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Abstracts Oral Sessions

I1

Tracking gold forgeries with X-rays

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Among the gold objects kept in museums, a few arrived from ancient private collections or were acquired in the antiquities market. Owing to the attention given by scholars and connoisseurs to the newly discovered ancient civilizations, some periods were characterized by a high production of pastiches and fakes. Queries on the authentication of gold work from these periods are difficult to achieve. The absence of documents either on the archaeological context of the finds or on the acquisitions as well as on the restorations carried out in the past complicates the task. These difficulties increase in the case of exceptional objects and less widespread civilisations.

In addition to the ability required to recognize and identify genuine items and fakes, non-destructive elemental analysis and exam can provide major information on the goldsmith's techniques and on the origin of the metal. The techniques based on X-rays (radiography, PIXE, SR-XRF, SEM-EDS…) are essential for authentication. By combining exam and analysis with studies on iconography, style and period and by comparing suspected with genuine objects it is possible to list criteria to distinguish the fakes. The aim of this work is to show the role of those techniques in the case of Etruscan and Pre-Columbian pastiches and repaired items from museum collections.

O1-1

Investigations on ancient Artemision gold objects using portable µ-XRF

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Within two measurement campaigns in summer 2006 and 2007 in the Archaeological Museum of Istanbul and in the Ephesus Museum of Selcuk/Turkey more than 80 ancient gold objects (e.g. small statuettes, brooches and coins) from the 8th-6th century BC, were analysed. Therefore, two self-built portable XRF instruments [1, 2] were used in order to gain information on the chemical composition and homogeneity of the artifacts discovered during excavations in the sanctuary of Artemis at Ephesus since the 1960s. The evaluation of the raw data was carried out using WinAxil software [3] These quantitative results and complementary studies on the manufacturing techniques of the objects will contribute to our knowledge of metalworking, trade, as well as the transfer of ideas and technologies at Ephesus and in Western Asia in the Archaic period.

The XRF data exhibited highly homogeneous alloys in most cases, mainly consisting of gold (Au), silver (Ag) and copper (Cu). A high compositional variation of these elements between different objects could be determined: the Au-content ranged between about 48 and 99.9%, the Ag-concentration between <dl and 51%, while copper was generally present at a comparably low level between 0.1 and 4.4%.

This has shown us the range of gold alloys represented within the collection and permitted us to distinguish between natural and artificial gold alloys (including the identification of “refined” gold !) and to obtain some information regarding the provenance of the raw materials (in most cases, presumably Lydia).

In some cases, gold objects which were closely related from a typological, stylistic and/ or technological point of view, were also very similar in composition, which differed only in the sub-percent range.

[1] V. Desnica, M. Schreiner, X-Ray Spectrometry 35 (2006), 280-286.

[2] Compact Portable Roentgen Analyzer, within the EU-Project No. SMT4-CT98-2237, project coordinator: Prof. Dr. K. Janssens, University of Antwerp

[3] Win Axil X-Ray Analysis Software, Canberra Eurisys Benelux, Belgium

O1-2

Discovery of a Hidden Van Gogh Painting by means of High-Energy XRF mapping

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The painter Vincent Van Gogh (1853-1890) is generally considered as one of the most important painters of the 19th-C. As a result, his short but very productive career is subject of intensive study by art historians, historians, (conservation) scientists, etc. In the past, traditional radiographies made clear that Van Gogh covered several of his paintings with a new composition. The recycling of canvases might have been prompted by his difficult financial situation. In addition, his style changed so dramatically at certain moments in time that he might have regarded preceding works of art as obsolete and thus eligible for overpainting.

An examination of the Van Gogh paintings and the corresponding radiographies of the Kröller-Müller museum (NL) confirmed the existence of these concealed compositions. However, radiographies usually allow only to discern some coarse outlines but prevent to observe further details. The visualization of such covered compositions would be of great interest to both Van Gogh specialists as the public audience.

This talk discusses the first successful attempt to re-establish a hidden portrait by means of elemental mapping with synchrotron based µ-XRF. A small canvas (ca. 30 x 20cm), representing a patch of grass (ca. 1886-'87) was transported to beam line L at the HASYLAB synchrotron facility in Hamburg. A conventional radiography of this painting reveals the outlines of a human face but no identification or correlation with the existing oeuvre of the artist was feasible. A square area of ca. 15x15 cm, corresponding with the position of the head, was scanned with a quasi monochromatic X-ray beam of 35.5 keV of 0.3x-0.3 mm2 cross-section.

One of the (trace) element maps obtained in this manner allows to visualize the covered portrait of a peasant woman with unprecedented detail. On-going spectroscopic research is focused on the identification of the nature of the pigmented compound with which the portrait was painted. Additionally, art historians are currently involved in a stylistic comparison between Van Gogh's existing oeuvre and the newly revealed portrait, including a re-examination the preserved correspondence of Van Gogh in an attempt to identify documentary links to this portrait.

O1-3

Archaeological analysis of Roman glassexcavated from Zadar, Croatia by a newly develped portable XRF spectrometer for glass

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A newly developed portable X-ray fluorescence spectrometer has been evaluated through the on site non-destructive analyses of 109 Roman glass artifacts excavated at a Roman necropolis found in Zadar, Croatia. The spectrometer has been designed for on site analysis of archaeological glass objects. The detector unit consists of X-ray tube with a Pd target operated at up to 40kV, SDD with a MOXTEK AP3.3 polymer window and an enlargeable vacuum sampling chamber. A capillary tube or a pyrolytic graphite monochromator can be selected to obtain white X-ray or Pd K line source. With this system, quantitative analysis of the light elements such as Na, Mg, and Al, important components of glass as well as heavy trace elements can be successfully made and the analytical results were used as characterization of the ancient glass objects.

The glass samples consist of several groups of square jug, small square flask, large cinerary urn and bell-shaped flask, dating from the 1st century to the beginning of the 5th century. The obtained results evidenced the use of Natron as fluxing agent in glass making process. The transition metals such as Mn, Fe, Cu and Co were found to be responsible for the colors of the pale bluish green, green, purple and deep blue glass vessels. We focused on the differences in the use of Mn and/ or Sb as decolorizing agent for colorless glass to classify a group of the bell-shaped flask which is believed to be an original product of at least one local workshop of Zadar in the Roman period (1) We will discuss the analytical results of the vessels excavated from 10 different localities along the coast of Croatia.

[1] S. Gluščević, *Annales du 14e Congrès, AIHV*, (1998), 182-189.

O1-4

Physical and chemical analysis of a 16th century manuscript

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This work is focused on a 16th century codex of the Chronicle of the Portuguese king Dom Fernando (1367-1383, b.1345), originally written by Fernão Lopes (c.1380 – c.1460), who was officially appointed chronicler of Portugal in 1434. No originals written by Fernão Lopes are extant, 47 copies remaining today of Chronicle of Dom Fernando, mostly anonymous and dated from the 16th to the 18th century. Our study includes microscopic analysis of the codex paper fibers, energy dispersive X-ray fluorescence analysis of the elemental content of the paper as well as regions where ink is present. Infrared and mass spectrometry analysis were also used in order to identify the type of ink used in the manuscript. The microscopic analysis of paper revealed the presence of textile fibers commonly used in papermaking before the 18th century. Ink analysis indicated a ferrogallic composition and elemental composition of the paper suggested three different origins, which has been corroborated by watermark analysis.

O1-5

Non-destructive determination of the Silver content in Roman coins dated to 308-310 A.D. by combined use of the PIXE-alpha, XRF and DPAA techniques

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The quantitative determination of the composition of ancient coins can give useful information to archaeologists, numismatists and conservators. The use of non-destructive techniques is preferable especially when a large number of samples have to be investigated. However analyses have to be performed with caution since ancient alloys present often surface effects due to corrosion/oxidation processes or to the manufacturing techniques (the presence of enriched patinas with nobles metals) that produce meaningful variation of the composition respect with the interior of the coins.

At the INFN/CNR LANDIS laboratory of Catania, a non-destructive protocol of analysis, based on the combined use of the portable PIXE-alpha [1] and XRF spectrometers and of the new DPAA (Deep Protons Activation Analysis) method [2], was developed for studying the Roman "folles" dated to 300 – 330 A.D. belonging to the Misurata treasure (Lybia), one of the most important finding of coins in the Mediterranean Area.

The use of the PIXE-alpha system allowed to determine the composition of the few microns thick silver-enriched patina of the bronze coins while the DPAA techniques, making use of high energy proton beams, was used to determine the silver content in the core of the samples, minimizing the surface effects due to the enriched patina; the XRF techniques was used to explore the composition of the interface between the patina and the substratum of the coins.

In the present work the data obtained from the analysis of 15 coins dated back to 308-310 A.D. are presented and discussed; results allowed archaeologists to make some historical hypothesis about this period of the Roman empire.

[1] L. Pappalardo, F.P. Romano, S. Garraffo, J. de Sanoit, C. Marchetta, G. Pappalardo, Archaeometry, 45 (2003) 333-339.

[2] G. Pappalardo, A. Esposito, G.A. Cirrone, G. Cuttone, S. Garraffo, L. Pappalardo, F. Rizzo, F.P. Romano, S. Russo, *in press in NIM B.*

O1-6

μ-XRF analysis of museum metal collections across the Mediterranean basin

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Micro- X-ray fluorescence spectrometry (μ-XRF) analysis has been well established during the last decade as an important diagnostic and analytical tool in archaeological and conservation science. The availability of relevant commercial and portable units is indicative, however, research groups have also developed portable setups to meet the needs of cultural heritage analysis [1-2]. Most of the reported studies have been undertaken in laboratories without exploring one of the main advantages of the μ-XRF which is the potential to analyze in the museum environment systematically collections of artefacts.

Analysis of archaeological and/or historical metal artefacts using micro-XRF encounters a number of analytical challenges related to the identification of corrosion products present on the surface, characterization of artefacts details, reliable compositional analysis etc. The development of analytical methodologies depending on the collection and the improvement of quantification aspects of the analysis can give important information about the raw materials, manufacture techniques and state of preservation supporting archaeometallurgical and conservation studies.

Within the FP6 project PROMET [3], a portable micro-XRF spectrometer, based on an industrial prototype with customized hardware components was characterized, optimized and used to analyse metal collections from the Mediterranean basin. More specifically, high-tin bronze mirrors of the 2nd cent BC from the museum of Ancient Messene in Greece, gilded mild steel 16th cent armours from the Palace Armoury in Malta, gilded copper and gold artefacts from the 3rd and 2nd Millennium B.C. from the Damascus National Archaeological Museum in Syria, Roman copper alloy artefacts from the Umm Qais site and gold Ottoman coins from the collection of the Numismatic museum of Yarmouk University, Jordan were analysed and will be presented. In addition, examples of the in situ synergistic use of LIBS and micro-XRF analysis will be discussed.

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[2] G. Buzanich, P. Wobrauschek, C. Streli, A. Markowicz, D. Wegrzynek, E. Chinea-Cano, S. Bamford, , Spectrochim. Acta 62B (2007) 1252-1256.
[3] PROMET, PROtection of METals, FP6-2002-INCO-MPC-1, www.promet.org.gr

O1-7

Provenance characterization of iron age ceramics from archaeological salvage excavations of Baku-Tbilisi-Ceyhan crude oil pipeline: Case of Erzurum and Erzincan sites (Turkey)

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The Baku-Tbilisi-Ceyhan (BTC) crude oil pipeline brings oil from the landlocked Caspian Sea to international markets. 1768 km pipeline winds its way through the historically fertile countries of Azerbaijan, Georgia and Turkey, considered to be among the world's most archaeologically wealthy countries. Turkey's cultural legacy is not only ancient, but it is also extremely complex. Archaeological salvage excavations were carried out at 17 sites in Turkey. Research Center for Archaeology of Gazi University (ARCED) was responsible for the cultural heritage management in accordance with ESIA.

This study was executed within the scope of the archaeological salvage excavations of the Baku-Tbilisi-Ceyhan (BTC) crude oil pipeline project. The qualitative and quantitative results of X-ray fluorescence analysis of thirty eight ceramic samples, dated to Iron Age, from Buyukardic-Erzincan and Gulludere, Tasmasor, Tetikom, Magaratepe-Erzurum archaeological sites and statistical evaluation of elemental XRF results of paste for selected ceramics were presented. Similarities and correlation between the samples were determined and compared for the investigation of the raw materials that used for the manufacturing of the ceramics. Multivariable statistical methods as well as hierarchic cluster and factor analyses were applied on the data set. In addition, mineral composition was identified for some samples in this group by means of XRD techniques for particular information. As a result, two sherds can be classified in different chemical composition while the others can be considered from similar provenance.

Furthermore, qualitative XRF measurements were accomplished on the ceramic bottle, metal slag and metal processed pot sherds that recovered from Buyukardic. The main purpose of these measurements is to prove metallurgical activities took place on site. The results indicate that the existence of a small –scale metal industry focused on processing iron and copper.

XRF and XRD results presented in this study are in line with the archaeological results, especially in determination of the local materials and imported objects which will help to enlight the cultural, social and technical relationships between the communities.

O1-8

Estimation of the interelement effects in applying the X-ray fluorescence method to the study of cultural heritage materials

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The particular features of the application of X-ray spectral analysis are discussed in this report to solve various problems related to the study of materials and objects which are of archaeological, historical and cultural heritage. The following objects were considered: glass- and ceramic products, different dishes, Fe-, Cu-, Ag-, Au-based metal alloys. The study of a chemical composition of particular materials, for example, several metal ores, obsidian and others is necessary very often in order to determine raw material sites: pre-historical mines, quarries and others. The X-ray fluorescence analysis is widely used for the control of chemical compositions of the materials considered owing to its compliance with these requirements and the availability of commercial instrumentation for the determination of most elements. The increasing number of publications on this problematics is noted [1, 2].

The following glass objects are considered: various dishes and ornaments, colouring pigments for glass, pictures painted on glass, vitreous coatings on ceramics and others. Main attention is given to the technology of sample preparation for an analysis and a problem of inhomogeneity of materials under study. The used techniques are considered in detail for the conversion of experimental intensities into concentrations of elements determined. The estimates of the theoretical intensities of the analytical lines of some elements, determined in glass, are presented, as well the intensities of coherently and incoherently scattered characteristic radiation of X-ray tube anode (for calculation procedure see [3]). Such estimates were made for the samples of ancient glass, obsidian, coloured mosaic glass, and glaze. The obtained data allow to choose the variants for taking into account interelement effects, which are optimal for each particular case.

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[2] Revenko A.G. Application of X-ray spectral method to the study of cultural heritage glass materials // Proc. Intern. Conf. Contemp. Phys.-IV “ICCP-IV". Ulaanbaatar: University Press, 2007. P. 225-247.

[3] Revenko A.G. X-ray fluorescence analysis of rocks, soils and sediments // X-Ray Spectrometry. 2002. V. 31. No. 3. P. 264-273.

O1-9

Portable EDXRF/UV-vis spectrometer, two complementary techniques on a mobile system used for Archaeometry research on the Noble tomb of Menna TT-69, Gourna, Egypt

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The Noble tomb of Menna (TT69) is one of the finest painted eighteenth Egyptian dynasty tombs. It is situated in the official's necropolis of Sheikh Abd el-Qurna In Thebes West. The tomb presents very well conserved paintings on the walls and ceilings. The two years Menna project is currently underway and is divided into several phases related to conservation, protection and scientific documentation. The fieldwork season for Archaeometry research has taken place from November 15 to December 20, 2007. Many different mobile analysis techniques (UV – Visible – Near Infrared spectrometry, Infrared spectrometry RAMAN spectroscopy, EDXRF spectroscopy) were involved in this project and worked in close collaboration. This scientific physico-chemical material approach will allow objective data to be contrasted with the formal and technological approach carried out by the Egyptologists of the Menna project, in order to have a better understanding of the manufacture processes of the decoration of Menna tomb. This project is the first attempt to carry out extensive analyses on wall paintings using complementary mobile equipments in archaeological fieldwork in Egypt. We will present here the technical aspect of the mobile EDXRF/UV-Vis spectrometer and its contribution to this project. Let us note that it is also the first time that these two different and complementary techniques are coupled on a mobile system in this field of research.

O1-10

Analysis of paintings from the XIX century Brazilian painter Rodolfo Amoedo using EDXRF portable system

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The pigments used in four of the most representative works of the Brazilian painter Rodolfo Amoedo were identified using EDXRF. The analyzed paintings, belonging to the National Museum of Fine Arts Collection, were: “The Last Tamoyo” (1883), “Study of a Woman” (1884), “Bust of Mrs. Amoedo” (1892) and “Bad News” (1895).

The analysis of the pigments is important to evaluate the artist working method and also for restoration and conservation purposes. Furthermore, the knowledge of the composition allows the pigment characterization through major or minor constituents and make possible to establish the provenance, historical period and, consequently, the authenticity of the painting.

Amoedo (1857-1941) was a renowned artist and contributing to the formation of several painters like Eliseu Visconti and Candido Portinari. In 1878, as student at the Imperial Academy of Fine Arts, he won the Europe Travel Prize and traveled to Paris – studying at the École Nationale des Beaux-Arts with the masters Alexandre Cabanel and Puvis de Chavannes. He returned to Brazil in 1887 and was designated acting professor at the Imperial Academy and later, in 1893, assistant director. In this same year, he won a medal at the Chicago International Exhibition.

EDXRF measurements were carried out with a portable system developed by the Nuclear Instrumentation Laboratory, consisting of an X-ray tube Oxford TF3005 with tungsten anode, operating at 25 kV and 100 μA, and a Si-PIN XR-100CR detector (Amptek). Several spectra were obtained, with an acquisition time of 300 s and a beam collimation of 2 mm. The spectra were analyzed using the software QXAS-AXIL (IAEA). Some pigments identified were: zinc and lead white, ochre, umbra, vermilion, Prussian blue, cobalt blue, cadmium yellow, black iron oxide and manganese violet. In one painting, which had been restored in the XX century, was identified titanium white in some alteration areas.

