl. Instr. Meth. Phys. Res. B **150** (1999), 254–259
820. T. Suzuki, A. Sasaki, I. Nakai, *Total reflection x-ray fluorescence analysis of cisplatin platinum in human cancerous tissues obtained by biopsy*. J. Trace Microprobe Techniques **19**(4) (2001), 547–561
821. J.M. Pérez, E.I. Montero, A.G. Quiroga, M.A. Fuertes, C. Alonso, C. Navarro-Ranninger, *Cellular uptake, DNA binding and apoptosis induction of cytotoxic trans-[PtCl₂(N,N-dimethylamine) (isopropylamine)] in A2780cisR ovarian tumor cells*. Metal Based Drugs **8** (1) (2001), 29–37
822. L. Tapia, M. Suazo, C. Hödar, V. Cambiazo, M. González, *Copper exposure modifies the content and distribution of trace metals in mammalian cultured cells*. BioMetals **16** (2003), 169–174
823. K. Günther, A. von Bohlen, *Simultaneous multi-element determination in vegetable foodstuffs and their respective cell fractions by total reflection X-ray fluorescence (TXRF)*. Z. Lebensm. Unters. Forsch. **190** (1990), 331–335
824. M. González, L. Tapia, M. Alvarado, J.D. Tornero, R. Fernández, *Intracellular determination of elements in mammalian cultured cells by total reflection X-ray fluorescence spectrometry*. J. Anal. At. Spectrom. **14** (1999), 885–888
825. A. Prange, H. Schwenke, *Trace element analysis using total reflection X-ray fluorescence spectrometry*. Adv. X-Ray Anal. **35** (1992), 899–923

826. V. Trunova, N. Parshina, V. Kondratyev, *Determination of the distribution of trace elements in human hair as a function of the position on the head by SRXRF and TXRF*. J. Synchrotron Rad. **10** (2003), 371–375
827. A. von Bohlen, P. Rechmann, J.L. Tourmann, R. Klockenkämper, *Ultramicro-analysis of dental plaque films by total reflection x-ray fluorescence*. J. Trace Elem. Electrolytes Health Dis. **8** (1994), 37–42
828. G. Bernasconi, M.C. Buoso, D. Ceccato, G. Cinque, M. Dargie, S. Galassini, G. Moschini, P. Passi, V. Valkovic, S. Varotto, A. Zadro, *PIXE and TXRF measurements of titanium levels in rabbit organs after endosseous implants insertion*. Nucl. Instr. Meth. Phys. Res. B **109/110** (1996), 372–374
829. D.M. Wamwangi, I.V.S. Rathore, S.K. Katia, M.J. Mangala, *Trace element analyses of pollen, bee tissue, and honey by total reflection and radioisotope excited x-ray fluorescence spectrometry*. J. Trace Microprobe Techniques **18** (2) (2000), 303–310
830. P. Kump, M. Nečemer, J. Šnajder, *Determination of trace elements in bee honey, pollen, and tissue by total reflection and radioisotope x-ray fluorescence spectrometry*. Spectrochim. Acta B **51** (1996), 499–507
831. T. Martinez, J. Lartigue, P. Avila-Perez, G. Zarazua, L. Cabrera, S. Tejeda, A. Ramirez, *Determination of lead in blood by TXRF and its correlation to environmental lead*. Nucl. Instr. Meth. Phys. Res. B **213** (2004), 584–589
832. C.D. Carrington, D.M. Sheehan, P.M. Bolger, *Hazard assessment of lead*. Food Additives and Contaminants **10** (3) (1993) 325–335
833. R.E. Ayala, E.M. Alvarez, P. Wobrauschek, *Direct determination of lead in whole human blood by total reflection x-ray fluorescence spectrometry*. Spectrochim. Acta B **46** (10) (1991), 1429–1432
834. A. Viksna, E. Selin, *Intercomparison between energy dispersive and total reflection X-ray fluorescence in whole blood analysis*. J. Trace Microprobe Techniques **14** (4) (1996), 763–774
835. J. Knoth, H. Schwenke, R. Marten, J. Glauer, *Determination of copper and iron in human blood serum by energy dispersive x-ray analysis*. J. Clin. Chem. Clin. Biochem. **15** (1977), 537–560
836. C.T. Yap, *X-ray total reflection fluorescence analysis of iron, copper, zinc, and bromine in human serum*. Applied Spectroscopy **42** (7) (1988), 1250–1253
837. A. Knöchel, U. Bethel, V. Hamm, *Multi-element analysis of trace elements in blood serum by TXRF*. Fresenius Z. Anal. Chem. **334** (1989), 673
838. U. Bethel, V. Hamm, A. Knöchel, *Untersuchungen zur Bestimmung von Spurenelementen in Blutserum mit Hilfe der Totalreflexions-Röntgenfluoreszenzanalyse*. Fresenius Z. Anal. Chem. **335** (1989), 855–859
839. P. Dogan, M. Dogan, R. Klockenkämper, *Determination of trace elements in blood serum of patients with Behçet Disease by total reflection x-ray fluorescence analysis*. Clin. Chem. **39** (6) (1993), 1037–1041
840. M.C. Buoso, D. Ceccato, G. Moschini, D. Bernardini, S. Testoni, A. Torboli, M. Valdes, *Assessment of serum selenium levels in 2-month-old sucking calves using total reflection X-ray fluorescence technique*. Spectrochim. Acta B **56** (2001), 2181–2186
841. I. Savage, S.J. Haswell, *The development of analytical methodology for simultaneous trace elemental analysis of blood plasma samples using total reflection x-ray fluorescence spectrometry*. J. Anal. At. Spectrom. **13** (1998), 1119–1122

842. J. Knoth, H. Schwenke, *An x-ray fluorescence spectrometer with totally reflecting sample support for trace analysis at the ppb level*. *Fresenius Z. Anal. Chem.* **291** (1978), 200–204
843. G. Bellisola, F. Pasti, M. Valdes, A. Torboli, *The use of total reflection X-ray fluorescence to track the metabolism and excretion of selenium in humans*. *Spectrochim. Acta B* **54** (1999), 1481–1485
844. M.A. Mansoor, C. Bergmark, S.J. Haswell, I.F. Savage, P.H. Evans, R.K. Berge, A.M. Svardal, O. Kristensen, *Correlation between plasma total homocysteine and copper in patients with Peripheral Vascular Disease*. *Clin. Chem.* **46** (3) (2000), 385–391
845. J. Messerschmidt, A. von Bohlen, F. Alt, R. Kockenämper, *Separation and enrichment of palladium and gold in biological and environmental samples, adapted to the determination by total reflection x-ray fluorescence*. *Analyst* **125** (2000), 397–399
846. C. Zarkadas, A.G. Karydas, T. Paradellis, *Determination of uranium in human urine by total reflection X-ray fluorescence*. *Spectrochim. Acta B* **56** (2001), 2505–2511
847. A. Knöchel, A. Prange, *Analytik von Elementspuren in Meerwasser*, *Fresenius. Z. Anal. Chem.* **306** (1981), 252–258
848. J.A. Liendo, A.C. González, C. Castelli, J. Gómez, J. Jiménez, L. Marcó, L. Sajo-Bohus, E.D. Greaves, N.R. Fletcher, S. Baumann, *Comparison between proton-induced x-ray emission (PIXE) and total reflection x-ray fluorescence (TXRF) spectrometry for the elemental analysis of human amniotic fluid*. *X-ray Spectrometry* **28** (1999), 3–8
849. B. Ostachowicz, M. Boruchowska, M. Lankosz, B. Tomik, A. Szczudlik, D. Adamek, *Application of the TXRF method to the elemental analysis of cerebrospinal fluid in amyotrophic lateral sclerosis*. *X-ray Spectrometry* **33** (2004), 46–49