I2

Quantification in XRF micro-analysis

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Capillary X-ray lenses have triggered major innovations in X-ray spectroscopy. The combination of these X-ray lenses with a new generation of low power micro-focus X-ray tubes and drift chamber detectors enabled tabletop units for micro-XRF with a few tens of µm lateral resolution.

Since the X-ray tube spectrum is altered significantly when the radiation passes the optical element in the excitation channel, fundamental parameter methods for the purpose of quantification have to be further developed, A variety of approaches to determine the altered excitation spectrum have been proposed and are under development.

A recent development is the additional application of a polycapillary half-lens in the detection channel. A confocal setup allows for three dimensionally resolved X-ray spectrometry.

Though they may be regarded as fundamental parameter methods, the quantification algorithms developed so far for 3D Micro-XRF substantially differ from the quantification of classical micro-XRF. In addition to the fundamental parameters, the appropriate modeling of the X-ray lens properties is of great importance for both fields of micro-XRF.

The author will give an overview on approaches to determine the X-ray lens properties, which are relevant for quantification. Furthermore, an introduction to the principles of quantification for 3D micro-XRF will be presented and its peculiarities will be discussed.

O2-1

Reference-free XRF including K- and L-lines by synchrotron radiation at multiple energy settings

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The paper discusses the complex situation that may arise when compound samples (such as rocks or ceramics) are analyzed by synchrotron radiation. In such cases several energy settings are often used in order to optimize the excitation of heavier and lighter elements, and occasionally K- and L-lines of an element are simultaneously observed. Proper evaluation of the obtained data requires:

- A description of the sample composition in terms of multielement components with known internal stoichiometric relationships, such as oxides, and reporting results in such terms rather than element contents;
- Accounting for the complex processes that are involved in the excitation of L-lines including cascades of electron transitions and Coster-Kronig/Auger-processes;
- Accounting for a variety of indirect excitation channels including excitation by electrons;
- An iteration algorithm that allows the integration of multiple lines for each element (such as K- and L-lines) that may be excited by different primary photon energies and therefore also affected by different secondary effects; and
- Availability of a consistent set of fundamental parameters.

Such schemes have already been applied to a variety of samples including ceramics and other oxide samples and showed that reference free analysis by using a well calibrated experimental environment is possible within an error-frame of 5-10% for the main constituents. This paper emphasizes the methodological side of these techniques and their implementation.

O2-2

Quantitative analysis of individual particles on TEM grids

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Electron probe X-ray microanalysis (EPMA) is particularly suited to characterizing morphology and elemental composition of individual microparticles. Besides, the use of ultrathin window X-ray detectors offer extended capabilities for low-Z element analysis. As C, N, and O are common constituents of environmental particles such as atmospheric aerosols, their detection allows a more realistic description of samples. A critical aspect of light element analysis however is the choice of collecting substrate material. Suitable substrates for single particle analysis by SEM-EDX should ideally not contribute to the electron and X-ray signals. When compared with commonly used bulk substrates, the use of thin-film substrates such as TEM grids results in lower X-ray background and thus lower detection limits [1]. Although carbon films of TEM grids offer advantageous characteristics as a collecting substrate, carbon interference can be quite strong for particle diameters less than 0.5 µm [2]. While conventional methods of quantification such as ZAF or normalization do not account for size-dependent substrate effects, Monte-Carlo simulations can accurately describe such electron-particle-substrate interactions [1].

In this study, TEM grid-supported C/Formvar film is evaluated for quantitative analysis of standard particles containing low-Z elements. TEM grids were mounted in a self-constructed sample holder which minimizes X-ray interferences. A correction procedure using a Monte Carlo simulation [3] allowing for input of substrate parameters (film thickness, substrate density, and composition), particle diameter, elemental intensities and excitation conditions was tested on $CaCO_3$ particles. The optimized substrate parameters were first determined using experimental data and Monte-Carlo simulations with different settings. Then carbon and oxygen corrections were successfully checked on $CaSO_4$ particles using the optimized parameter settings.

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[2] A. Laskin and J.P. Cowin, Analytical Chemistry, 73 (2001) 1023 – 1029.

[3] C.-U. Ro et al., Analytical Chemistry, 75 (2003) 851 – 859.

O2-3

The necessity of maximum information utilization in x-ray analysis

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There are significant differences in the experimental data needed in the analysis of x-ray spectra [1]. If we look deep into the problems many of them contradict simple logic, elemental arithmetic [2], even parity and angular conservation laws [1]. We have identified that the main source of the problems, other than the human factor, is rooted in the signal processing electronics.

We have developed a line of fully digital signal processors [1] that not only have excellent resolution and line shape [3] but also allow proper accounting. This is achieved by processing all events and separating them into two or more spectra where the first spectrum is the accepted or good spectrum and the second spectrum is the rejected spectrum. It is not enough to know that an event was rejected, and increment the input counter, it is necessary to know, what, why and when it happened, whether it was pure noise, a noisy or disturbed event, a true event, or any pile up combination of the above in order to account properly for true event input rate and processor dead time.

The data processing methodology cannot be established on the partial and fractional information offered by other approaches. The availability of all the events allows one to see the other part of the spectrum. To our surprise the total information explains many of the shortcomings and contradictions of the x-ray database. We call this a maximum information utilization approach in signal processing.

To supplement the concept of maximum information utilization, we have developed front end electronics that keep the maximum information from the detector available for the processor. Also a fundamental parameter XRF program (CSX-XRF) has been developed to utilize all the information offered by the signal processor as well as an inverse fundamental parameter program package for equipment characterization.

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O2-4

The quest for a fundamental algorithm in XRF analysis and calibration

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When the author began his career in X-ray Spectrometry, he was looking for a XRF analysis method able to analyse any type of bulk and solid samples such as rocks, ores, cements, metals, etc., prepared either as fused discs, pressed pellets or metallic specimens.

At that time, a multitude of algorithms relating concentration to intensity had been proposed to calculate sample compositions. In this case, the problem is to select the most appropriate one to an analytical context. Another solution is to try to find a fundamental algorithm, theoretically exact, that would serve as a common mathematical basis to generate all the models proposed to date and that can be applied to any analytical context.

The solution proposed by the author is the Fundamental Algorithm (FA) [1]. It was found to be of a sound theoretical foundation from which one can deduce all the other algorithms proposed up to now [2]. Furthermore, it explains all the XRF phenomena observed in practice and contains all the XRF knowledge accumulated since the beginning of the XRF analysis.

The next step is to develop a special calibration procedure [1] to adapt theory to the experimental data of each spectrometer, knowing very well that theory cannot account for all variations in all the instrumental parameters.

Finally, it will be shown how to apply the Fundamental Algorithm in practice to fused discs, pressed pellets and alloys [3]. Three optimized methods will be presented that cover the complete analytical range (0-100%). The proposed three approaches combine the practical flexibility of the influence coefficient concept and the theoretical exactness of the Fundamental-Parameters method.

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O2-5

3D Micro X-ray Fluorescence Spectroscopy – Validation of the three-dimensional model and scattering

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3D micro X-ray fluorescence spectroscopy (3D Micro-XRF) enables three-dimensional resolved, nondestructive investigation of elemental distribution in samples in the micrometer regime. A procedure for the quantitative reconstruction of the composition of stratified material by means of 3D Micro-XRF has been developed [1] and validated [2], recently. The procedure is based on a model of the spatial distribution of the sensitivity of the probing volume defined by the overlapping foci of the confocal setup.

In this presentation, the validity of the model is shown. As no adequate reference samples were available for validation, stratified reference material has been developed that is appropriate for 3D Micro-XRF or other depth-sensitive X-ray techniques. The samples are made of five polymer layers with varying ZnO concentration. Measurements have been carried out at the mySpot beamline of the Berlin synchrotron BESSY. The reconstructed layer thickness and the respective Zn concentration of the individual layers show an excellent agreement with the manufacturers' values.

As further development of the quantification model the scattering of a sample was included in the analysis process. With this additional information the overall density of a layer can be estimated, which leads to a better understanding of the 'dark matrix' of a sample. As an example highly inhomogeneous parchment samples will be discussed.

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O2-6

Confocal XRF quantification procedures applied to the cometary matter returned by NASA's STARDUST mission

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Stardust is an interplanetary spacecraft launched on February 7, 1999, by NASA, whose primary purpose was to investigate the make up of comet Wild2 and its coma. The spacecraft was equipped with aerogel (highly porous silica foam with an extremely low density) collectors, in order to facilitate the capture of cometary dust particles. After the return of Stardust to Earth on January 15, 2006, the acquired samples were distributed among more than 150 researchers worldwide, including the X-Ray Micro-Spectroscopy and Imaging group of Ghent University (XMI-UGent) [1-3].

Each presented sample contains an elongated cavity (called *track*) produced by the impact and deceleration of a single comet coma particle through the aerogel. Multiple experiments were performed on such tracks and their terminal particle at the ESRF (beamline ID13) using several non-destructive X-ray based methods such as conventional 2D scanning nano X-ray fluorescence (XRF) and confocal nano-XRF. The latter technique is characterized by the mounting of a polycapillary half-lens in front of the detector, thereby effectively reducing the volume defined by the intersection of the incoming beam and the sample to a volume defined by the acceptance of the polycapillary. The nanobeam of X-rays was produced by a linear Fresnel lens assembly which reduced the dimensions of the beam to the 100-200 nm level.

The data has been evaluated using xmi-quant, a software-package dedicated to the evaluation of confocal XRF spectra, under development at our research group. This package includes an implementation of the fundamental parameter method allowing the modeling of the complex STARDUST particles. The presented quantitative results confirm the earlier findings concerning the presence of Ca-Al-rich inclusions in the cometary dust[2].

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O3-1

Synchrotron radiation induced Total Reflection X-ray Fluorescence Analysis- absorption spectroscopy (SRTXRF-XAS)

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Synchrotron Radiation induced Total Reflection X-ray Fluorescence Analysis (SR- TXRF) using a multilayer monochromator allows to achieve detection limits in the fg range due to the more effective excitation using synchrotron radiation and the background reduction. TXRF is specially suited for samples where only small amounts are available. A crystal monochromator selects a smaller energy bandwidth from the white synchrotron spectrum than the multilayer. Though it reduces the intensity it allows absorption spectroscopy measurements (XANES) in fluorescence mode to perform speciation at trace levels. [1-2]

Various applications of K- edge XANES measurements will be shown: Speciation of Arsenic in xylem sap of cucumber plants at concentration levels of 30 ng/g. [2] , Fe in aerosols collected in a size fractioning impactor, Fe contamination on Si wafer surfaces at contamination levels of E12 atoms/cm^2. Furthermore absorption effects for higher concentrated standard solutions have been studied and will be discussed.

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O3-2

High speed 2-dim. X-ray imaging spectroscopy at BESSY and FLASH

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For experiments at the present and future X-ray lasers (FLASH, LCLS, XFEL) we are developing large format backside illuminated fully depleted pnCCDs with column parallel readout. In a first phase a 1024 x 1024 format detector with 75 x 75 μm^2 pixels will be ready for use in 2009. The detector chip has recently been fabricated. First basic properties are actually being measured. The full system will be described in detail and its prospects will be discussed in the light of the potential applications. In phase II a 2048 x 2048 format system will be made available. The design of the pnCCD is being finished, fabrication starts in early 2008; the system could be ready for use in 2011 for phase II.

Recently we have performed two demonstrator experiments with a 256 x 512 format pnCCD system (a) at the white X-ray beam of BESSY with energies up to 30 keV and (b) with monochromatic radiation of 90 eV at the FLASH X-ray (VUV) laser. Due to the high frame rate of the pnCCDs the measurements were made in a full frame mode with up to 500 frames per second. The results of both experiments will be presented, the propects of future experiments will be discussed. They are in excellent agreement with the pnCCDs performance in the laboratory. A detailed analysis of the pnCCD data of both beamline experiments, (a) the X-ray diffraction experiment at BESSY and the Xe-nanocluster imaging at FLASH will be given.

O3-3

Measuring and interpreting X-ray fluorescence from planetary surfaces

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As part of a comprehensive study of X-ray emission from planetary surfaces and in particular the planet Mercury, we have measured fluorescent radiation from a number of planetary analogue rock samples using monochromatized synchrotron radiation provided by the BESSY II electron storage ring. The experiments were carried out using a purpose built X-ray fluorescence (XRF) spectrometer chamber developed by the Physikalisch-Technische Bundesanstalt (PTB), Germany's national metrology institute. The XRF instrumentation is absolutely calibrated and allows for reference-free quantitation of rock sample composition, taking into account secondary photon and electron induced enhancement effects. The fluorescence data, in turn, have been used to validate a planetary fluorescence simulation tool based on the GEANT4 transport code. This simulation can be used as a mission analysis tool to predict the time dependent orbital XRF spectral distributions from planetary surfaces throughout the mapping phase.

O3-4

Development of a Low Energy X-ray Fluorescence system with high spatial resolution

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In the present paper we report a recently developed Low Energy X-ray Fluorescence spectrometer (LEXRF) system combined with a soft X-ray Microscope.

The LEXRF setup is a modular system based on the use of multiple windowless Silicon Drift Detectors (SDD), with the option of up-scaling it to 8 detectors. The detectors are read-out by a custom designed fast multichannel acquisition system, optimized for the use with SDDs [1]. The LEXRF set up has been designed and adapted to the European TwinMic [2] microscope station located at Elettra synchrotron light facility in Trieste, Italy. TwinMic is a Transmission X-ray microscope working in the energy range 200-2000 eV. It is a multipurpose end station that combines the advantages of full-field imaging and those of Scanning Transmission X-ray Microscopy (STXM), with easy switch between the two modes. By using zone plate diffractive optics the X-ray beam can be focused down to sub-100 nm spot size.

The developed XRF system coupled with the STXM operation mode of TwinMic enables the simultaneous acquisition of XRF maps, absorption images and phase contrast images [3] with high spatial resolution for the sample under analysis. This allows combining chemical specificity with morphological information.

Some examples of XRF maps, absorption images and phase contrast images collected on environmental and biological samples (human cells) will be shown and discussed. Moreover the design and performances of the developed system will be presented. Preliminary results include XRF maps of Ca ($L\alpha$ and $L\beta$ lines, 341 and 344 eV respectively), Na ($K\alpha$ line, 1041eV), Mg ($K\alpha$ line 1253 eV) and other chemical elements.

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O3-5

High resolution X-ray absorption and X-ray emission spectroscopy of titanium compounds

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Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy and high resolution X-ray emission spectroscopy (XES) are powerful tools for the non-destructive chemical speciation of compounds.

The NEXAFS of Ti *K*- and $L_{\mathrm{II,III}}$-edges of different binary titanium compounds were investigated and related to $L_{\alpha,\beta}$ X-ray emission spectra of the same specimens. The aim was to compare the information obtained from absorption techniques to those gained from emission spectroscopy. All measurements took place in the laboratory of the Physikalisch-Technische Bundesanstalt at the electron storage ring BESSY II. All measurements in the soft X-ray regime, where the Ti *L*-shells are located, were carried out at the plane-grating monochromator beamline for undulator radiation. The structure of the Ti *K*-edge was measured at the four crystal monochromator beamline for dipole radiation.

For the sake of comparison, the compounds were sorted according to the oxidation state of the bonded titanium. Thus, it is possible to differ between inner atomic effects due to different oxidation states and external effects related to the ligand and the crystal structure. It becomes evident, that certain compounds, while nearly indistinguishable in their *K*-NEXAFS spectra, still show significant differences in their emission characteristics. On the other hand, the strength of NEXAFS spectroscopy for speciation of different site geometries and ligands can be affirmed.

O3-6

Reference-free quantification of multielemental nanolayered systems

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Layered systems in the nanometer range acting as conducting or non-conducting interfaces become more and more important in the semiconductor industry. The non destructive characterization of such steadily redesigned nanolayered systems e.g. consisting of transition and noble metals is an important task. Appropriate reference materials are often not available due to the rapid developments. Here, reference-free quantification in X-ray fluorescence analyses may be a flexible and reliable solution for this task.

Reference-free XRF requires the accurate knowledge of all experimental values both in the excitation and detection channels as well as of the fundamental parameters involved. Due to the use of a set-up with only calibrated devices the experimental values are well known. The energy-dispersive detectors to record the fluorescence spectra are calibrated with respect to their efficiency as well as to their response behavior. The relative uncertainty of the experimentally determined data in total is about 3 %. Besides contributions from the instrumentation, the relative uncertainties of the XRF analytical results are furthermore affected by the tabulated fundamental parameters of the elements, some of which only have estimated uncertainties.

Using reference-free XRF carried out at BESSY II, different fundamental parameter databases have been compared and supplemented by own values determined by transmission measurements of self-supporting one-elemental foils. These transmission measurements have been carried out with monochromatized synchrotron radiation of high spectral purity and well-known flux to obtain absorption correction factors depending on both the exciting and the fluorescent energy. Moreover the energy dependency of the absorption jump ratio has been included in the algorithms to further reduce the uncertainties of the standard-free XRF.

With these improvements a significant reduction of the relative uncertainties for reference-free quantification from XRF measurements can be achieved and is shown for relevant nanolayered systems and bulk materials in the present work.

I4

The latest directions and trends in Ion Beam Analysis of fine particle air pollution

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In recent times fine particle air pollution (particles with diameters less than 2.5μm, also known as PM2.5) has been related to adverse health outcomes in USA and Europe, poor visibility in Asia and long range pollution transport. In 1997 the US EPA introduced a PM2.5 standard of 15 μg/m^3 for annual average and 65 μg/m^3 for 24 hour maximum. The 24 goal was reduced to 35 μg/m^3 in 2006. Several countries in Europe and Asia have followed suit, in Australia our current PM2.5 goals are 8 μg/m^3 annual and 25 μg/m^3 for 24 hour maximum, much tighter than many other countries. These air pollution goals or standards recognize the deleterious effects of fine particle pollution.