850. A. Wittershagen, P. Rostam-Khani, V. Zickermann, I. Zickermann, S. Gemeinhardt, B. Ludwig, B.O. Kolbesen, *Determination of metal-cofactors in respiratory chain complexes by total reflection x-ray fluorescence spectrometry (TXRF)*. *Fresenius J. Anal. Chem.* **361** (1998), 326–328
851. S. Steinmeyer, B.O. Kolbesen, *Capability and limitations of the determination of sulfur in inorganic and biological matrices by total reflection x-ray fluorescence spectrometry*. *Spectrochim. Acta B* **56** (2001), 2165–2173
852. M. Mertens, C. Rittmeyer, B.O. Kolbesen, *Evaluation of the protein concentration in enzymes via determination of sulfur by total reflection x-ray fluorescence spectrometry – limitations of the method*. *Spectrochim. Acta B* **56** (2001), 2157–2164
853. W. Michaelis, A. Prange, *Trace analysis of geological and environmental samples by total reflection x-ray fluorescence spectrometry*. *Nucl. Geophys.* **2** (4) (1988), 231–245
854. A. Viksna, V. Znotina, J. Boman, *Concentrations of some elements in and on Scots pine needles*. *X-Ray Spectrometry* **28** (1999), 275–281
855. V.G. Mihucz, E. Tatár, A. Varga, G. Záray, E. Cseh, *Application of total reflection X-ray fluorescence spectrometry and high-performance liquid chromatography for the chemical characterization of xylem saps of nickel contaminated cucumber plants*. *Spectrochim. Acta B* **56** (2001), 2235–2246

856. H. Miesbauer, G. Köck, L. Füreder, *Determination of trace elements in macrozoobenthos samples by total reflection x-ray fluorescence analysis*. Spectrochim. Acta B **56** (2001), 2203–2207
857. M. Mages, S. Woelfl, W.V. Tümpling, jun., *A method for trace element determination of single Daphnia specimens using total reflection x-ray fluorescence spectrometry*. Spectrochim. Acta B **56** (2001), 2209–2217
858. K. Friese, M. Mages, K. Wendt-Potthoff, T.R. Neu, *Determination of heavy metals in biofilms from the River Elbe by total reflection x-ray fluorescence spectrometry*. Spectrochim. Acta B **52** (1997), 1019–1025
859. K. Günther, A. von Bohlen, *Multi-element speciation in vegetable foodstuffs by gel permeation chromatography (GPC) and total reflection x-ray fluorescence (TXRF)*. Spectrochim. Acta B **46** (10) (1991), 1413–1419
860. R. Görgl, P. Wobrauschek, P. Kregsamer, C. Strel, M. Haller, A. Knöchel, M. Radtke, *Total reflection x-ray fluorescence analysis excited by synchrotron radiation (SRTXRF): variation of excitation conditions and sample geometries*. X-Ray Spectrometry **26** (1997), 189–194
861. C. Strel, *Development of total reflection X-ray fluorescence analysis at the Atominsitute of the Austrian Universities*. X-Ray Spectrometry **29** (2000), 203–211
862. A.T. Ellis, M. Holmes, P. Kregsamer, P.J. Potts, C. Strel, M. West, P. Wobrauschek, *Atomic spectrometry update x-ray fluorescence spectrometry*. J. Anal. At. Spectrom. **13** (1998), 209R–232R
863. H. Yuying, W. Yingrong, Z. Limin, L. Guangcheng, H. Wei, Y. Lizhen, C. Jiapei, L. Jiangfu, Z. Tongcun, C. Enhua, *Beijing synchrotron radiation total reflection x-ray fluorescence analysis facility and its applications on trace element study of cells*. Spectrochim. Acta B **56** (2001), 2057–2062
864. R.S.S. da Costa, M. das G.T. do Carmo, C. Saunders, R.T. Lopes, E.F.O. de Jesus, S.M. Simabuco, *Trace element content of Colostrum milk in Brazil*. J. Food Compos. Anal. **15** (2002), 27–33
865. S. Muratsu, T. Ninomiya, Y. Kagoshima, J. Matsui, *Trace elemental analysis of drugs of Abuse using synchrotron radiation total reflection X-ray fluorescence analysis (SRTXRF)*. J. Forensic Sciences **47**(5) (2002), 944–949
866. K.M. Kemner, W. Yun, Z. Cai, B. Lai, H.-R. Lee, J. Maser, D.G. Legnini, W. Rodrigues, J.D. Jastrow, R.M. Miller, S.T. Pratt, M.A. Schneegurt, C.F. Kulpa Jr., *Using zone plates for x-ray microimaging and microspectroscopy in environmental science*. J. Synchrotron Rad. **6** (1999), 639–641
867. B. Lengeler, C. Schroer, J. Tümmler, B. Benner, M. Richwin, A. Snigirev, I. Snigireva, M. Drakopoulos, *Imaging by parabolic refractive lenses in the hard x-ray range*. J. Synchrotron Rad. **6** (1999), 1153–1167
868. M. Haller, A. Knöchel, *X-ray fluorescence analysis using synchrotron radiation*. J. Trace Microprobe Technol. **14**(3) (1996), 461–488
869. F. Adams, K. Janssens, A. Snigirev, *Microscopic x-ray fluorescence analysis and related methods with laboratory and synchrotron radiation sources*. J. Anal. At. Spectrom. **13** (1998), 319–331
870. K. Janssens, L. Vincze, B. Vekemans, F. Adams, M. Haller, A. Knöchel, *Use of leadglass capillaries for micro-focusing of highly-energetic (060 keV) synchrotron radiation*. J. Anal. At. Spectrom. **13** (1998), 339–350
871. S. Hayakawa, S. Tohno, K. Takagawa, A. Hamamoto, Y. Nishida, M. Suzuki, Y. Sato, T. Hirokawa: *Ultra trace characterization using an X-Ray microprobe at SPring-8 BL39XU*. Anal. Sci. **17** (Suppl.) (2001), i115–i117

872. R. Simon, G. Buth, M. Hagelstein: *The X-ray-fluorescence facility at ANKA, Karlsruhe: Minimum detection limits and micro probe capabilities*. Nucl. Instr. Meth. B **199** (2003), 554–558
873. K. Proost, L. Vincze, K. Janssens, N. Gao, E. Bulska, M. Schreiner, G. Falkenberg: *Characterization of a polycapillary lens for use in micro-XANES experiments*. X-Ray Spectrometry **32** (2003), 215–222
874. A. Somogyi, M. Drakopoulos, L. Vincze, B. Vekemans, C. Camerani, K. Janssens, A. Snigirev, F. Adams: *ID18F: a new micro-x-ray fluorescence end-station at the European Synchrotron Radiation Facility (ESRF): preliminary results*. X-Ray Spectrometry **30** (2001), 242–252
875. C.A. Pérez, M. Radtke, H. Sánchez, H. Tolentino, R.T. Neuenschwander, W. Barg, M. Rubio, M.I. Silveira Bueno, I.M. Raimundo, J.J.R. Rohwedder: *Synchrotron radiation X-Ray fluorescence at the LNLS: Beamline instrumentation and experiments*. X-Ray Spectrometry **28** (1999), 320–326
876. K.W. Jones, W.J. Berry, D.J. Borsay, H.T. Cline, W.C. Conner jr., C.S. Fullmer, *Applications of synchrotron radiation-induced x-ray emission (SRIXE)*. X-Ray Spectrometry **26** (1997), 350–358
877. J. Maser, D. Wagner, B. Lai, D. Legnini, I. Moric, L. Bermudez, *Trace metals and their relation to bacterial infections studied by x-ray microscopy*. J. Phys. IV France **104** (2003), 283–288
878. M. Szczerbowska-Boruchowska, M. Lankosz, J. Ostachowicz, D. Adamek, A. Krygowska-Waijs, B. Tomik, A. Szczudlik, A. Simionovici, S. Bohic, *Application of synchrotron radiation for elemental microanalysis of human central nervous system tissue*. J. Phys. IV France **104** (2003), 325–328