This paper discusses fine particle characterisation by X-ray and ion beam analysis (IBA) techniques and recent developments in their application to source fingerprinting and apportionment. In particular the positive matrix factorisation (PMF) technique will be discussed and its advantages over chemical mass balance methods highlighted. Examples of these applications and their potential will be demonstrated with recent long term datasets obtained in Asia between January 2001 and June 2007. It will also show how wind and back trajectory data can be included to plot fine particle pollution transport and identify possible sources several thousands of kilometers from the sampling site.

O4-1

Depth investigation of aerosols in PM10-filter with 3D micro particle induced X-ray emission (3D Micro PIXE)

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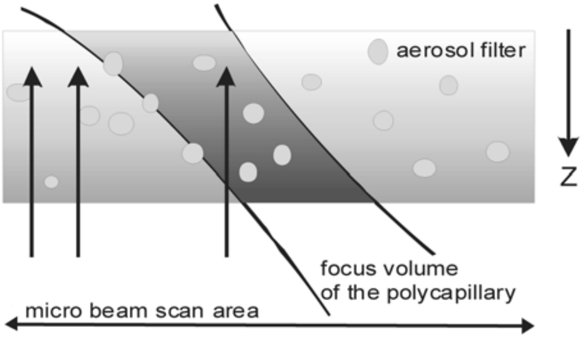
The successful implementation of two X-ray lenses in a X-ray Fluorescence set-up (3D Micro XRF) [1] motivated the establishment of a novel experimental technique, 3D micro Particle-induced X-Ray emission (3D Micro PIXE). The 3D Micro-PIXE is realized by inserting a polycapillary X-ray lens in front of the X-ray detector. The intersection of the lens focus ($FWHM_x$ ~29 μm at 6.4 keV) with the proton micro-beam space distribution ($FWHM_b$ ~2 μm) creates a probing micro-volume. By moving the sample in the beam direction or by 2D beam scanning, depth resolved measurements on elemental distribution become possible at the micrometer regime, whereas the combination of the two approaches allows 3D elemental analysis. For the experimental realization of this technique, the nuclear microprobe of the Jožef Stefan Institute was used [2] in order to establish, characterize and apply the confocal setup for 3D Micro PIXE [3].

In the present work, a new application of 3D Micro PIXE is presented in the field of the environmental science. The 3D site probing of different aerosol particles collected in a PM10 quartz filter was investigated by 3D Micro PIXE analysis by moving the sample in the bean direction and performing micro-beam scanning at each position (Figure 1). An analytical methodology is proposed based on the acquired semi-quantitative information (depth intensity profiles of sulfur, calcium and iron) that allows the determination of the position of different aerosol particles within the micro-beam scanned sample volume.

Figure 1:



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O4-2

Theoretical description of 3D Micro–PIXE intensities. Case 1: Layered materials

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In a typical Micro-PIXE set-up the insertion of a polycapillary half-lens, in front of the X-ray detector in combination with the focused ion beam defines a confocal geometry and the intersection of two foci a probing micro-volume. By moving the sample across the probing-volume, the characteristic X-ray intensities produced only within this probing-volume are detected. This experimental procedure will result, finally, into intensity profiles versus position. It has been demonstrated very recently the feasibility of such kind of depth resolved elemental analysis with Micro-PIXE [1].

This work presents a complete theoretical description of 3D Micro-PIXE intensities for layered materials. The proposed model utilizes an analytical description for the energy dependent spatial response function of the X-ray lens at the focal region in an analogues manner to the one for 3D Micro-XRF [2]. Incorporating together the beam profile, the probing-volume is analytically described through a sensitivity function expressed in spatial coordinates. Particle induced X-ray intensities are calculated taking into account all the well known processes that involve in the PIXE process (ionization, stopping power, and self-attenuation) and through convolution with the sensitivity function 3D Micro-PIXE intensities can be simulated. The model developed accounts for both experimental approaches aiming to depth resolved analysis in 3D Micro-PIXE, i.e. sample displacement inside the probing volume or micro-beam scanning inside the lens focus volume. In the first case, simulated in-depth intensity profiles are generated, whereas in the second case two dimensional intensity maps are obtained.

The influence of various experimental parameters (beam energy, spatial resolution of the X-ray lens, micro-beam dimensions, irradiation and detection angles), as well as of the sample characteristics like the structure (thickness, composition) of the individual layers that compose the analyzed sample, on the simulation of the PIXE intensity profiles is examined and discussed. Examples of the advantages and benefits of the Micro-PIXE analysis in confocal geometry are given.

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O4-3

Lapis lazuli characterization at the LABEC external microbeam

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Characterization of stones and minerals is usually carried out with optical microscopy and in vacuum analytical techniques (e.g. SEM-EDS, cathodoluminescence) typically requiring some treatments of samples, like slicing and/or metallization. These treatments are not possible when precious artworks are to be studied, so that it is necessary to exploit non-destructive techniques like PIXE/PIGE and ionoluminescence (IL). At the LABEC external scanning microbeam of Firenze, we started to study raw lapis lazuli samples of different known origins and precious lapis lazuli artworks of the Collezione Medicea of Museum of Natural History, University of Firenze, aiming to characterise their composition and provenience.

Thanks to the PIXE/PIGE spectra and to the intercomparison of elemental maps, we were able to identify minerals constituting the samples and trace elements in the minerals. Just basing on these results it was possible to interpret IL spectra of lapis lazuli standards. Since the IL technique is sensitive to chemistry of materials, in favourable cases, we can recognize minerals and activators in minerals. Thanks to its high efficiency which permits to get high statistics with low doses, the IL technique is a powerful tool to analyze lapis lazuli artworks. The minerals in lapis lazuli stones and the presence of impurities can characterize the provenience of lapis lazuli; for the Chilean lapis lazuli, we were actually able to point out a clear correlation between the IL spectrum and the provenience.

O4-4

Multiparameter and digital pulse processing for μ-PIXE applications

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X-ray detection and measurement using high resolution detectors usually requires fast and low noise front-end electronics for pulse processing. Programmable digital filters are superior alternative to the traditional analog electronic counterparts in terms of throughputs and flexibility. In addition, as a compact alternative to bulky analog electronics a digital pulse processing can be great benefit in the applications that needs more detectors.

The implementation of the digital pulse processor on FPGA's has several benefits, with emphasis on parallelism and amount of functionality that can be placed into the silicon. In this work a Virtex-4 SX FPGA based PCI card with two 14-bits, 105-MSPS ADCs and two 14-bit DACs was used as a hardware platform for development of a multi-channel digital pulse processor suitable for μ-PIXE applications. Two boards are chained together and signals from four detectors can be processed simultaneously.

In order to utilize ADCs input range as best as possible a four channel analog pre-filter has been designed and produced. The pre-filter includes digitally controlled differentiation, pole-zero cancellation, linear amplification and finally anti-aliasing filter.

The main FPGA design was divided into two asynchronous clock domains. The first clock domain, related to the pulse processing, is driven by 105-MHz clock. It includes (per channel) the following subsystems which name and functionalities are equal to their analog counterparts: pulse shapers – continuously time domain trapezoidal filters (fast and energy) followed by base line restorer (BLR), pile-up rejector (PUR), live time corrector (LTC) and pulse height analyzer (PHA). The second clock domain is driven by 40-MHz clock and includes subsystem blocks for communication with host computer.

O4-5

Trace Element Profiling of Gunshot Residues by PIXE and SEM-EDS: A Comparative Study

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The identification of gunshot residues found on a suspect has challenged forensic scientists for many years [1]. SEM-EDS is the technique of choice for analysing such samples because as well as being non-destructive, the technique can be used to study the morphology in addition to the composition of the spherical particles that make up the residue. The technique is used routinely by police authorities in the UK to identify gunshot residue, and it has been shown that the technique can be used to distinguish between residues from different types of ammunition powders [2]. However, it is probably impossible to distinguish between some ammunition powders using this method [2],[3], particularly for lead free ammunition powders.

In this work, we evaluate the usefulness of particle induced X-ray emission (PIXE) compared with SEM-EDS for the characterisation of gunshot residues. Samples of gunshot residue from several different ammunition powders were collected from different shooters hands by swabbing with carbon tape. Individual particles of gunshot residue were analysed by SEM-EDS and PIXE using a 2.5MeV proton beam focussed to 3 microns. The PIXE technique revealed trace elements in the samples that were not detected by EDS because of the lower sensitivity of the latter technique. We demonstrate that the PIXE technique can be used to distinguish between gunshot residues that cannot be resolved using conventional methods.

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[2] Z Brozek-Mucha et al, Evaluation of the possibility of differentiation between various types of ammunition by means of GSR examination with SEM-EDX method, Forensic Sci. Int. (2001).39-47

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O4-6

EPMA investigations of soil cover in lake Baikal region

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Soil is an informative indicator of environmental pollution. Therefore, environmental investigation of soil cover is actual task of soil science and geochemistry. In this connection, it is very important to have information both about chemical soil composition and about phase distribution of substance, shapes of phase separation, sizes and structure of surface.

The results of investigations of soil cover in Baikal Region obtained by X-ray electron probe microanalysis (EPMA) are presented in this work. Samples of soils were collected in ecologically clean (background) regions and regions with high man-caused loading degree.

The EPMA technique is developed for soil particles using Superprobe-733 and JXA-8200 (Jeol Ltd, Japan) devices with energy-dispersive and wavelength-dispersive spectrometers. The surface of particles, shapes of phase separation, sizes and homogeneity of their distribution were studied using scanning electron microscope.

The results of investigations indicated that, soil cover consists of mixture of mineral phases separated as individual particles of different shape and various sizes. The change of phase and chemical composition of soils from regions with various man-caused loading degree differs in proportion of natural and anthropogenic particles. The natural particles of faceted shape are observed in background regions. They generally include silicate minerals. Industrial regions contain along with natural particles the anthropogenic particles shaped as rounded, orbicular and irregular semi-faceted caused by industrial processes. These particles include the phase with carbon compounds, carbonates, metal oxides, metallic grains and spherules.

Thus, detailed investigations of soil cover in Baikal Region by EPMA allows identification of basic pollution sources and their influence on the environment and estimation of anthropogenic accumulation in clear background regions and regions with high man-caused loading degree.

O4-7

Application of X-ray spectroscopy to study of alkali-silicate glasses irradiated with electrons

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Glasses are frequently used in the applications where they are exposed to particle irradiation of different energy (materials for the fixation of radioactive waste, insulating glass fibres in nuclear power plants, electron multipliers, telescopes located in open space, etc.). The need of seeking for the limiting glass properties increases in connection with material-tailoring technologies, which enable to improve the glass properties (durability, fatigue, weathering, and mechanical properties) and to use glass in new applications.

Alkali-silicate glasses irradiated with electrons show changes in their structures, which can be characterized via measuring of intensity of alkali metal X-ray line. Intensity versus time curve, so called decay curve, can be recorded by X-Ray spectrometer during the electron bombardment. The decay curve generally reveals two distinguished parts; the first one is constant or linear and after some time, called the incubation period, breaks into the exponential-like one.

Potassium silicate glasses were irradiated with 50 keV and 2.5 MeV. The decay curves were recorded for both pristine glass and that irradiated with high-energy electrons. Both decay curves were compared; the changed incubation times enabled to estimate the radiation damage caused by 50 keV and 2.5 MeV. Changes of composition within and around the exposed volumes were measured by EPMA (Electron Probe Microanalysis). Absorption spectra of glass irradiated with high-energy electrons in the visible range revealed a clustering in glass. The electron irradiation is also accompanied with volume changes. AFM revealed volume contraction at small doses and expansion at high doses.

O4-8

Measurement of a certified standard of hydroxyapatite by PIXE, EDS, and simultaneous PIXE and RBS – a comparative study

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Determination of the Ca:P ratio in biomedical samples such as bone is of interest in biomedicine, and small variations in the Ca:P ratio are frequently studied in order to understand conditions such as osteoporosis [1]. X-ray spectrometry methods are particularly suitable for such studies because the mapping capability of the techniques allows researchers to locate spatial variations in the Ca:P ratio.

In this paper, we will present a comparative study of different X-ray spectrometry methods (PIXE and EDS) for the determination of the Ca:P ratio in a certified standard of hydroxyapatite. The certified value was accurately verified by Rutherford Backscattering Spectrometry (RBS) which is a simply traceable technique depending on the scattering cross-section given (analytically) by the Coulomb potential, and typically using a probe beam of 2MeV alpha particles. RBS is one varant of ion beam analysis (IBA), and PIXE spectra can be collected simultaneously with RBS spectra.

The Ca:P ratio was measured using EDS, the PIXE code GUPIX [2], and the newly implemented PIXE module in the IBA DataFurnace code [3,4] which accurately determines elemental depth profiles by self-consistently fitting the PIXE and RBS spectra. RBS spectra have depth profile information available directly, so a PIXE/RBS analysis is very powerful for samples which are not homogeneous in depth, a common case which can can seriously distort EDS results. It is also interesting to compare EDS with IBA since the information depth for all the techniques is different.

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I5

Photoinduced atomic inner-shell processes investigated by means of high-resolution x-ray spectroscopy

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High-resolution x-ray spectroscopy represents a powerful and sometimes unique tool for the investigation of atomic inner-shell processes. Indeed many aspects of the mechanisms governing the atomic excitation and decay channels can be studied by means of this technique which has played a central role in our present understanding of atomic structures and dynamics. The wealth of x-ray based applications in many domains of modern physics and other fields of sciences and technology and the recent advent of new tools such as synchrotron radiation facilities and heavy-ion storage rings combined with increasingly sophisticated instrumentation have given a new boost to the domain.

In the first part of the talk, basic aspects of wavelength dispersive instruments will be presented. Bragg-type and Laue-type spectrometers will be outlined and their advantages and drawbacks discussed. Two high-resolution crystal spectrometers constructed in Fribourg will be then described in more details: a Laue-type DuMond bent crystal spectrometer used for the measurements of photons of energies higher than 12 keV and a Bragg-type von Hamos bent crystal spectrometer employed for photon energies between 0.6 keV and 16 keV.

In the second part, examples of some recent projects performed by means of high-resolution x-ray spectroscopy will be presented. Some typical results obtained in our long-term work on the metrology of x-ray transitions will be first presented. Studies concerning the resonant inelastic x-ray scattering (RIXS) and the hyper-satellite transitions induced by impact with heavy-ions, electrons and photons will be then discussed. Finally, before concluding some results concerning the determination of low-Z trace impurities on the surface of silicon wafers by means of the novel high-resolution total reflection x-ray fluorescence (TXRF) technique will be outlined.

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[2] J. Hoszowska et al., Nucl. Instr. Meth. Phys. Res., A 376 (1996) 129 - 138.

O5-1

Large area silicon drift detectors

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Silicon Drift Detectors (SDDs) are commercially available for more than 10 years. They are widely used in XRF, TXRF, electron microprobe analysis systems and synchrotron applications.

The big benefit of SDDs compared to other x-ray detectors as Si(Li)s or pin-diodes is the spectroscopic performance principally being independent of the sensitive area. As there is a growing demand for larger detector areas, KETEK has developed SDDs with active areas up to 100 mm².

We will present spectroscopic measurements of SDDs with areas varying from 10 to 100 mm². Energy resolution below 130 eV for the Manganese $K\alpha$ line and peak to background values of more than 10,000 will be shown for devices with active areas of 100 mm² when cooled down to -60°C. Count rate dependency of the energy resolution and the peak position is shown to be negligible up to count rates of 100,000 counts per second.

Temperature dependent measurements of the energy resolution will be shown for different detector areas. We will present improved cooling techniques for KETEK VITUS modules which allow detector temperatures down to -50°C at an ambient temperature of +20°C. Energy resolutions below 135 eV for 100 mm² SDDs and 130 eV for 30 mm² devices at -50°C are achieved.

O5-2

Advances in the technology of silicon drift detectors (SDD) and multiple element SDD

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Over the past few years, Silicon Drift Detectors (SDD) have become more and more popular in the field of X-ray detection and are about to replace lithium-drifted silicon detectors (Si(Li)), [1]

Improvement have made it possible for state of the art SDD, as represented by the forth generation XFlash 4000 series, to exceed the performance of Si(Li) in almost every respect that matters to analytical x-ray spectrometry. High resolution type SDD show energy resolutions of 125eV or even better at Mn-Kα. Optimised detector radiation entrance windows [2] provide an excellent low energy response with minimal shelf and tail. Improved electronics with pulsed charge restoration methodology maintain this energy resolution even at extremely high count rates, allowing all XFlash detectors to achieve full specification at 100 kcps input count rate.

Multiple element SDD structures with four separate detectors integrated on one chip provide even higher count rates without increasing pile-up or dead time. Quad SDD with four separate detectors are capable to deliver up to 1,000,000 cps output count rate. The multi element concept also allows a larger solid angle without degrading energy resolution because of a larger effective area, e.g. detectors which consist of four 10mm² (left) and 15mm^2 SDD (right), offering effective detector areas of 40 and 60mm^2, respectively.

The especially designed annular QUAD XFlash 4060 with four 15 mm^2 SDD centered around a hole for the primary beam can be placed directly before the sample in order to cover an extremely large solid angle of about 0.9 sr because of its flat and perpendicular structure and good performance at count rates of up to 500kcps [2], Fig. 1.

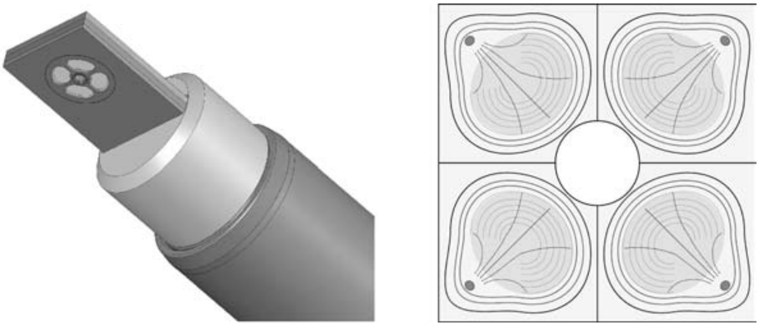

Fig. 1. Flat annular detector (QUAD XFlash 4060) which covers a solid angle of 0.9 sr when placed 5mm above the sample. Left: design, right: sketch of the four detector segments.