879. C.T. Dillon, P.A. Lay, B.J. Kennedy, A.P. J. Stampfl, Z. Cai, P. Ilinski, W. Rodrigues, D.G. Legnini, B. Lai, J. Maser, *Hard x-ray microprobe studies of chromium(VI)-treated V79 Chinese hamster lung cells : intracellular mapping of the biotransformation products of a chromium carcinogen*. J. Biol. Inorg. Chem. **7** (2002), 640–645
880. M. Kirchgeßner, *Ernährungsphysiologische Grundlagen der Spurenelementversorgung* in: Spurenelemente und Ernährung (G. Wolfram, M. Kirchgeßner, (Eds.)), Wiss. Verlagsgesellschaft Stuttgart 1990, pp. 135–149
881. J. Kawai, K. Takagawa, S. Fujisawa, A. Ektessabi, S. Hayakawa, *Microbeam XANES and x-ray fluorescence analysis of cadmium in kidney*. J. Trace Microprobe Techniques **19**(4) (2001), 541–546
882. F. Vittur, C. Tuniz, S. Paletti, R. Rizzo, K.W. Jones, *Elemental analysis of growth plate cartilage by synchrotron-radiation-induced x-ray emission (SRIXE)*. Biochem. Biophys. Res. Commun. **188**(3) (1992), 1010–1017
883. C.J. Sparks jr., *Synchrotron radiation research* (H. Winick, S. Doniach (Eds.)), Plenum Press, New York, 1980, pp. 459–512
884. S. Bohic, A. Simionovici, A. Snigirev, R. Ortega, G. Devès, D. Heymann, C.G. Schroer, *Synchrotron hard x-ray microprobe: Fluorescence imaging of single cells*. Appl. Phys. Lett. **78**(22) (2001), 3544–3546
885. P.J. Potts, A.T. Ellis, P. Kregsamer, J. Marshall, C. Strehli, M. West, P. Wobrauschek, *Atomic spectrometry update x-ray fluorescence spectrometry*. J. Anal. At. Spectrom. **18** (2003), 1297–1316
886. K.P. Koutzenogii, T.I. Savchenko, O.V. Chankina, G.A. Kovalskaya, L.P. Osipova, A.V. Bgatov: *Synchrotron Radiation X-Ray Fluorescence Analysis (SRXRF) for measuring the multielement composition of samples of biogenic nature*. J. Trace Microprobe Techn. **21**(2) (2003), 311–325

887. N. Schulmann-Choron, P. Chevallier, J. de Ceaurriz, C. Souleau, *Determination of selenium in rat brain by synchrotron radiation x-ray fluorescence*. *Analyst* **28** (2000), 316–323
888. T. Pfister, H. Feng, E. Wimmer, K.W. Jones, *Synchrotron radiation-induced x-ray emission to identify metal ions in preparations of purified protein*. *BioTechniques* **32** (2002), 134–141
889. Y. Gao, C. Chen, Z. Chai, J. Zhao, J. Liu, P. Zhang, W. He, Y. Huang, *Detection of metalloproteins in human liver cytosol by synchrotron radiation x-ray fluorescence combined with gel filtration chromatography and isoelectric focusing separation*. *Analyst* **127** (2002), 1700–1704
890. Y. Gao, C. Chen, P. Zhang, Z. Chai, W. He, Y. Huang, *Detection of metalloproteins in human liver cytosol by synchrotron radiation x-ray fluorescence after sodium dodecyl sulphate polyacrylamide gel electrophoresis*. *Anal. Chim. Acta* **485** (2003), 131–137
891. G. Weseloh, M. Kühbacher, H. Bertelsmann, M. Özaslan, A. Kyriakopoulos, A. Knöchel, D. Behne, *Analysis of metal-containing proteins by gel electrophoresis and synchrotron radiation x-ray fluorescence*. *J. Radioanal. Nucl. Chem.* **259**(3) (2004), 473–477
892. M.L. Carvalho, J.P. Marques, J. Brito, C. Casaca, A.S. Cunha, *Hg, Bi, Cu and Zn distribution in human teeth treated by dental amalgam measured by synchrotron microprobe*. *Nucl. Instr. Meth. B* **196** (2002), 148–154
893. I. Nakai, R. Iwata, K. Tsukamoto, *Ecological study of the migration of eel by synchrotron radiation induced x-ray fluorescence imaging of otoliths*. *Spectrochim. Acta B* **54** (1999), 167–170
894. T. Yoshitomi, C. Nakayasu, S. Hasegawa, A. Iida, N. Okamoto, *Site-specific lead distribution in scales of lead-administered carp (*cyprinus carpio*) by non-destructive SR-XRF analysis*. *Chemosphere* **36**(10) (1998), 2305–2310
895. A.M. Ektessabi, M. Rokkum, C. Johansson, T. Albrektsson, L. Sennerby, H. Saisho, S. Honda, *Application of synchrotron radiation in investigation of metal-ion release from a hip replacement prosthesis*. *J. Synchrotron Rad.* **5**, 1136–1138 (1998)
896. A. Ektessabi, S. Shikine, N. Kitamura, M. Rokkum, C. Johansson, *Distribution and chemical states of iron and chromium released from orthopedic implants into human tissues*. *X-ray Spectrometry* **30**, 44–48 (2001)
897. Y.Y. Huang, J.X. Lu, R.G. He, L.M. Zhao, Z.G. Wang, W. He, Y.X. Zhang, *Study of human bone tumor slice by SRXRF microprobe*. *Nucl. Instr. Methods A* **467–468**, 1301–1304 (2001)
898. R.R. Martin, T.K. Sham, G. Wong Won, K.W. Jones, H. Feng, *Synchrotron x-ray fluorescence and secondary ion mass spectrometry in tree ring microanalysis: applications to dendroanalysis*. *X-Ray Spectrometry* **30** (2001), 338–341
899. R.R. Martin, S.J. Naftel, W. Skinner, K.W. Jones, H. Feng, *Micro-synchrotron x-ray fluorescence of the metal distribution in a black spruce tree stem: evidence for radial mobility*. *X-Ray Spectrometry* **32**, 402–407 (2003)
900. N. Shimojo, S. Homma-Takeda, K. Ohuchi, M. Shinyashiki, G.F. Sun, Y. Kumagai, *Mercury dynamics in hair of rats exposed to methylmercury by synchrotron radiation X-ray fluorescence imaging*. *Life Sci.* **60**(23) (1997), 2129–2137
901. F. Briki, C. Mérigoux, F. Sarrot-Reynauld, M. Salomé, B. Fayard, J. Susini, J. Doucet, *Evidence for calcium soaps in human hair shaft revealed by sub-micrometer x-ray fluorescence*. *J. Phys IV France* **104** (2003), 337–340

902. R. Ortega, G. Devès, M. Bonnin-Mosbah, M. Salomé, J. Susini, L.M. Anderson, K.S. Kasprzak, *Chromium mapping in male mice reproductive glands exposed to CrCl₃ using proton and x-ray synchrotron radiation microbeams*. Nucl. Instr. Methods B **181** (2001), 485–488
903. C. Paluszkiwicz, W.M. Kwiatek, *Analysis of human cancer prostate tissues using FTIR microspectroscopy and SRIXE techniques*. J. Mol. Struct. 565–566 (2001), 329–334
904. W.M. Kwiatek, A.L. Hanson, C. Paluszkiwicz, M. Gaka, M. Gajda, T. Cichocki, *Application of SRIXE and XANES to the determination of the oxidation state of iron in prostate tissue sections*. J. Alloys Comp. **362** (2004) 83–87
905. T. Pinheiro, L.C. Alves, A. Barreiros, F. Araujo, S. Bohic, A. Simionovici, *Imaging and quantification of trace metals in thin biological specimens using microprobe techniques: synchrotron induced x-ray fluorescence microprobe and nuclear microprobe*. J. Phys. IV France **104** (2003), 321–324
906. S. Yoshida, A. Ide-Ektessabi, S. Fujisawa, *Application of synchrotron radiation in neuromicrobiology: role of iron in Parkinson's disease*. Struct. Chem. **14**(1) (2003), 85–95
907. M. Kühbacher, G. Weseloh, A. Thomzig, H. Bertelsmann, G. Falkenberg, M. Radtke, H. Riesemeier, A. Kyriakopoulos, M. Beekes, D. Behne, *Analysis and localization of metal- and metalloids-containing proteins by Synchrotron-Radiation X-Ray Fluorescence*. X-Ray Spectrometry **34**(2) (2005), 112–117.