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[2] P. Kotula et al., Proceedings of the ACMM-20 & IUMAS-IV (2008) 50-51

O5-3

Silicon drift detector spectrometers for high count rate XRF applications

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A 50 mm^2 silicon drift detector (SDD) has been successfully applied to TXRF (total reflection x-ray fluorescence), synchrotron and other XRF applications. The SDD offers a large solid angle, excellent energy resolution (<130 eV FWHM at 5.9 keV, 4-6 μs peaking time), and high count rate performance (> 600 kcps throughput at 0.25 μs peaking time).

The SDD has recently been applied to collect synchrotron XRF spectra in several astrophysics applications. For example, the chemical composition of particles from the “Wild 2” comet, collected and returned to Earth from a NASA mission, have been analyzed using the SDD in synchrotron XRF techniques at the Stanford Synchrotron Radiation Laboratory.

Multi-channel XRF spectrometers, offering larger solid angle and higher count rate performance, have been developed based on multiples of the 50 mm^2 SDDs. Two unique multi-element systems have recently been developed and are currently being used in high count rate synchrotron applications at the Advanced Photon Source at Argonne National Laboratory.

Results from several XRF applications, using both the single-element and multi-element SDD spectrometers, will be presented.

O5-4

High througput digital pulse processing hardware

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Practical applications of X-ray spectrometry frequently require the user to trade off a substantial degradation of energy resolution in order to achieve an increase in the detector throughput. Traditional approaches to digital pulse processing allow this by implementing linear filtering techniques to decrease the required pulse-shaping time. However, a point is rapidly reached beyond which the majority of data is corrupted by pulse pileup degrading the throughput, energy resolution, or both.

This paper presents an optimal pulse detection technology for the processing of digitised pulse trains from X-ray detectors. Using a multi-stage, nonlinear digital signal-processing algorithm, this approach is able to decode pileup events in real time dramatically improving the count-rate, throughput, and resolution performance of XRF and XRD systems.

The performance of the digital pulse processing technology has been analysed over a range of input count-rates using a digital nuclear pulse generator. Results indicate that over a 100-fold increase in input count-rate (from 10 kc/s to 1,000 kc/s) system throughput and energy resolution both degrade by less than 10%.

Implemented on a PCI based computer card, in a Virtex-IV FPGA, the technology is able to decode pulse pileup events in real-time dramatically improving the performance of a wide range of X-ray spectrometry systems.

O5-5

Enhanced detection sensitivity of micro X-ray Fluorescence by using advanced X-ray optic chain

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Both polycapillary X-ray optics and doubly curved crystal (DCC) optics have been widely used in X-ray analytical instruments and a variety of research applications. A polycapillary optic is a broad-band optic that consists of up to millions of small channels that are precisely curved to a designed profile to efficiently transmit X-rays by multiple external total reflections off the inner surface of each individual capillary channel. The optic collects a large solid angle of X-rays from a divergent X-ray source and redirects them to either a parallel beam of a focused beam. A focusing polycapillary optic can generate a focal spot less than 10μm while delivering an X-ray intensity equivalent to a pinhole collimator of millimeters in diameter, making it an inevitable tool to use for many applications. A doubly curved crystal (DCC) optic, on the other hand, is a diffractive X-ray optic that collects X-rays from a divergent X-ray source and redirects a narrow band of them by diffraction to form a focused, monochromatic beam. The two optic technologies have their own characteristics and advantages, but also have their limitations. We will report in this paper the use of a DCC-polycapillary optic chain to achieve a monochromatic beam with the focal spot size less than 10μm and the use of such configuration for micro X-ray fluorescence applications. The performance will be compared with that of other technologies to demonstrate the capability of the innovative approach in achieving higher detection sensitivity, higher measurement precision and other analysis benefits.

O5-6

Detection of a heavy metal inclusion in the tissue with the use of ED XRF approach

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Energy Dispersive X-Ray Fluorescence (ED XRF) spectrometer X-Art M produced by JSC “Comita” is used to determine position and size of a spherical heavy metal inclusion formed by injection at a certain depth in the tissue. This problem appears in Neutron Capture Therapy when the tumor is saturated with ^{157}Gd solution [1]. It is important to check the real boundaries of the inclusion just before the tumor is irradiated by neutron flux.

Thick Si(Li) detector in the X-Art M spectrometer allows effective detection of Gd $K\alpha,\beta$ lines excited in the tissue by ^{241}Am source. To interpret the experimental spectra a new Monte Carlo code is developed which includes non-standard imitation of the photon path length in the media with variable parameters.

It is shown that the Gadolinium concentration of about 25 mg/ml can be seen at a depth up to 4 cm in the tissue, and for 80 mg/ml the depth is up to 5 cm.

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O5-7

The difficult way to excellent analytical results

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Everyone who deals with elemental analysis is probably striving after the most ideal results and thus calibration curves. Sometimes, it is indeed a long and difficult way obtaining an excellent and trustable result with an X-ray spectrometer (let it be an ED- or a WD-XRF). Too often, providers of analytical equipment get confronted with the question or even statement “the machine/spectrometer does not run stable, it gives me wrong results!”

There are some steps in the analytical process which have to be taken care of in order to get precise and accurate results. It is not only measuring a sample and picking up your results. No, that is only the final step in a process of many actions.

This presentation will deal with the different sources of error which can take place, before we measure the actual specimen, in the XRF analysis. First of all we need to take a representative sample and we also need to transform this sample into an appropriate specimen which we can measure with our spectrometer. Of course, also the instrument stability will play a role; every equipment needs some basic maintenance. If we are setting up a calibration line then we must be sure that we have a set of certified reference materials or at least some standards of which we know that they are of high quality. And last but not least, we must take care that we do use the right calibration model; did we calculate line overlaps where it is necessary, did we calculate matrix effects? It is necessary to check the quality of our result by means of some standard.

Further, we can not expect the same quality in our results when we compare the today so popular “black box – standardless analysis” with quantitative analysis. Nevertheless, today both methods can give us good results, but again we must realise that analysis with X-ray spectrometers also needs some human input.

In the end WE are the largest source of error.

O5-8

Response function of semiconductor detectors : comparison between experimental measurements and Monte Carlo simulation

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Response function of semiconductor detectors is a key element for accurate analysis of experimental spectra obtained by X-Ray fluorescence or PIXE. The interest of the use of monochromatic radiation to accurately know the detector response function has been previously pointed out.

In the present study, the SOLEX X-ray source [1] is used to produce a tunable monochromatic X-ray beam in the 1-20 keV range. With this facility, it is possible to record spectra around the binding energies of the elements constituting the detector (active crystal, electrode, etc.). The comparison between spectra just below and above the binding energies allows demonstrating the effects of primary photons and secondary fluorescence X-rays, Auger electrons and photoelectrons on the spectrum shape. Indeed, the spectrum shape strongly depends on the photons and photoelectrons interactions at the level of the semiconductor crystal-electrode interface.

The PENELOPE Monte Carlo code [2] is used to simulate the spectra corresponding to experimental conditions, and to follow the interactions of elementary particles in each constituent of the detector. This is applied to a high-purity germanium detector that has been previously characterized using SOLEX [3] and whose constituents' thicknesses have been measured.

Comparison between experiment and simulation allows validating assumptions on the composition of the low energy side of the full-energy peak

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O5-9

A new X-ray astronomy spectro-imaging detector based on a micro-calorimeters array using tantalum absorbers

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For the next generation X-ray space observatories, such as XEUS mission, cryogenic X-ray microcalorimeter arrays are expected to outperform CCDs in terms of spectral resolution, energy bandwidth and count rate. In this context, we are now developing an X-ray spectro-imaging camera operating between 0.05 and 0.1 K [1] using silicon thermistors thermally and mechanically linked to Ta absorbers.

The camera is a 32x32 pixels matrix with a 500 µm pitch. Each pixel is made of a purified tantalum X-ray absorber thermally linked in a flip chip configuration to a thermistor. This last is obtained by P and B implantation and high temperature diffusion in 1.5 µm thin and very brittle silicon membranes, electrically connected to a read out circuit for data processing. Thanks to its high atomic number, a 25 µm thin tantalum foil allows almost complete absorption of photons between 0.1 and 10 keV. Due to the high number of pixels, a flip chip collective hybridization of tantalum absorbers on brittle implanted silicon thermistors array has been performed with a pure indium solder. Indium bumps were first fabricated on silicon wafers and then transferred onto tantalum foils. These were singulated maximizing the filling factor, i.e. with a minimum space between pixels. Collective hybridization of pixels onto thermistors array is then carried out using a Suss Microtec FC 150 bonding machine by a reflow process.

We will first discuss the materials choice and implementation techniques imposed by the severe detector's specifications. Then we will present in details, the main challenging technical issues of the construction of the detector. Collective hybridization of singulated tantalum absorbers on brittle silicon membranes will be shown. First measurements of the thermal impedance of the link will be presented.

[1] A. Aliane et al, J. Low Temp. Phys., (2008) doi: 10.1007/s10909-007-9664-7

O5-10

X-ray Microanalysis by a Transition-Edge Sensor Microcalorimeter mounted on a low voltage FE-SEM

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We have developed an EDS system for scanning electron microscope utilizing a transition-edge sensor (TES) microcalorimeter X-ray detector and mounted it on a FE-SEM (JEOL: JSM-7000F). The microcalorimeter is composed of a gold X-ray absorber, a bilayer Au/Ti thermometer, a heat sink and a thermal isolation structure with a SiN$_x$ membrane. The operating temperature of 100 mK is obtained via a dilution refrigerator. The achieved energy resolution was 19 eV for Al Kα (1487 eV) at an acceleration voltage of 5 kV. An EDS spectrum of euxenite, (Y, Ca, U, Th) Nb$_2$O$_6$, was measured and compared with the SSD data in Fig. 1. TES gives well resolved peaks of the heavy elements Y,Nb,Th,U as well as the light element of Ca showing the high resolution of the detector.

The TES system was applied for the first time to reveal the cellular distribution of Cd in a cadmium hyper-accumulating plant. The elemental maps of the light element P as well as the heavy elements Cd and Zn were also successfully obtained. Similarly, the simultaneous analysis of As L*α* and Mg K*α* in an arsenic-accumulating fern was possible with this system. In addition, a single particle of natural particulate matter was successfully analyzed by this spectrometer at a low acceleration voltage. These results suggest that this system has high potential in application to X-ray microanalysis of environmental samples including various biological samples.

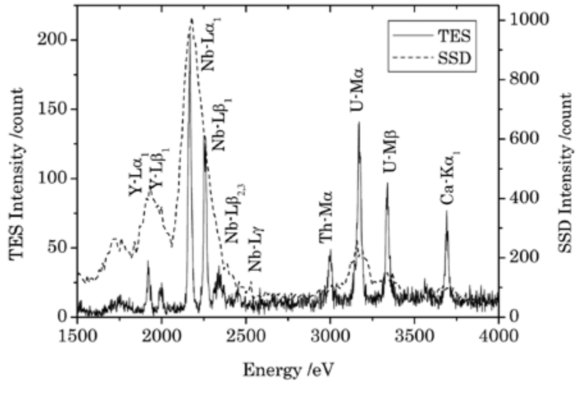

Fig.1μ-cal EDS spectrum of euxenite, (Y,Ca,U,Th)Nb$_2$O$_6$.

O5-11

High-resolution X-ray spectroscopy with the TES microcalorimeter X-ray detector

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[2]National Institute of Standards and Technology, Boulder, Colorado, 80305 USA

The NIST microcalorimeter x-ray detector using a superconducting transition edge sensor (TES) has reached a point of practical development at which we have already carried out programs in x-ray spectroscopy and quantitative x-ray microanalysis[1,2]. The ability to measure x-ray spectra with relatively high resolution (up to 4.4 eV) over an extended energy range (8 keV) means that we are able to resolve spectra due to compositions of multiple chemical elements and to make intercomparisons of spectral lines. These include both the energies and intensities of lines and accompanying satellite lines. We describe the current performance of the detector and applications that we have carried out using electron excitation. Future improvements in resolution that will allow us to observe oxidation states and chemical valence features in the x-ray fluorescence spectra will also be described.

[1] T. Jach, J. A. Small, and D. E. Newbury, Adv. X-ray Anal. **48** (2005) 216-218.

[2] T. Jach, N. Ritchie, J. Ullom, and J. A. Beall, Adv. X-ray Anal. **50** (2007) 51-53.

O5-12

Calculation of scattering spectra for the determination of the actual transmission of an X-ray mini-lens for µXRF

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The knowledge of the X-ray excitation spectrum is a prerequisite for XRF quantification. In the case of small-spot XRF the excitation spectrum is the X-ray tube spectrum multiplied with the transmission function of the X-ray mini-lens. The tube spectrum is usually calculated by fundamental equations. The transmission function is conventionally determined by *measuring* two scattering spectra with and without mini-lens and dividing them to each other [1]. The measurement without mini-lens is costly, requiring a calibrated double collimator to be interchanged with the mini-lens – therefore carried out mostly by manufacturer.

The alternative to the measurement of the scattering spectrum without lens is its *calculation* from Rayleigh and Compton scattering of the specimen. The procedure was verified with an *iMOXS* X-ray source (IfG, Berlin) with known tube spectrum [2] and being attached to a SEM equipped with a calibrated EDX spectrometer [3]. The transmission function obtained was in a good agreement with that resulted from two measured scatter spectra. It will be presented how the procedure exactly works and how secondary effects not yet included into the scattering model can be circumvented.

The major benefits of the new procedure are that the user is able quickly to determine the actual transmission function. This is very likely modified after a change of the X-ray tube or of the X-ray mini-lens (meanwhile routine practice in our lab when looking for the optimal excitation). Additionally, the procedure is sensitive to the effect of possible degradation of the tube target or window.

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O5-13

X-Ray plasma source for fs-pulses

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Examination of material structure is possible with X-Ray techniques. A very often used method is X-Ray diffraction. This method typically gives time averaged information about the arrangement of atoms in a crystal. But more and more it will be interesting to see their changes or also changes in electronic structure. In that case time dependent measurements are necessary. Due to time constants for these processes in the range of picoseconds and down to femtoseconds special pump-probe-experiments are used. They need X-Ray sources that generate pulses of hard X-Rays in the fs-range. X-Ray pulses of this duration can be generated by beam slicing experiments at synchrotrons, by free electron lasers or by laser pumped plasma sources. These plasma sources are table top instruments that can be used in laboratory environment. They produce incoherent pulses with duration in the range of 100 fs and with up to 107 photons/(pulse*4π) and a repetition rate in the kHz range.

The paper discusses the development of a plasma-X-Ray-source of this type and their mechanical design. First results of operation will be presented.

I6

X-ray phase contrast imaging and tomography of malaria transmitting mosquitoes

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X-ray phase contrast imaging technique was applied to examine the morphology of malaria transmitting mosquitoes in support to the development of the sterile insect technique (SIT) [1, 2]. The aim of the experiment was to detect eventual damage induced by the sample preparation procedures, to perform X-ray phase-contrast imaging on freshly prepared (not fixed) and live mosquito species, and to test the new beamline set up.

The ability to perform X-ray phase-contrast imaging of live mosquito specimens was confirmed. The collected still images provided data on a relatively large population of mosquitoes. The CT data were very useful to compare selected mosquito species. They confirmed that the sample preparation procedures are critical for examining the morphological details. The procedures must by further optimized in order to stabilize the sample without inducing significant damage. The most interesting results should be obtained with the high-resolution (~ 0.5 micrometer) set up. If there are differences between the control and irradiated populations of mosquitoes they should show up first at the tissue level. Using the high-resolution set up it should be possible to detect such differences, if present

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O6-1

Combined micro-XRF/XRPD tomography on historical and modern paint multilayer samples

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The combination of X-ray powder diffraction (XRPD) and X-ray fluorescence (XRF) used together in a micro-tomography experiment at a synchrotron end station allows the reconstruction of phase and elemental distributions within objects on the micro scale [1]. Several parameters can be extracted from the XRD data and plotted against the tomographic translation and rotation coordinates to construct sinograms which form the basis for image reconstruction. Using the intensity of individual (hkl) reflections will result in phase distribution maps in a plane through the scanned powder sample, i.e. where all crystal orientations are evenly present. For polycrystalline material with less grains in the x-ray microbeam, the intensity will depend on the orientation under which the diffractograms are collected. This results in irregular sinograms, showing strongly fluctuating diffraction intensity as a function of the object rotation angle, making the reconstruction very difficult.

The Pawley intensity scaling factor can be used instead of individual peak intensities to smooth out this orientation effect. When performing Rietveld refinement, additional semi-quantitative information (i.e. phase weight percentages) can be obtained for the scanned area.

Recent results from tomographic experiments on paint multilayer samples, performed at HASYLAB Beamline L, are presented. A ~700 µm thick car paint was found to be composed of nine layers, containing six different crystalline compounds. Furthermore, a paint fragment was investigated from a 17th C. painting from P.P. Rubens. Reconstruction shows a distinct calcite grounding on which a mixed hydrocerussite/azurite layer is deposited, which explains the light-blue tint used to depict the clouded sky in the painting.

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O6-2

Three dimensional SR-confocal micro XRF combined with absorption microtomography on *Daphnia magna*: Instrumental developments and recent advances in dataprocessing

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Daphnia Magna (also called “water fleas”) are being used to study the mechanism of intoxication by metals (Zn, Cu, Ni) and to develop so called biotic ligand models (BLM’s). It has been shown that *Daphnia magna* responds differently to Zn-exposure via the water and/or via the food [1].