908. M. Szczerbowska-Boruchowska, M. Lankosz, J. Ostachowicz, D. Adamek, A. Krygowska-Wajs, B. Tomik, A. Szczudlik, A. Simionovici, S. Bohic, *Topographic and quantitative microanalysis of human central nervous system tissue using synchrotron radiation*. X-Ray Spectrometry **33**(1) (2003), 3–11
909. H. Shen, Q.G. Ren, Y. Mi, X.F. Shi, H.Y. Yao, C.Z. Jin, Y.Y. Huang, W. He, J. Zhang, B. Liu, *Investigation of metal ion accumulation in Euglena gracilis by fluorescence methods*. Nucl. Instrum. Methods B **189** (2002), 506–510
910. R. Ishihara, A. Ide-Ektessabi, N. Kitamura, Y. Fujita, Y. Mizuno, T. Ohta, *Investigation of interactions of nano-particles within cells using micro-beam imaging techniques*. X-Ray Spectrometry **32** (2003), 418–422
911. D.X. Balaic, Z. Barnea, Z. Cai, M. Cholewa, G.B. Deacon, C.T. Dillon, P. Ilinski, P.A. Lay, D. Legnini, D. Phillips, S. Rainone, G. Shea-McCarthy, A.P.J. Stampfl, T. Talarico, L.K. Webster, W. Yun, B. Lai, *High resolution nuclear and x-ray microprobes and their applications in single cell analysis*. Nucl. Instr. Methods B **181** (2001), 715–722
912. R. Ortega, B. Fayard, M. Salomé, G. Devès, J. Susini, *Chromium oxidation state mapping in human cells*. J. Phys IV France **104** (2003), 289–292
913. K. Takemoto, T. Ueki, B. Fayard, A. Yamamoto, M. Salomé, S. Scippa, J. Susini, T. Uyama, H. Michibata, H. Kihara, *Local distribution of vanadium in living blood cells of ascidians by fluorescence scanning x-ray microscopy ID21 at ESRF*. J. Phys IV France **104** (2003), 333–336
914. C.T. Dillon, P.A. Lay, B.J. Kennedy, A.P.J. Stampfl, Z. Cai, P. Ilinski, W. Rodriguez, D.C. Legnini, B. Lai, J. Maser, *Hard x-ray microprobe studies of chromium(VI)-treated V79 Chinese hamster lung cells: intracellular mapping of the biotransformation products of a chromium carcinogen*. J. Biol. Inorg. Chem. **7** (2002), 640–645
915. Van Grieken RE, Markowicz AA (2002) Handbook of X-Ray Spectrometry. 2nd Edn, Marcel Dekker, New York

916. Potts PJ (1992) *A Handbook of Silicate Rock Analysis*. Blackie, Glasgow and London, p. 240
917. Reynolds RC (1967) Estimation of mass absorption coefficients by Compton scattering: improvements and extensions of the method. *Am Mineral* 52:1493–1502
918. Tertian R, Claisse F (1982) *Principles of Quantitative X-ray Fluorescence Analysis*. Heiden, London
919. Potts PJ (1992) *A Handbook of Silicate Rock Analysis* Blackie, Glasgow and London, p. 240
920. Spatz R, Lieser KH (1977) Kritischer Vergleich des Meßbereichs und der Nachweisgrenzen für die energiedispersive Röntgenfluoreszenzanalyse mit Röhrenanregung (Sekundärtarget) und mit Radionuklidanregung (109Cd und 241Am) am Beispiel von Pulverschüttproben auf Kieselgelbasis. *Fresenius Z Anal Chem* 319:732–734
921. Strecker H, Harding G, Bomsdorf H, Kanzenbach J, Linde R, Martens G (1993) Detection of Explosives in Airport Baggage Using Coherent X-Ray Scatter. *Proc. SPIE* 2092:377
922. Luggar RD, Farquharson MJ, Horrocks JA (1998) Multivariate analysis of statistically poor EDXRD spectra for the detection of concealed explosives. *X-Ray Spectrom* 27:87
923. Henrich A, Hoffmann P, Ortner HM, Greve T, Itzel H (2000) Non-invasive identification of chemical compounds by energy-dispersive X-ray fluorescence spectrometry, combined with chemometric methods of data evaluation. *Fresenius J Anal Chem* 368:130–138