In order to distinguish critical tissue from whole body accumulation in these small organisms (~3 mm size), we explored the potential of combined X-ray techniques as a complementary approach to the above problem. Fast dynamic 2D micro XRF scanning and XRF micro CT experiments on *Daphnia magna* at Beamline L (HASYLAB, Hamburg, Germany) allowed the semi-quantitative investigation of the accumulation of metals within specific organs with microscopic resolution. Combining these results with micro CT data sets unravelled the tissue specific 2D/3D distribution of metals within delicate organic samples on the 3-15 µm resolution level in an essentially non-destructive manner [2].

As demonstrated, recent developments at beamline L, involving a dedicated confocal µ-XRF set-up with a resolution of 5 µm and full 3D dynamic scanning algorithms allowed to explore microscopic 3D substructures within *Daphnia magna* (also called “top-down” methodology) aiding ecotoxicological research towards the tissue and even cellular level. Three dimensional isosurfaces of the elements of interest were obtained within a 300 µm *Daphnia magna* egg (5µm resolution). Moreover, K-means clustering allowed us to isolate 3D clusters of interest of which the elemental content can be investigated in closer detail [3]. Finally, using laboratory micro CT (0.9 µm resolution) we obtained full 3D correlation between elemental and absorption datasets on the micrometer scale within biological samples.

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[2] Three-dimensional elemental imaging by means of synchrotron radiation micro-XRF: developments and applications in environmental chemistry, Anal. Bioanal. Chem. (2008) 390:267-271

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O6-3

Quantitative elemental imaging of fragments of the Dead Sea scrolls with a combination of micro-XRF and 3D micro-XRF

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With a combination of Micro-XRF and 3D Micro-XRF an investigation of very inhomogeneous, archaeological samples was carried out. For Micro-XRF a portable spectrometer [1] was used for which a quantification procedure was developed. 3D Micro-XRF measurements were performed at the µSpot beamline of the synchrotron storage ring BESSY. The quantification of the elemental depth profiles was obtained by a self-developed reconstruction algorithm which was validated and applied recently [2,3]. The combination of both methods allows reliable quantitative elemental imaging even for very inhomogeneous samples.

The mutual benefits of this combination will be exemplified by the investigation of some fragments of the Dead Sea Scrolls. It shows its capacity especially for samples from the field of Cultural Heritage.

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O6-4

X-Ray fluorescence microtomography analysis under various excitation conditions

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X-ray fluorescence microtomography (XRFCT) can be used to investigate the distribution of the chemical elements inside a sample. This makes it a powerful tool for several fields of research, like biology, archaeology and medicine. XRFCT is based on the detection of fluorescence photons emitted by the elements in the sample. As the energy of photons of fluorescence has a particular value for each element, is possible to obtain the distribution of all the elements in a sample, since that a minimum of fluorescence signal is detected.

The main of this work is to compare three different excitation conditions in XRFCT for analyzing reference samples and to determine the elemental distribution map in breast tissue samples in order to verify the concentration of some elements correlated with characteristics and pathology of each tissue observed by the transmission CT.

The experiments were performed at the X-Ray Fluorescence beamline (D09B-XRF) of the Brazilian Synchrotron Light Source (LNLS), Campinas, Brazil. In this works, it was used a multilayer monochromator at photon energies near 12 keV, a monochromatic beam at 9.8 keV using a Si(111) and a white beam for the excitation of the elements inside the samples. The sample was placed on a high precision goniometer and translation stages that allow rotating as well as translating it perpendicularly to the beam. The fluorescence photons were collected with an energy dispersive HPGe detector placed at 90º to the incident beam, while transmitted photons were detected with a fast Na(Tl) scintillation counter placed behind the sample on the beam direction.

The transmission CT images were reconstructed using a filtered-back projection algorithm and the XRFCT were reconstructed using a filtered-back projection algorithm with absorption corrections.

O7-1

High-energy polarised-beam EDXRF for the determination of palladium residues arising from catalysts used in the synthesis of active pharmaceutical ingredients

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Pharmaceutical industries are required by legislation to restrict the amounts of residual metals used as process catalysts in the synthesis of drug substances [1]. Metals are classified in three categories based on their potential risk to human health and concentration limits are set according to the maximal daily dose, duration of treatment, route of administration and permitted daily exposure. For example, in the case of Platinum Group Elements (Pt, Pd) a limit of 10 $mg \cdot kg^{-1}$ in active pharmaceutical ingredients (APIs) for oral exposure has been established.

All pharmacopoeias include a test for heavy metals, which is commonly carried out by sulphide precipitation in a weakly acidic medium. However, such test is not suitable for quantitative determination of the actual levels of some metal residues such as Pd and then spectroscopic techniques including atomic absorption spectrometry or inductively coupled plasma optical emission spectrometry are preferred. However, numerous drugs are practically insoluble in water, weak acids or alcohols and therefore laborious sample preparation procedures for the total destruction of the matrix by mineralization, using corrosive and toxic reagents, are needed.

In the present work, we study the feasibility of using High-Energy Polarised-Beam EDXRF (HE-P-EDXRF) spectrometry as an alternative analytical tool for the analysis of Pd residues in APIs. The combined use of selective excitation using a CsI secondary target, a Gd anode X-ray tube and a high-energy Ge semiconductor detector allowed the determination of Pd in APIs and synthetic cellulose standards in the low mg kg^{-1} range. Moreover, typical validation characteristics proposed by the ICH guide [2] were evaluated to study the real capability of the method for the intended purpose.

The results obtained show that HE-P-EDXRF is a promising analytical alternative since it involves a really simple sample preparation (i.e. pelletisation) without losing analytical performance compared to techniques used in the daily routine at the pharmaceutical laboratories.

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O7-2

Chemical character of BC_xN_y nanolayers

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Binary and ternary compounds of the light elements boron, carbon, and nitrogen were predicted to have extraordinary properties for hard coatings, and as semiconductors of varying band gaps. Layers of BC_xN_y were produced in a CVD process using the precursor trimethylamine borane and inert or reactive gases as He, N_2, and NH_3, respectively [1]. These layers deposited on Si wafers were characterized chemically by TXRF-NEXAFS and XPS. As a result, the chemical bonds were identified by comparison of the spectra with those of reference materials, and with spectra from the literature [2].

In the product synthesized without NH_3 nearly only B-C bonds could be characterized. By adding NH_3 with a partial pressure of up to about 1.3 Pa to the precursor a material with atomic relations B:C:N = 2:2:1 was found. Increasing the partial pressure of NH_3 to about 1.7 – 2.1 Pa the product was enriched in nitrogen yielding a material with atomic relations B:C:N = 1:1:1.

The ternary products exhibit a hexagonal structure, which can be characterized as h-BN, in which some of the nitrogen atoms are substituted by carbon atoms. In the contribution the results will be discussed in detail.

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O7-3

XUV diffraction from a self-assembled 2D array of close-packed 200nm diameter PMMA Spheres

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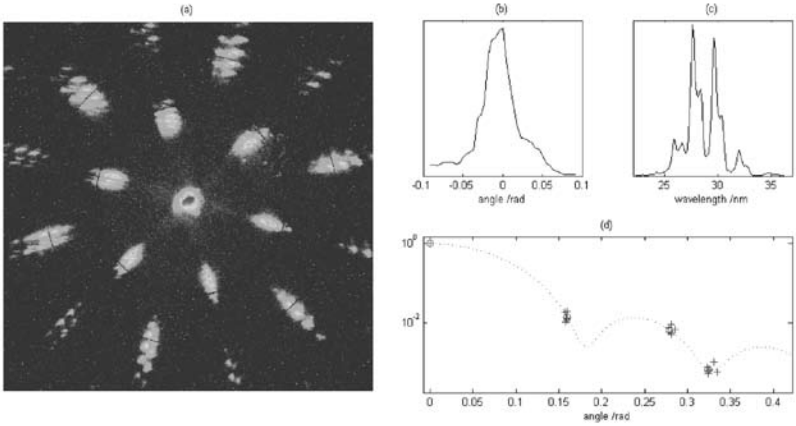
Laser-generated XUV and soft x-ray radiation sources using high-harmonic generation (HHG), typically producing 10^8 photons per pulse per harmonic (~5nm to ~50nm) in a coherent low-divergence beam [1], are a promising source for nanometer scale imaging [2]. Here we present XUV diffraction from a single-layer self-assembled hexagonal-close-packed (HCP) array of 200nm diameter PMMA nanospheres. Such a lattice is too small to diffract from using visible light, and hence XUV wavelengths are required. Figure (a) shows the far-field pattern from the single crystal at a 22μm focus, and overlaid with 100 mrad contours. The interference peaks are a convolution of a Bragg peak with both the distribution of lattice planes (due to crystal defects) and the harmonic spectra. However, as these convolutions are in orthogonal directions, they can be independently resolved (figures b & c), providing information on the crystal quality and generated wavelengths.

The far-field diffraction pattern from a single-layer HCP array of spheres is the Fourier Transform (FT) of a hexagonal grid of delta functions multiplied by the FT of a the scattering function from a single sphere, which can be calculated using Mie theory. Figure (d) shows, (+) the measured intensity for each of the eighteen interference peaks for the harmonic at 27.6nm, (.) the theoretical intensity versus angle distribution for a single sphere, and (o) the predicted intensity at each interference peak. The excellent agreement indicates that Mie scattering predicts an appropriate form factor for this analysis and enables us to extract the complex refractive index of PMMA at this wavelength.



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O7-4

An EDXRF method for determination of uranium and thorium in AHWR fuel after dissolution

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Thorium, uranium and plutonium based fuels are used in nuclear reactors for electricity generation [1]. X-ray Fluorescence in different geometries: Energy Dispersive, Total Reflection and Wavelength Dispersive, can be used as a non-destructive, fast technique for bulk analysis of Th, U and Pu in these fuel materials [2]. The main advantage of X-ray spectrometric methods is that the samples can be analysed without dissolution. However, such determinations suffer from laborious sample preparation and are encountered with severe matrix effects. In present work, an EDXRF method for uranium determination with a special emphasis on Advanced Heavy Water Reactor (AHWR) fuel using a Jordan Valley EDXRF spectrometer EX-3600 TEC having a Rh target has been developed. Studies were carried out for uranium and thorium determinations in the samples in form of solutions. Synthetic uranium and thorium mixtures covering the U% in (U+Th) from 0 to 70% were prepared by mixing uranium and thorium standard solutions. Y was added as internal standard in these solutions. About 20 microlitre of solution was taken on circular Whatmann 541 filterpaper of 30 mm diameter and dried. From the EDXRF spectrum of such samples, a calibration plot between the amount of uranium and intensity ratios of U $L\alpha$ / Y $K\alpha$ was made. A few synthetic mixtures prepared in similar way were analysed using this calibration. In order to use this method specifically for AHWR fuel, synthetic mixtures were prepared in U % range of 1 to 5 % and the calibration curve obtained from these mixtures was used to analyse a few unknown samples. The precision of the method for uranium determination was found to be 4 % (1 σ RSD) and the results deviated from the expected uranium concentrations within 3 %. Thorium was determined in similar way using uranium as internal standard and the precision and accuracy values of 5% were achieved. Compared to solid sample analysis by XRF, this method is fast gives better precision and accuracy, requires easy sample preparation and avoids laborious and time consuming processes e.g. grinding and pelletisation. However, it requires dissolution of the sample.

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O7-5

Crystallinity measurement of modified SiO_2 samples by laser produced-plasma

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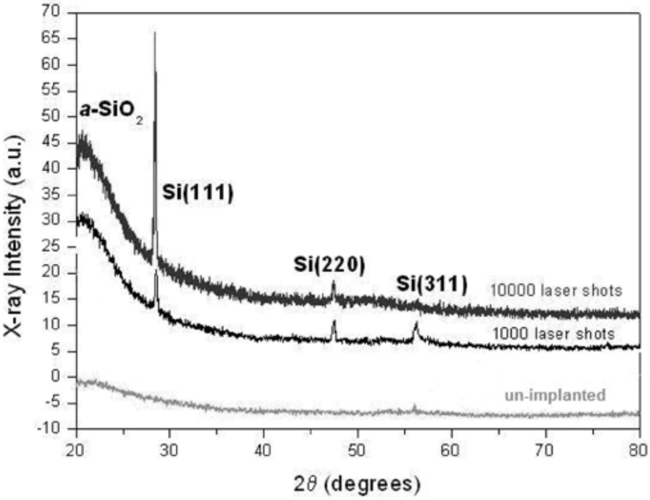
In this work the preliminary results of plasma influence onto SiO_2 films and the glancing-angle X-ray diffraction analyses are reported. The samples were processed by a Si plasma source which emits ion, clusters and X-rays. We developed a new apparatus composed of a plasma source having the source target polarized as well as the substrate support. The plasma source was able to generate ions of some hundreds eV of intrinsic energy and soft X-rays[1]. The laser source consists of a KrF excimer laser and a generating vacuum chamber made of stainless steel. The laser energy was 45 mJ/pulse, providing a laser fluence of about 4.5 J/cm^2 and a power density of 2.25x10^{8}W/cm^2 by means a convergent lens. The ion dose and the X-rays energy were estimated by a fast Faraday cup in two separate steps. In order to highlight changes in the material degree of crystallinity, as-implanted samples were studied by X-ray diffraction (XRD) in both Bragg and glancing angle geometry (GAXRD) using a Rigaku D/MAX-Ultima+ diffractometer equipped with a thin film sample stage and an Eulerian cradle. This analysis, suitable to investigate thin film properties, is well used to study the superficial implantation profile due to the low intrinsic energy involved. Fig 1 shows the XRD results obtained from a sample at three different conditions.



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O7-6

Getting an insight into soft polymeric systems properties by X- ray techniques

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Soft polymeric systems include from quasi-homogenous dispersions, in which the number, the position and the size of pores are fluctuating, to porous heterogeneous rigid structures. Transport phenomena of dispersed systems of different nature have recently acquired special meanings for theoretical and experimental investigation. This is due to the fact that this knowledge is essential in a great variety of technologies applied to diverse areas of engineering: preparation of emulsions, gel permeation chromatography, operations of separation and filtration, enhanced oil recovery, medicinal and cosmetic production, foods, etc. In order to design technological devices for such purposes, it is necessary to have an understanding of the transport properties of the diffusing species in a given matrix (polymer-solvent) which are influenced by changes in structural characteristics.

X-Ray Microfluorescence is a spectrometric technique with high resolution properties that allows studying dynamic systems. In this work instrumental and practical parameters were optimized to make possible subsequent transport properties studies in these systems for varied applications. The originality of the measurements required the design of a special cell for this type of systems. Measurements were realized at the D09–XRF line in the National Laboratory of Synchrotron Light, Campinas, Brazil.

Results of Small Angle Scattering Light experiments with different concentration solutions of scleroglucan (neutral polysaccharide), xanthan (polyanion) and polyoxyethylene (neutral polyether) of similar molecular mass help us to studying the structural changes which have polymers and linked with transport properties. SAXS measurements were performed in the line SAXS2 National Laboratory of Synchrotron Light, Campinas, Brazil.

Results show that in aqueous solution the scleroglucan has a triple helix structure that behaves as statistical ball at low concentrations (<0.1%), with the same structure but with local behavior of rodlike to average concentrations (0, 1% and 1%) and there are larger aggregates and gels (<1%). The xanthan shows a similar behavior while the POE presents in all areas of concentration structure of the statistical sphere with a radius of gyration almost invariant. It has been found that the semidiluted solutions in all cases are those with higher retention power, it can be understood on the basis of accessibility to the active sites of the macromolecules.

O7-7

Nanoresolution interface studies in thin films by synchrotron x-ray diffraction and by using x-ray waveguide structure

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Using computer simulations, it was shown [1] that on nanoscale, for strongly composition-dependent diffusion coefficients, an initially diffuse A/B interface can become chemically abrupt even in ideal systems with complete mutual solubility. This sharpening is surprising at first sight because the macroscopic Fick I law states that the direction of diffusion is always opposite to the direction of the composition gradient. This predicted behaviour is interesting not only from fundamental research point of view, but, if confirmed experimentally, it is very promising in terms of applications as well. It could provide a useful tool for the improvement of interfaces and offer a way for fabrication of e.g. better X-ray or neutron mirrors, microelectronic devices or multilayers with giant magnetic resistance. In this contribution we will present theoretical results [1] and experimental evidence [2] for interface sharpening. The latter is shown in situ during heat-treatments at gradually increasing temperatures by scattering of synchrotron radiation in coherent Mo/V multilayers containing initially diffuse interfaces.

Moreover, X-ray standing wave technique has been used to measure the kinetics of CoSi intermetallic phase growth in a-Si/Co/a-Si sandwich structure. The a-Si/Co/a-Si arrangement were placed into a waveguide structure formed by two Ta films. X-ray fluorescence and extended X-ray absorption fine structure analysis has been used in a combination with X-ray standing wave technique for depth profiling with sub-nanometer resolution. The position and the thickness of the growing CoSi intermetallic phase have been monitored and thus the kinetics of the growth could be determined.

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O7-8

XANES and EXAFS analyses of manganese local environment in porous silicate catalysts

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One of the major challenges in environmentally benign catalysis is the search for highly active and stable catalysts for the selective oxidation of organic substrates with molecular oxygen [1]. In recent years, manganese(III)-containing porous catalysts have received considerable attention as catalysts for the selective oxidation of hydrocarbons using molecular oxygen (air) as the oxidant [2].

Porous silicates are used as catalytic supports in chemical reactions [1]. They possess pore openings with diameters in the range from 1.2 to 2 nm (microporous) and 2 to 10 nm (mesoporous). Incorporation of metals into their framework generates catalytically active sites. Catalytic properties of metal-functionalised porous silicates depend on the structure type, location and the nature of incorporated metal.

Here we report on synthesis and structure analysis of microporous silicate catalysts with structure type silicalite-1 and mesoporous silicate structure types MCM-41 and MCM-48, functionalised by manganese. The porosity of the products was determined by X-ray powder diffraction (XRD), high-resolution transmission electron microscopy (HRTEM) and nitrogen adsorption isotherms. The evidence for the presence of catalytically active Mn sites in the framework was obtained by Mn K-edge XANES and EXAFS analysis, which provided direct information on valence state and local environment of Mn in these products. Experiments were performed at XAFS beamline of synchrotron radiation facility ELETTRA (Trieste, Italy). The analysis revealed a presence of predominatly Mn^{3+} cations located at distorted tetrahedral coordination silicate framework sites in all three structural types. First catalytic tests of the products revealed successful oxidation of alkyl aromatics hydrocarbons to the corresponding aromatic ketones by molecular oxygen.

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I8

The nature of X-ray absorption spectra: Novel theoretical and experimental tools

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The theoretical interpretation of X-ray absorption spectroscopy is briefly introduced. The XAS spectral shape is determined by the empty density of states, including phenomena such as multiplet effects, charge transfer effects and non-local screening [1,2].

Multiplet effects are caused by the overlap of core and valence wave functions. They destroy the interpretation of the XAS spectral shape in terms of the empty density of states. The 2p XAS spectra of 3d metal systems are dominated by large 2p3d multiplet effects, yielding many fine details [3]. This allows for the detailed analysis of the spectral shapes, which in turn gives a precise determination of the ground state, including phenomena such as differential orbital covalence, the effects of π-bonding and mixed-spin ground state, i.e. a state that is a mixture of two spin states due to spin-orbit coupling combined with strong covalency.

An important addition to X-ray absorption spectroscopy is the use of high-resolution X-ray emission detectors, both in the hard and soft X-ray Resonant X-ray Emission (RXES) experiments. In this talk, I limit myself to a few cases where the combination of multiplet effects and coherence plays a role in spectral shape distortions in XAS. This includes non-linear decay ratios between radiative and non-radiative channels and the effects of broken coherence in the radiative decay channels.

Scanning Transmission X-ray Microscopy (STXM) experiments make it possible to measure metal L edges with a spatial resolution of 20 nm. With the use of a new in-situ reactor, we have performed STXM experiments at 1 bar and 500 C. This allows for the in-situ spectroscopic study of a single catalytic nanoparticle (in action). Recent STXM results show the spatial distribution of the degree of reduction of iron-oxide nanoparticles.

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O8-1

EXAFS measurements at the micrometer-scale spatial resolution using achromatic multilayer-based focusing optics

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When performing spectroscopy using a microbeam it is crucial to maintain both the size and the position of the beam fixed during the total acquisition time. While this constraint applies to both micro x-ray fluorescence and x-ray absorption spectroscopy techniques, the problem is severer in EXAFS since the energy of the probe beam is varied. In this context an achromatic focusing optics is preferable.

We have developed a Kirkpatrick-Baez (KB) optics system in which both mirrors were coated with aperiodic multilayers to increase the collection angle as compared to total reflection mirrors and to deliver a large energy bandpass (15%) and. Hence, the KB optics can remain in a steady state, thus preserving the beam size and position while scanning the x-ray energy with an upstream silicon double-crystal monochromator.

A series of measurements were performed at various absorption edges (Zn, As, Se) at the ESRF synchrotron bending-magnet beamline BM5 to demonstrate the performance of the system in the 6-13 keV energy range [1] and to assess the beam stability. The relative variation of the size and the position of the microbeam at the sample never exceeded 7% of the beam nominal size, for typical spot sizes of the order of 2.0 μm (V) and 2.2 μm (H). Another set of measurements was performed at the Fe K-edge at the ESRF BM29 beamline to compare the spectra classically obtained at an EXAFS beamline, i.e., without focusing, with spectra obtained under a microfocused beam. When comparing the results in a $k^3.\chi(k)$ plot a difference between the spectra could only be noticed at large k (>15 $Å^{-1}$). For high-pressure experiments where the sample is located inside a pressure cell, the combination of the large energy range available from a bending-magnet source with a microfocused achromatic beam is particularly interesting.

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O8-2

XAS analysis of Cd coordination in Cd hyperaccumulating plants

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Cd pollution of environment results mainly from Cd-containing fertilizers, smelting and sewage sludge disposal. From the polluted soils Cd can be taken up by different plants and translocated to the food chains. Cd is extremely toxic even at low concentrations of a few µg g-1 of dry weight (DW). In some plant species (as for example *Thlaspi*) Cd absorption from polluted soils is found to be very efficient. Recently, *Thlaspi praecox* was shown to hyperaccumulate up to 5960 µg g-1 DW of Cd under field conditions [1]. Such hyperaccumulating plants are a promising way for metal removal from polluted soil. However, more knowledge on metal accumulation and detoxification is needed to understand soil-plant interactions for the use of phytoextraction in practice.

In addition, *Thlaspi praecox* was found to massively accumulate Cd not only in roots and leaves, but also in seeds (up to 1350 µg g-1 DW), without drastically affecting seed viability [2]. Micro-PIXE (proton-induced x-ray emission) localization study showed that Cd is mainly accumulated in the epidermis of cotyledons, away from photosynthetically active embryonic tissues [2].

In this study we use Cd K-edge EXAFS and XANES analysis of different organs (roots, shoots, leaves and seeds) of *T. praecox* to obtain information on the local structure around Cd cations bound in different plant tissues, in order to identify the Cd complex responsible for Cd immobilization. X-ray absorption spectra were measured at BM29 beamline of ESRF and C beamline of HASYLAB. Cd concentrations in plant organs were determined by XRF analysis.

Comparison of chemical coordination of Cd in different plant organs gives insight in detoxification mechanism and Cd transporters and/or antioxidant-based defense at the molecular level that contributes efficiently to Cd tolerance in hyperaccumulating species [3].

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O8-3

Possibilities of polycapillary based μ-EXAFS at DUBBLE, a non-fixed exit monochromator bending magnet beamline

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X-ray absorption spectroscopy (XAS) based experimental techniques like XANES and EXAFS are widely used for structural characterization. Conventional XAS measurements involve the use of millimetre sized beams. When a microscopically inhomogeneous sample is measured with such beam dimensions, an average spectrum over the illuminated area is recorded in which the information on the local structure is lost. To obtain spatially resolved spectra of such inhomogeneous samples, beams of micrometer dimensions are needed.

Focusing optics such as compound refractive lenses and Fresnel lenses are less suitable for XAS due to their achromaticity. A Kirkpatrick-Baez (KB) mirror system is therefore often used at bending magnet beamlines, but these mirror systems typically have relatively small acceptances which leaves a large amount of the available flux unused. Glass polycapillaries are known focussing elements in for instance in μ-XRF experiments and can present an alternative focusing optic for μ-XAS. The main advantage being the relatively large acceptance angles (some mm horizontally and vertically). Also their use in μ-XANES has been demonstrated [1].

A focussing system based on a polycapillary optic was tested at the DUBBLE (BM26A, ESRF) beamline for transmission and fluorescence EXAFS. Beam sizes (FWHM) of 12-16 μm, transmission efficiencies of 25-45% and intensity gain factors, compared to the non-focussed beam, of about 2000 were obtained in the 7-14 keV energy range. The vertical height variations during a typical EXAFS energy scan hardly influences the experimental results and positional accuracy, as the focusing by the polycapillary reduces this vertical movement strongly. Spectra on several standards were recorded. As a practical application, an As XANES study on plant roots and stems was performed.

The experiments show that polycapillary optics are suitable focusing elements for μ-XANES and μ-EXAFS at bending magnet beamlines equipped with a non-fixed exit monochromator.

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In situ defect microscopy during the electric-field-driven insulator-to-metal transition in Cr:SrTiO$_3$

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SrTiO$_3$ doped with Cr can be conditioned such that it exhibits a bistable resistance state. Voltage pulses of opposite polarity switch the resistance between a high-resistance and a low-resistance state, making it a possible material for memory device applications. X-ray absorption near edge spectroscopy on the Cr *K* edge indicates the presence of an oxygen vacancy. Spatially resolved X-ray fluorescence microscopy images of Cr:SrTiO$_3$ show the introduction and the evolution of oxygen vacancies during the conditioning process, the electric-field-driven insulator-to-metal transition. The vacancies are introduced at the anode, diffusing through the crystal towards the cathode, and thereby creating a conducting path through a network of locally conducting defects. The spatial distribution of vacancies is explained by a model describing the electrical breakdown as a percolation process with fractal growth. The resistance after the transition shows the previously reported bistable state with highly reproducible resistance switching. Strong differences in the conducting path are found between samples electrically treated in air and in a hydrogen enriched atmosphere. In air, the vacancy network seems to rearrange inside the crystal. In hydrogen, where electrochemistry plays a critical role, the path forms closer to the surface, (Figure).

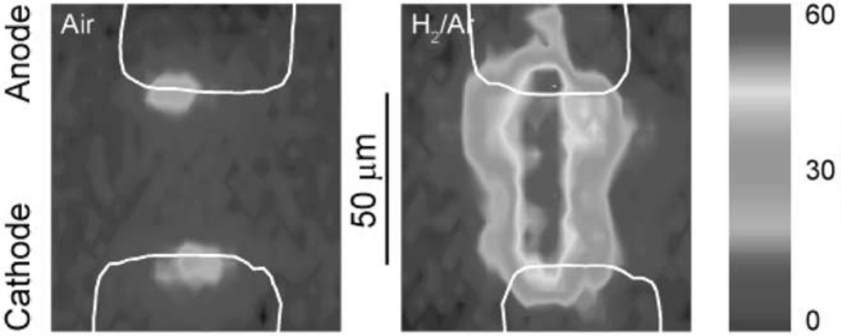

Figure: X-ray fluorescence microscopy images of the memory device electrically treated in air and in a mixture of hydrogen and argon (H$_2$/Ar). In case of air, the vacancy concentration is highest close to the electrodes; while in the case of H$_2$/Ar the vacancy concentration shows a higher ridge between the electrodes. This indicates that the conducting vacancies are closer to the surface in the latter case.

O8-5

Non-destructive probing of the chemical state of buried TiO_x nanolayers

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Near edge x-ray absorption fine structure (NEXAFS) in combination with grazing incidence x-ray fluorescence (GIXRF) analysis provides a good approach for a depth-sensitive characterization of buried nanolayers with respect to both elemental composition and speciation. This idea offers the specific advantage of a high tunability of the information depth. The GIXRF regime implicates the occurrence of the x-ray standing waves (XSW) field above, at and below the surface affecting directly influence on the fluorescence intensity. The XSW field and the related mean penetration depth are dependent on both the incident angle and photon energy. The variation of the photon energy during a NEXAFS study requires to correct the angle of incidence to keep the mean information depth constant.

The sample system investigated here consists of several 30 nm titanium nanolayers oxidized to different extents and being buried below 5 nm of carbon. These layered structures were produced by means of ion beam sputtering deposition. The measurements were carried out at the plane grating monochromator (PGM) beamline for undulator radiation in the PTB laboratory at BESSY II, providing tuneable radiation of both well-known flux and high spectral purity for GIXRF-NEXAFS studies. The results of angular corrected high-resolution Ti L3,2 edge NEXAFS spectra exhibit an electronic structure presumably comparable to that measured in total electron yield (TEY) and confirm the potential of this method. GIXRF-NEXAFS provides a complementary approach to different non-destructive techniques based on electron detection, the reach of which restricts the effective detection sensitivity for deeply buried thin layers.

O8-6

Microstructure of quantum dots ensembles by EXAFS spectroscopy

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The Ge/Si and GaN/AlN quantum dots vertical and lateral alignment have been recently demonstrated. Interpretation of QDs ensembles energy spectra must take into account the peculiarities of local structure of such formations, due to the strain field near the interfaces.

Ge or GaN sandwich heterostructures (from 1 up to 20 monolayers) were prepared by molecular beam epitaxy growing procedure with follow-up deposition of blocking Si or AlN layers (from 30 up to 500 Å). EXAFS spectra of the GeK- and Ga*K*- edges were measured at the VEPP-3 storage ring of the BINP (Novosibirsk) and at the DUBBLE beamline of the ESRF (Grenoble) [1,2].

Lowering of the Si spacer deposition temperature from 500°C to 300°C leads to a substantial decrease of the diffusion between the Ge- and Si- phases and the formation of sharp phase boundaries. It was found that the first shell R_{Ga-N} interatomic distance in heterostructure GaN/AlN is 0.02 A smaller compared to crystalline GaN.

It was established an influence of blocking layers (Si, AlN) thickness and number of QDs layers (Ge, GaN) in geterosystems, contains vertically aligned QDs, on the microstructure characteristics of QDs. This result is in accordance with electron spectroscopy and electron diffraction results. It was found the same, but more feebly marked results, for GaN/AlN heterostructure. This result suggests increasing of average GaN clusters size for structures with more thin AlN films.

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O8-7

Electronic structure of Copper films in aqueous solutions

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Possibility of using x-ray absorption spectroscopy (XAS) and resonant inelastic x-ray scattering (RIXS) to probe the Cu oxidation state and changes in the electronic structure during interaction between copper and groundwater solutions were examined. Surface modifications induced by chemical reactions of oxidized 100Å Cu films with Cl^-, SO_4^{2-} and HCO_3^- ions in aqueous solutions with various concentrations were studied in-situ using liquid cells. Copper corrosion processes in groundwater were monitored up to 9 days. By comparing Cu 2p - 3d, 4s transitions for a number of reference substances previously measured, electronic structure changes of the Cu films were analyzed. The XAS and RIXS spectral shape at the Cu edge, the chemical shift of the main line for Cu^{2+}, and the energy positions of the observed satellites served as a tool for monitoring the changes during the reaction.

I9

Spin-state studies with X-ray spectroscopy, and applications to Earth's lower mantle constituents

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We report on the study of spin-crossover compounds of Fe^{3+}, Fe^{2+} and Co^{2+} in their high-spin and low-spin forms to show that hard X-ray spectroscopies provide sensitivity to the spin state of 3d transition metal ions, combined with unique qualities: element selectivity, bulk sensitivity, compatibility with extreme conditions (e.g., high pressure), and relatively straightforward experimental conditions. It is shown that all features of the X-ray emission spectrum (XES) are sensitive to the spin state. Variations of the Kα and the Kβ emission line shapes, which are in agreement with theory, can be used as quantitative probes of the spin state; it is suggested that with appropriate reference experiments one can extract the spin momentum for a general case. Resonant X-ray emission spectra unveil details of the redistribution of electrons on the 3d levels associated with the spin-state change by revealing features at the X-ray absorption pre-edge hardly accessible through standard absorption measurements [1].

The properties of the main constituents of Earth's lower mantle, (Mg, Fe) SiO_3 and (Mg, Fe)O are decisive for the inner dynamics of the Earth, which is driven by the heat transport towards the surface. Both of these minerals contain iron, which can be either in high or in low spin-state. Different spin states imply very different physical properties, including density, optical and infrared absorption, and transport properties. Therefore, reliable geodynamical modelling of the mantle requires detailed knowledge on the state of iron in these minerals at high pressure and temperature. To procure such information, we have applied XES to samples at lower-mantle conditions [2,3].

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O9-1

In-situ X-ray analytical methods in applied earth sciences – advantages and shortcomings -

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X-ray analytical methods are used for a great range of applications in earth sciences. Uses include qualitative and quantitative element identification and distribution, mass transport processes, and derivation of phase relationships. Among these methods, high resolution in-situ energy dispersive X-ray fluorescence analysis (EDXRF) techniques play an increasing role. They are used to supplement traditional methods such as wavelength dispersive X-ray fluorescence analysis (WDXRF). Major advantages include high spatial resolution of the acquired data, strongly reduced sample preparation and the ability to analyse even very fragile samples such as wet sediment drill cores. Applications range from screening analyses for subsequent sampling in isotope studies of hydrothermal fluids over time sequence analyses of palaeoclimate proxies, to mineral exploration.

We compare and statistically validate classical WDXRF (PANalytical Axios™) measurements, commercial handheld XRF (INNOV-X CLASSIC™) and in-situ µ-EDXRF analyses (single point and along profiles) [1]. Sensitivity of the methods to matrix and surface effects as well as to sample inhomogeneity was taken into account. Sample types include ore, silicates and carbonates and preparation includes sawn or polished hand specimens, crushed rocks, powder and fusion pellets. Results are validated by qualitative ICP-OES and ICP-MS analyses.

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O9-2

Analysis of different U and Pu particles by means of μ-XRF, μ-XANES and μ-XRD

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Due to the crash accidents of two American B-52 bombers carrying plutonium-bearing weapons, large amount of plutonium as well as uranium were dispersed over a terrestrial area in the Mediterranean village of Palomares (Spain) and on the sea ice in Bylot Sound (Greenland). Moreover during the Kuwait and Balkan conflicts depleted uranium (DU) ammunition were expended by NATO forces which after impact on hard targets generated large amounts of a DU dust contaminated soil around.

In this work, the study of oxidation states of uranium and plutonium in individual particles from these four regions were of interest since various oxidation states can cause different environmental behavior. A number of particles were repeatedly investigated by means of μ-XRF and μ-XANES at the U- and Pu-L3 edges.

By means of these methods, which predominantly provide information on the chemical state of U and Pu at/near the surface of the particles, we observed that U was predominantly present as U(IV) , but that higher oxidation of U was partially apparent especially in the Palomares, Kuwait and Kosovo samples. Due to lack of suitable reference compounds for Pu, the conclusions concerning Pu were less certain.

In order to complement this information with data on the entire bulk of the particles, the same samples were reexamined by means of transmission μ-XRD. The 2θ-pattern obtained from Palomares particle is matching very well to the U_4O_9 ICDD database entry, but also coinciding adequately well with the pattern of UO_2. PuO_2 , a 1:1 solid solution of UO_2 and PuO_2. Also the actual nature of the uranium species from Kuwait and Kosovo is more complicated than a simple mixture of two well-known uranium compounds. The μ-XRD results from DU samples revealed presence of several phases such as $Ti_{0.06}U_{0.94}$, UO_2, $UO_{2.34}$ and Schoepite.

O9-3

Heavy metals in soils and their biogeochemistry significance

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In order to reveal the environmental and toxic effects of heavy metals in ecological system on bio-chains and human health, the soil samples were taken from the farmlands near a Pb mine in the suburban of Nanjing City in the southeast of China. Biogeochemistry investigation was conducted. Potential pollution was evaluated by means of x-ray fluorescence spectrometry, several related analytical techniques and the biogeochemistry methods.