924. Hofmann T, Hoffmann P, Lieser KH (1984) In-line determination of Uranium, Plutonium and Neptunium in process streams by energy-dispersive X-ray fluorescence analysis (EDXRF). *J Radioanal Nucl Chem* 82:201–204
925. Heckel J, Ryon RW (2002) Polarized Beam X-ray Fluorescence Analysis. in Van Grieken RE, Markowicz AA Eds. (2002) *Handbook of X-Ray Spectrometry*, 2nd Edn, Marcel Dekker, New York, p 603
926. Szegedi S, Tun KM, Ibrahim SM (1996) Determination of ash content in coals by gamma reflection method. *J Radioanal Nucl Chem* 213:403–409
927. Confalonieri L, Crippa R, Milazzo M (1987) Experimental approach to analysis of binary alloys by Rayleigh-Compton back-scatter ratio method. *Appl Radiat Isot* 38:139–142
928. Kunzendorf H (1972) Quick determination of the average atomic number $\bar{Z}$ by X-ray scattering. *Nucl Instr Meth* 99:611–612
929. Miranda J, Andrade E, Lopez-Suarez A, Ledesma R, Cahill TA, Wakabayashi PH (1996) A receptor model for atmospheric aerosols from a southwestern site in Mexico City. *Atmos Environ* 30:3471–3479
930. Remola JA, Larrechi MS, Rius FX (1993) Chemometric characterization of 5th century A.D. amphora-producing centres in the Mediterranean. *Talanta* 40:1749–1757
931. Benninghoff L, von Czarnowski D, Denkhaus E, Lemke K (1997) Analysis of human tissues by total reflection X-ray fluorescence. Application of chemometrics for diagnostic cancer recognition. *Spectrochim Acta Part B* 52:1039–1046
932. Majcen N, Rius FX, Zupan J (1997) Linear and non-linear multivariate analysis in the quality control of industrial titanium dioxide white pigment. *Anal Chim Acta* 348:87–100
933. Molt K, Schramm R (1997) Application of factor analysis in EDXRF. *Fresenius J Anal Chem* 359:61–66

934. Scan for Windows (1995) Users Manual, Version 1.1. Minitab, State College, PA
935. Friedman JH (1989) Regularized discriminant analysis. *J Am Stat Assoc* 84:165–175
936. Frank IE, Friedman JH (1989) Classification: oldtimers and newcomers. *J Chemom* 33:463–475
937. Wu W, Mallet Y, Walczak B, Penninckx W, Massart DL, Heuerding S, Erni F (1996) Comparison of regularized discriminant analysis, linear discriminant analysis and quadratic discriminant analysis, applied to NIR data. *Anal Chim Acta* 329:257–265
938. Baldovin A, Wen W, Massart DL, Turello A (1997) Regularized discriminant analysis RDA—Modelling for the binary discrimination between pollution types. *Chemom Intell Lab Syst* 381:25
939. Kessler T, Hoffmann P, Greve T, Ortner HM (2002) Optimization of the identification of chemical compounds by energy-dispersive X-ray fluorescence spectrometry. *X-Ray Spectrom* 31:383–390
940. Ernst T, Bartels M, Ohm M, Beckenkamp K (2003) Automatische Identitätsprüfung von Feststoffen mit der energiedispersiven Röntgenfluoreszenzanalyse. *GIT-Labor-Fachz* 47:392–396
941. Gigante GE, Pedraza LJ, Sciuti S (1985) Analysis of metal alloys by Rayleigh to Compton ratios and X-ray fluorescence peaks in the 50 to 122 keV energy range. *Nucl Instr Meth B12*:229–234

D. Rammlmair, M. Wilke, K. Rickers, R.A. Schwarzer,
 A. Möller and A. Wittenberg
 Methodological Developments and Applications
 Chapter 7.6 Geology, Mining, Metallurgy.
 in: B. Beckhoff, B. Kanngießner, N. Langhoff,
 R. Wedell and H. Wolff (eds.):
 Handbook of Practical X-Ray Fluorescence Analysis.
 Springer-Verlag Berlin Heidelberg 2006, S.640–687
 ISBN 3-540-28603-9