Heavy metals and other minor and trace elements in the soil samples were determined by a polarized energy dispersive x-ray fluorescence spectrometer. Powder pellet was used in the sample preparation. Four targets were used to excite different elements in the samples.

Analytical data and research results show that the high concentrations of Pb, Cd and As exist in the farmland soils. Some of them exceed the national health regulation limits. The high concentrations of heavy metals were also detected in plants, animals and human blood at the same area. That means the heavy metals, which come from the lead mine, may have potential toxicity effects on the plants and animals, especially on the human health.

O9-4

EDXRF for fingerprinting fine-grained sediment sources in the Demer basin, Belgium

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The EU Water Framework Directive demands good water quality by 2015. In order to meet this target, water managers need reliable information on catchment sediment dynamics, since sediment represents a key vector governing the transfer and fate of important pollutants. In order to gain a reliable understanding of sediment dynamics one must focus on the principal sources involved. Traditional techniques for investigating sediment provenance face many limitations and constraints. In view of these problems, sediment fingerprinting is increasingly recognized as a reliable alternative means of assembling information on sediment sources at catchment scale.

Sediment source fingerprinting requires analysis of elemental composition for identifying a range of fingerprint properties for distinguishing different sources. EDXRF offers potential in this respect. Accordingly, an ongoing study is applying the fingerprinting approach to investigate sediment sources in the Demer basin, Belgium. Potential sediment sources were classified as agricultural soils, channel banks and authigenic sediment produced in-channel due to groundwater upwelling. The various sources imply different matrices, so developing a robust method, capable of handling this variety of matrices, was a challenge. The sample matrix is expected to be composed mostly of low-Z elements, so the high-Z elements can be determined with a method based on Compton correction. In order to validate this approach an ICP-AES procedure, involving HF to ensure complete digestion of the matrix, was used. The agreement with ICP-AES was very satisfying; even low-Z elements could be determined when applying a correction factor.

The promising results of the validation demonstrate that EDXRF can be used to generate fingerprint property datasets and thus to support sediment source fingerprinting studies designed to improve the information available to catchment managers concerned with diffuse pollution problems.

O9-5

External estimation of the quality of content determinations of a number of elements in GeoPT geological samples by X-ray fluorescence method

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Institute of the Earth's Crust, SB RAS, Russia

The authors discuss the results obtained by XRF group of the Analytical center participated in 13 rounds of an international proficiency testing programme for analytical geochemistry laboratories (GeoPT) [1]. The analyses were made according to the requirements that were stated in the Protocol [2]. The tested samples are rocks of different types. The analyses were carried out by X-ray fluorescence method of analysis (XRF) using VRA-30 and S4 PIONEER spectrometers [3].

The quality of results of analysis, made by XRF in the Analytical center, corresponds to II category of accuracy and is assessed by the criterion Z'. The statistical treatment of the analytical results over 13 rounds of this programme has shown that in most cases the presented results fall into the range $|Z'| \leq 2$ and are satisfactory (73%). 15% of the analytical results fall into the range $2 < |Z'| < 3$, which are questionable and must be discussed. For some elements determined the unsatisfactory values of the error of the analytical results (13%), i.e. $|Z'| \geq 3$. The possible reasons for the significant systematic source of error were judged: contents of some elements determined are close to detection limits; insufficient number of the certified reference materials, close in a chemical composition to a matrix of GeoPT samples; possible inhomogeneous distribution of an element analyzed in a sample; insufficient consideration of overlapping of analytical lines, which have wavelengths close to ones of elements determined.

The participation in the GeoPT programme allows to assess the quality of the determination of contents of a number of trace elements in samples by XRF and to consider the results of analysis to be satisfactory in most cases. The testing of our center in the framework of GeoPT programme allowed to compare the obtained results of routine analysis with the results of other laboratories and exhibited the need for the improvement of the available measurement techniques.

The work was made under support of RFBR, grant No 07-05-01061.

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O9-6

Elemental analysis of ambient aerosol samples with synchrotron XRF

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Samples of ambient aerosols often contain minuscule amounts of trace elements at or below the detection limit of conventional analysis methods. Synchrotron x-ray fluorescence spectroscopy (SR-XRF) allows the detection of such small concentrations of elements (a few µg/m^3) without further treatment [1,2]. Therefore the sampling time can be significantly reduced compared to filter analysis and allows for the detection of diurnal variations. Rotating Drum Impactors (RDIs) were deployed to collect ambient aerosols in three different size bins (PM10-PM2.5, PM2.5-PM1 and PM1) on a thin Mylar foil. These samples were analyzed subsequently with SR-XRF at the Swiss Synchrotron Light Source at PSI using monochromatic light of around 11 keV, and at Hasylab at DESY, Hamburg using a polychromatic beam.

Ambient samples had been collected in three different settings in winter 2006/07 and thus allow for a comparison of different emission scenarios (wood combustion, abrasion of vehicles, etc). With the analysis at lower excitation energies the range of elements form Al – Ge could be detected while at higher energies elements up to Ba are detectable. Heavier elements were found mainly in the largest size fraction, which is usually considered to originate from (mineral) dust re-suspended into the air or from mechanical abrasion. The smaller particle size fraction is more typical for combustion processes. Additional measurements of different wood-burning stoves were performed with a testing set-up. The results obtained with RDI samples are also compared to complementary measurements.

Results of this analysis will feed into source apportionment studies (applying positive matrix factorization, PMF) to get more insight into possible sources of emissions and therewith helping to formulate mitigation strategies.

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I10

The effect of chemical bonding on high-resolution X-ray spectroscopy

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The earliest X-ray spectroscopy used wavelength-dispersion, and chemical effects were observed very early in X-ray emission spectra. However, prediction and interpretation of these effects remains something of a challenge. The effects can be grouped into three main categories: changes in the absorption cross sections, energy shifts, and changes in the basic line shapes. All of these effects are most pronounced at low energies, where atomic levels involved in the transition are at or near the bonding/anti-bonding or conduction electron levels. This talk will mostly focus on the third effect, although the other effects will be mentioned and some surprises from the first effect, which sometimes confuse the issue, will also be discussed. Modern theoretical methods are now able to predict chemical effects with improving precision. We have performed measurements as well as molecular and solid state simulations on several nitrogen and chromium compounds of molecular and metallic nature. These simulations used different methodologies and will be compared to synchrotron and laboratory measurements to see how well the various effects can be predicted with modern theories, and to illustrate some successes, failures, and pitfalls. We will also demonstrate how information from different theoretical methodologies can be integrated to obtain a more complete understanding of the systems. The measurements are from both electron beam and X-ray excitation, and all are wavelength-dispersive, high-resolution measurements of the X-ray emission line shapes. The measurements with electron beam excitation were made on readily-available commercial laboratory equipment.

O10-1

High-resolution soft X-ray emission spectrometry for the determination of atomic fundamental parameters related to the Ni-L fluorescence process

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The reliability of XRF quantitation, in particular its reference-free variant [1], strongly depends on the knowledge of the respective atomic fundamental parameters like fluorescence yields, transition probabilities and Coster-Kronig coefficients. For an accurate XRF analysis, e.g. involving light matrix elements or transition metal nanolayers, a reliable determination of these parameters in the soft X-ray range with small uncertainties is essential.

Measurements based on calibrated instrumentation employing energy-dispersive detectors can very well contribute to the determination of fundamental parameters [2]. However, the energy resolution of energy-dispersive detectors is not sufficient to determine all parameters of interest, especially for the L-fluorescence lines of transition metals. Hence, a wavelength-dispersive grating spectrometer (WDS) was designed and built for dedicated experiments at the plane grating monochromator beamline for undulator radiation of the Physikalisch-Technische Bundesanstalt at the electron storage ring BESSY II. The WDS was experimentally characterized with respect to both its detection efficiency and response functions. This characterization allows for absolute measurements of fundamental parameters with small relative uncertainties.

As an example, we present a study of the L-fluorescence emission of Ni and the related transition probabilities. Taking advantage of the tunability of monochromatized undulator radiation, we could study the evolution of the Ni-L emission spectra with increasing incident photon energy. In particular, specific spectral features such as resonant Raman scattering and satellite lines show strong dependencies with respect to the photon energy of the exciting radiation.

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O10-2

Spectroscopic analysis of the water-window range with Cr/Sc multilayers

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The water-window range, between the C K (≈280 eV) and O K (≈530 eV) absorption edges, is difficult to study in WDS analysis due to the lack of efficient diffractive optics. This is particularly true for the N K emission band, which is presently analysed by using periodic multilayers having a poor reflectivity (≤10%) in this photon energy range. Recently, the use of Cr/Sc multilayers has been suggested to study the N K emission and theoretical reflectivity as high as 45% is expected.

The aim of this communication is to report on the performances of Cr / Sc periodic multilayers as Bragg dispersive devices for the analysis in wavelength dispersive spectrometry of samples containing N or Sc atoms [1], such as BN, CrN, Sc_5Si_3 and ScN. The possibility to distinguish the chemical state of the emitting N or Sc atoms is evidenced by using Johan-type and double-crystal spectrometers.

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O10-3

Micro spot analysis using policapillary lens in standard WDXRF

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The demand of micro spot measurement such as for the analysis of micro-electronics devices and parts has increased. X-ray optics using capillary lens is an effective method to obtain high intensity x-rays for small spot measurement and is mainly utilized in EDXRF system.

We have developed a WDXRF spectrometer which is added a poly-capillary lens to a standard sequential spectrometer that enables 100 micro meter spot size measurement. And this spectrometer can also be used as regular spectrometer. The spectrometer is equipped with sample stage and electric camera to observe sample image for point analysis and mapping measurement of small area

Owing to WDXRF type, high spectral resolution and high sensitivity for light element can be achieved. The measurable energy range is wide from low energy (e.g. C-Kα) to high energy (e.g. Sn-Kα). The data reduction function of the spectrometer allows semi-quantitative analysis using fundamental parameter method for bulk and film in addition to quantitative analysis. Minor elements such as impurities could also be analyzed in addition to major elements for stoichiometric analysis with high power of 4kW x-ray tube.

The spectrometer configuration and some application examples will be presented.

O10-4

High resolution X-ray fluorescence study of Sulfur in various compounds

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Among the geochemically abundant elements sulfur is characteristic for its wide range of oxidation states, exhibiting states from 2^- to 6^+. The inorganic sulfur species encountered in the nature among other include sulfide (S^{-2}), native sulfur (S^0), sulfite (SO_3^{-2}), and sulfate (SO_4^{-2}). Due to its important role in the fundamental mechanisms such as volcano-climatic interactions, genesis of ore deposits as well as for its role in the industrial glass-forming processes it is extremely important to study chemical state of sulfur in order to better understand these mechanisms.

In order to determine electronic configuration and coordination geometry high energy resolution Kα and Kβ X-ray emission spectra of sulfur in numerous compounds from sulfides to sulfates were recorded at the ID26 beamline at the ESRF synchrotron employing Johansson type wavelength dispersive spectrometer. Excellent energy resolution of our experimental setup enabled precise measurement of energy shifts and main spectral features. The energy of Kα emission line clearly correlates with the valence state of S and can be effectively employed for such analysis. Much more complex Kβ spectral structures give important information about local coordination around S. Ab initio quantum-chemical calculations using the StoBe code, based on density functional theory, were performed in order to explain the measured Kβ spectral structures.

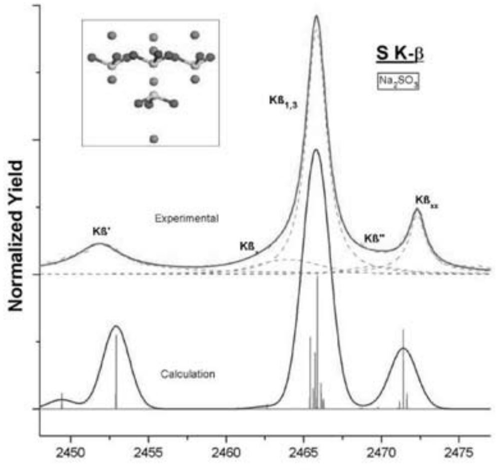

Figure 1: The comparison between the experimental Na_2SO_3 spectrum and the theoretical calculation using the density functional theory (StoBe code), with four sulfite ions and 8 sodium atoms.

O10-5

The use of WD-XRS Spectrometry and XRD to prepare a series of reference materials of geological samples

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Reference materials play an important role in geoanalytical laboratories as materials for calibrating instrumental techniques, and for quality assurance and control. However, few reference materials are accompanied by analysis certificates with uncertainties as recommended in the guide for the calculation of uncertainties. This impedes appropriate traceability in the measurements that are made using these materials.

In this work, a series of reference materials of geological samples of clays, kaolin, silica sand, feldspars, dolomite and calcium carbonate have been prepared.

In order to achieve this objective, it has been necessary to attain a number of specific tasks: a) selection and collection of the geological samples for analysis; b) preparation of the samples selected for characterisation, which includes: crushing, quartering and milling, and the determination of particle size distribution; c) homogeneity test and distribution of the homogeneous material between the participating laboratories, after evaluation; d) chemical and mineralogical characterisation using different analytical techniques: Wavelength Dispersive X Ray Fluorescence Spectrometry (WD-XRF), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), Atomic Absorption Spectrophotometry (AAS); thermogravimetric techniques for the determination of loss on ignition (LOI); and X Ray Diffraction (XRD); e) analysis of the results obtained for each element by the different chemical analysis techniques by the participating laboratories; f) and finally, preparation of the reference material with the data obtained in the foregoing phases, in accordance with ISO Guide 31.

The validation of the methodology used to obtain the chemical composition was carried out by:

1) using standard reference materials,
2) comparing the results from independent methods (WD-XRF and ICP-OES), and,
3) doing an interlaboratory test.

The results show very good agreement between WD-XRF and ICP-OES methods for all the analysed elements and it was concluded that, for geological samples, the WD-XRF method is more accurate and reproducible for major and minor elements, probably due to simple sample preparation needed and the measurement technique itself.

The XRD allows the mineralogical composition to be known and it is extra useful information in the certificate of the reference material, for future use, specially when a material is going to be used as a calibration standard in the WD-XRF method when the sample preparation is in the pellet form.

O10-6

Absolute X-ray wavelength standards to determine the wavelength of important X-ray lines with double reflection in single crystal X-ray Spectroscopy

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An X-ray beam (in the range of about 0.7- 5 Angstrom) reflected twice in one crystal by two different crystal planes (h,k,l,) and (h',k',l') might be recorded if the indices of the reflection having the sum of the successive reflections ((h+h'),(k+K'),(l+l')) is a crystallographically forbidden reflection. This occurs for limited cases of crystal symmetries [1].

Adjustment for obtaining double reflection is made by rotating the crystal in the plane of the forbidden reflection to a precalculated azimuthal position, while the beam makes a Bragg angle with the plane.

Double reflection of a POINT SOURCE yields on a film (film has the best resolution) a POINT for every wavelength emitted. A strong point will indicate an X-ray transition, while a line represents the continuous white spectrum.

For every forbidden reflection there are several double reflections possible. Let us look at the diamond lattice forbidden reflection (2,0,0). As an example, the following double reflections represent a multitude of double reflections which may be used: ((1,1,1),(1,-1,-1)); ((3,1,5), (-1,-1,-5)); ((5,3,1),(-3,-3,-1)). These double reflections are seen on film as a group of lines of the white spectrum, intersecting between them [2].

THE WAVELENGTH OF AN INTERSECTION IS A CONSTANT OF THE CRYSTAL LATTICE. With several such constants on a line of the white spectrum, they may be used to determine the wavelength value of a point seen on the line, this point representing a spectral transition. It may be argued that crystal constants are dependent on X-ray wavelength, but this has been overcome by using a DesLattes interferometer [3].

For example we obtained on film two intersections along a white spectrum line at 1.287829 A and 1.280169 A, assuming an agreed upon lattice constant for the Ge crystal involved. The sharpness of the lines is better than 1/300 of the distance between those intersections [2]. This was done with a fine focus tube. With a micro-focus tube one may expect much better resolution.

The description of obtaining intersections for determining the near absolute wavelength values of the main lines of Fe XXVI and Fe XXV will be given.

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I11

Biomedical applications of micro-PIXE

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Nuclear microscopy is a generic term referring to a large panel of ion beam analysis techniques carried out using light ion micro-beams in the MeV energy range (typically H^+, D^+ and He^+). After twenty years' experience by world-wide research groups in the use of those micro-beams, nuclear microscopy is now recognised as a powerful technique for routine chemical microanalysis and elemental mapping in the frame of biomedical applications.

The lateral resolution achieved by advanced facilities is about 50 nm in low current mode for pure imaging and 300 nm in high current mode for trace elements analysis and mapping. Since MeV ions may induce both nuclear reactions and ionisation of atomic shells, a non-exhaustive list of available methods includes PIXE (Particle Induced X-ray Emission), NRA (Nuclear Reaction Analysis), RBS (Rutherford Backscattering Spectrometry) and STIM (Scanning Transmission Ion Microscopy). PIXE is the basic method employed for routine elemental mapping. Numerous applications in biomedicine take advantage of its versatility and easy operation, either at the tissue or individual cell scale. In addition, micro-PIXE and other micro-beam techniques complement each other to offer unique information. This is particularly true for RBS and STIM for sample mass monitoring and ultra-structure elucidation.

The first CENBG micro-beam was commissioned in 1989 at the old Van de Graaff accelerator. This beam-line was recently transferred on the AIFIRA facility and a new high resolution line has been constructed. Since the first microprobe was initially designed for easy and reliable micro-PIXE analysis of biological samples, biomedicine has been the main research area developed on this system. In this review, different examples of investigation will be presented with emphasis placed on dermatology, pathology and pharmacology. Development and prospective studies of STIM-PIXE Tomography will be also discussed.

O11-1

Trace element mapping using hard X-ray nanobeam focused by a Kirkpatrick Baez mirror system

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X-ray fluorescence spectroscopy is a powerful tool for trace elements because of non-destructive and high-sensitivity analysis. To visualize elemental distributions with high resolution and high sensitivity, we developed a Kirkpatrick Baez mirror system which enables us to utilize hard X-ray nanobeam having a size of 30 x 50 nm^2, and constructed a scanning X-ray fluorescence microscope (SXFM) with the focusing system, a high resolution scanner and a silicon drift detector in BL29XUL of SPring-8.

We demonstrated high-resolution elemental mapping using test patterns having 50-60 nm line widths. As a result, the best spatial resolution was found to be better than 50 nm. Additionally, we demonstrated application for biological samples, in which high-sensitivity detection is required. To observe frozen hydrated samples, a cryogenic system, which is capable of imaging samples at temperature of 120K, was installed on the scanner. As a result of observation of fast frozen cells at cryogenic temperature, we could visualize intercellular elemental distributions same as that of living cells, compared with fixed cells with chemicals.

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[2] S. Matsuyama et al., Proc. SPIE, 6317 (2006) 631719.
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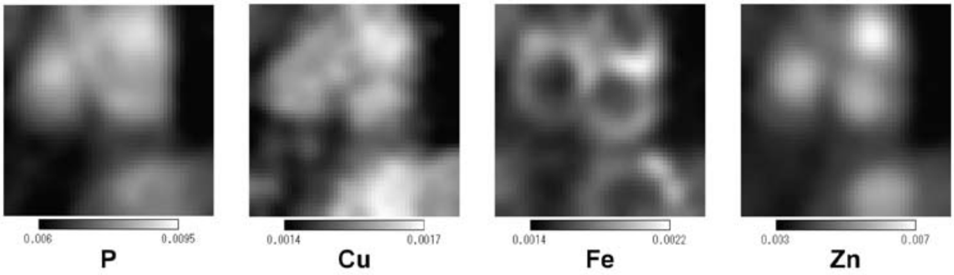

Fig. Intracellular elemental distributions of fast frozen NIH/3T3 mouse cells. Area: 50 x 50 um^2, Exposure: 0.5sec/pix., X-ray energy: 15keV, Temperature: 150K.

O11-2

Micro-XRF imaging and micro-XANES analysis of cadmium hyper-accumulating plant, *Arabidopsis halleri* ssp. *gemmifera*, using high-energy synchrotron radiation

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Arabidopsis halleri grows in Europe and are known to contain more than 10,000 mg kg^{-1} of cadmium and zinc in the shoot [1]. This trait in *A. halleri* has the potential to be exploited in phytoremediation, a soft method in which plants are used for the cleanup of heavy metal-polluted soils. Subspecies of this plant, *Arabis gemmifera*, a native species of Japan, is also known as a cadmium and zinc hyperaccumulator [2]. Since Cd is a highly toxic metal for plants, it is interesting to reveal the mechanism involved in the Cd accumulation of this plant.

The monochromatic high-energy X-rays (37 keV) focused to a microbeam (3.8 × 1.3 μm^2) with a Kirkpatrick-Baez mirror allows us for the first time to reveal a striking sub-cellular distribution and the chemical form of cadmium in the cadmium hyperaccumulating plant, *Arabidopsis halleri* ssp. *gemmifera* by detecting the Cd Kα line. Micro X-ray fluorescence (μ-XRF) analysis and micro X-ray absorption near-edge structure (μ-XANES) analysis were used for the nondestructive analysis of Cd distribution and chemical form of Cd at a cellular scale in the plant in order to investigate the accumulation mechanism of Cd. It was clearly observed by two-dimensional μ-XRF imaging that Cd was highly accumulated in a part of the trichomes, epidermal hairs existing at the surface of leaves. The bases of trichomes contained Cd, Zn and Mn at a high concentration and these distribution patterns were similar to each other. These elements were located near the surface of the trichome in the form of a ring. The μ-XANES analysis revealed that the majority of Cd exists as divalent state and bound to O and/or N ligands. This study has demonstrated the potential of Cd K-edge μ-XANES spectroscopy, which was applied here for the first time to plant samples.

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O11-3

Quantification of manganese in teeth *via* wavelength-dispersive X-ray fluorescence spectrometry: A pilot study

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With the recent study by Smith and co-workers [1] outlining how classical biological specimens (*i.e.* blood, plasma and urine) do not act as viable biomarkers of manganese exposure, the search for a suitable biomarker has been in place. Teeth are known to accumulate trace and minor elements during full mineralization and have a high half-life for trace elements (on the order of 14-24 years). As such, teeth, in particular baby teeth can potentially be used as a means of studying a population's environmental exposure to manganese (as well as other trace and minor elements). Wavelength-dispersive X-ray fluorescence spectrometry (WDXRF) provides unparalleled resolution of X-ray lines (reducing Mn/Fe line interferences) and although suffers from relatively high detection limits, a method has been developed that can be used as a means to quantify manganese in teeth at the expected concentrations (1-10 ppm). The WDXRF system (Bruker-AXS, S4 Explorer) equipped with LiF(200), PET and OVO-55 analyzing crystals and an 8 mm mask, is conveniently able to provide a means of non-destructively and simultaneously quantifying for the elements between Be-U in the small sample size (~100-300 mg per tooth) providing a full multielemental analysis of the minor and major elements (Ca, P, Sr) while also being optimized for the trace quantification of manganese. The system allows for an adequate estimate of the light element content in teeth which allows for a "standardless" algorithm to be used successfully. An investigation into the use of a standardless algorithm will be reported.

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O11-4

Human prostate cancer – is zinc the prime suspect?

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Prostate cancer is one of the most commonly diagnosed cancers in men throughout the world. Investigating possible reasons for cancerogenesis process on molecular level lead to zinc. The suspicion is not groundless for the reason of unique capability of prostate epithelial cells in accumulating zinc that plays role in a wide range of cellular processes such as immune system function, antiangiogenesis or apoptosis. Zinc has a significant antioxidant function and its presence in prostate cells is strongly connected with their metabolism [1].

Searching irrefutable proofs in that investigation we used synchrotron radiation based techniques to look insight human prostate cancer tissues and cultured human prostate cell lines (DU-145, LNCaP and PC-3). Analysis of prostate tissue samples revealed complexity of structures that can be reflected by bioimaging methods, while cell culture samples provided areas of required homogeneity. SR X-Ray Fluorescence analysis let to connect concentration of zinc with pathological status of tissue (healthy, hyperplastic and cancerous) and obtain bioimaging on cellular level. X-Ray Absorption Near Edge Spectroscopy (XANES) provided sophisticated studies of environment of absorbing zinc atom including determination of Zn K-edge position and local structure description [2].

Role of zinc in prostate cancer etiology is still an open question but the solution of this riddle seems to be closer.

This work was supported by the European Community under the Contract RII3-CT-2004-506008 (IA-SFS) (Hasylab project No I-20070071 EC).

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O11-5

The role of chemical elements in the formation of aneurism of aorta (SRXRF)

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The efficiency of the surgical treatment of the ascending part of aorta in many respects depends on the knowledge of pathogenesis of aorta diseases. One of the reasons of aorta pathology formation is the occurrence of microelements disbalance. The researches in this direction are not numerous, and the results are inconsistent. The most part of researches deal with the contents of calcium in an aorta wall [1]. The analysis of Ca, Mg, Zn, and Cu in aorta wall, atherosclerosis plaque and aneurism of aorta has shown that concentration of Zn, Cu, Mg, and Ca in atherosclerosis plaque is higher than in a surrounding tissue [2]. At the same time, according to the other author's data, the content of Cu, Zn, and Cr in the plaque was considerably below the norm [3].

The purpose of our research is to reveal the role of the chemical elements in the development and forming of aneurism of aorta versus the anatomic-morphological changes of its wall. We have revealed the marked disbalance of the chemical elements expressed disbalance of the chemical elements in a wall of aorta at patients with aneurism of the ascending part of an aorta and with stratification of an aorta in comparison with ischemic heart disease patients, that testifies to the important role of macro- and microelements in the metabolic processes connected with the formation of aneurysm of aorta. It has been shown, that V, Ni, Cr, Sr, Mn, Co provide structural integrity of an aorta as the development of aneurysms of aorta is accompanied by decrease in their concentration. Increased contents of As at an aneurysm of aorta and, especially, at stratification of its wall testifies to inflammatory process. It proves to be true morphological data. Probably, such microsomal elements as Se, As, K, and Rb are markers of aneurysms of aorta.

The given researches are executed by SRXRF method, experimental station XFA, BINP, Novosibirsk. Measurements have been executed in different conditions of primary excitation energies.

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O12-1

Double 1s ionization of Al and Si by photon and electron impact

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Double ionization leading to an empty 1s shell is a sensitive probe of electron correlation effects in the initial and final states. For low-Z neutral atoms, experimental data on double-to-single 1s ionization are scarce or nonexistent.

We report on the energy dependence of the double 1s photon and electron ionization of metallic Al and Si. The double K–shell vacancy production was studied by means of high-resolution x-ray emission spectroscopy. Measurements of the photoinduced x-ray spectra were carried out using the Fribourg high-resolution von Hamos Bragg curved crystal x-ray spectrometer [1] installed at the ID21 and ID26 beam lines at the ESRF, Grenoble. The electron impact double ionization cross sections were measured in-house by means of an electron gun. The double to single 1s ionization cross sections were derived from the hypersatellite ($1s^{-2} \rightarrow 1s^{-1}2p_{1/2}^{-1}$) $K\alpha_2^h$ to diagram Kα ($1s^{-1} \rightarrow 2p^{-1}$) line intensity ratios as a function of the photon and electron energy spanning the range from threshold for double ionization to 7 keV for Al and 10 keV for Si in case of photoionization, and 20 keV for electron impact. It was found that the maximum values of P_{KK} for electron double ionization are an order of magnitude lower than those obtained with photons.The energies and linewidths of the $K\alpha_2^h$ x-ray emission lines were determined. Further, the peak values of the ratio of double to single ionization cross sections were compared to the Z-dependence reported in [2] and different theoretical models for double 1s photoionization of He-like atoms. The relative importance of the dynamical electron-electron scattering contribution to hollow low-Z atom production was evinced.

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O12-2

Effect of excitation energy on the Pb Lα/Lβ intensity ratio

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Pb Lα lines overlap with As Kα lines. The overlapped lines are separated by a Pb Lα/Lβ intensity ratio. The Lα/Lβ intensity ratio is not actually constant, though the statistical ratio of Lα/Lβ is 2 [1]. In order to quantify Pb accurately, it is necessary to know changing factors of the Pb Lα/Lβ intensity ratio. We have measured dependence of the Pb Lα/Lβ intensity ratio on applied voltages of an X-ray tube. Pb Lα and Lβ X-ray fluorescence spectra of Pb metal and several compounds were measured using an energy dispersive X-ray spectrometer with a Rh target X-ray tube. Changing the applied voltage, the $L\alpha_{1,2}$ (L_3-$M_{5,4}$) / $L\beta_{1,2}$ (L_2-M_4, L_3-N_5) intensity ratio changed from about Lα/Lβ = 4 at 15 kV to Lα/Lβ = 1 at 45 kV (Fig.1). The calculation values of the Pb Lα/Lβ intensity ratio of the Pb metal using the Shiraiwa's formula [2] were in good agreement with the experimental ones (Fig.2). The Pb Lα/Lβ intensity ratio modifications of metal and compounds were smaller than 5%. We concluded that the Pb Lα/Lβ intensity ratio modifications by the applied voltage were due to the changes of the L_3 and the L_2 ionization probabilities and that the rate changes of Auger transitions had little effect on the Pb Lα/Lβ intensity ratio.

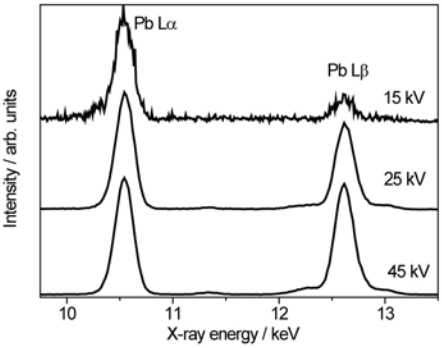

Fig.1 Pb Lα and Lβ X-ray fluorescence spectra of Pb metal.

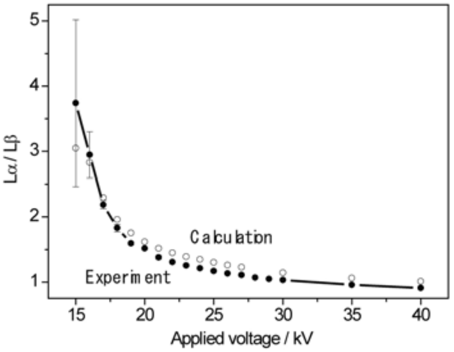

Fig.2 Experimental and calculated Pb Lα/Lβ intensity ratios plotted against the applied voltage.

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O12-3

Helium induced L X-ray production cross-section in Pt and Bi

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L-Shell X-ray production cross-sections induced by helium on Pt and Bi elements have been measured in the incident energy range of 2.0 to 3.0 MeV. The present values will be compared with available data of Vigilante et al [J. Phys. B: At. Mol. Opt. Phys. 24 (1991) 2521] and with the theoretical calculations by ECPSSR model [W. Brandt and G. Lapicki, Phys. Rev. A23 (1981) 1717]

O12-4

On features of extreme X-Ray focusing

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New scientific applications of intense coherent x-ray beams require focusing of the beams to sub-micron spot sizes. In order to propose suitable technological solutions for sub-micron x-ray imaging one becomes necessary to understand the basic features of x-ray focusing at the extreme diffraction limited conditions.

In this report, recent studies on x-ray micro- and nano-focusing by means of various guide systems, performed by different research groups in the world, will be analyzed [1]. The fine features of x-ray propagation both in ultra narrow collimators and at glancing reflection from a smooth surface, plane or curved, can be described within the unified theory of trapped radiation propagation: surface channeling in micro-guides and bulk channeling in sub-micron/nano-guides [2].

[1] S.B. Dabagov, and H. Uberall, Nucl. Instr. Meth. **A580** (2007) 756.

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O12-5

Self enhancement effects on XRF K-lines due to natural width

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It is well known that, due to the Heisenberg's uncertainty principle, the energy levels in the atom are defined within an energy width. Any electronic transition involving two or more levels shows a natural width given by the sum of the widths of the participating levels. Moreover, any XRF line appears to have a Lorentzian like distribution whose FWHM is the natural width.

Since the Lorentzian distribution has long tails on both sides, the tails may cross above neighbor absorption edges giving rise to enhancement effects of a certain complexity.

In this article we discuss the self enhancement effects on XRF K-lines in pure element samples having atomic numbers Z=11-92. This study is performed with both deterministic and MC calculations.

O12-6

A method for measuring K, L and higher shell photoionisation cross sections at 59.5 keV

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A simple and direct method has been developed to measure the K, L and other higher shell photoionisation cross-sections of several element at 59.5 keV. The K and L_i (i=l, α, β, γ) x-ray intensities emitted by these elements, from irradiating their samples by the photons of above energy are measured using a Si(Li) spectrometer system. The Kα and L_i x-ray fluorescence cross sections of the above elements are determined, after the total K and L shell photoelectric cross sections are evaluated. The present experimental results are agreed with the theoretical values.

O12-7

Intensity distribution of Compton scattered gamma rays from K-shell electrons using coincidence technique

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Compton scattering generally refer to the scattering of photons from free and stationary electrons. Scattering from bound electrons modifies the general relationship between energy of the scattered photons and the scattering angle in a number of ways. Various relativistic and non-relativistic theoretical investigations of the Compton scattering from bound electrons are based upon either form factor approximation, which is valid for low photon energy and low binding energy or the incoherent scattering function approach, whose validity requires that the photon energy to be appreciably greater than the electron binding energy. Due to different approximations introduced in various theories, the prediction made by these calculations is very often in disagreement with each other.

In the present work, the measurements are made to determine the intensity distribution of Compton scattered photon from K-shell electrons of medium atomic number elements at 145, 279 and 662 keV gamma photons at scattering angles ranging from 30° to 150°. The scatterer is viewed by two detectors, one sensitive to characteristic x-rays emitted from the element and the other to the scattered gamma rays. The scattered photons are detected by a 51 mm diameter and 51 mm thick NaI(Tl) crystal and the K X-rays are detected by a 38 mm diameter and 2 mm thick NaI(Tl) crystal. A coincidence set up using Canberra ARC timing amplifiers in the fast channels and having 30 nsec resolving time is used for recording the events.

The intensity distribution of measured K-shell to free electron Compton collision, absorption and scattering cross section ratio, $d\sigma_K/d\sigma_F$ will be presented for the energies, elements and scattering angles mentioned above. The general trend of K-shell to free electron Compton collision cross section ratio increases with the increase in scattering angle. Our experimental results are compared with the available theoretical and experimental data.

I13

Synchrotron-radiation-based hard X-ray nanobeam by Kirkpatrick-Baez mirrors

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We developed a surface-figuring method to realize atomic-level smoothness and 0.1nm (RMS)-level figure accuracy over the large area of 100mm scale, and applied the method to fabricate total-reflection optics for hard X-ray nano-focusing [1]-[3]. The fabricated optics were evaluated at the 1km-long beam-line (BL29-XUL) of SPring-8, and a nearly diffraction-limited focusing with the spot size of 25nm x 30nm was obtained at the X-ray of 15keV. The fabrication methods, the performances of the focusing optics, and the application examples will be introduced.

We are now trying to realize sub-10nm X-ray nano-beam in which wave-front error smaller than 0.01nm is required. To evaluate such small phase error, we developed a novel at-wavelength interferometry using a phase retrieval technique [4,5]. A compensation method of the phase error was also proposed. The latest results on the research will be also presented.

[1] Y. Mori et al., Rev. Sci. Instrum., 71 (2000), 4627-4632.
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[5] H. Mimura et al., Phys Rev A 77, 015812 (2008)

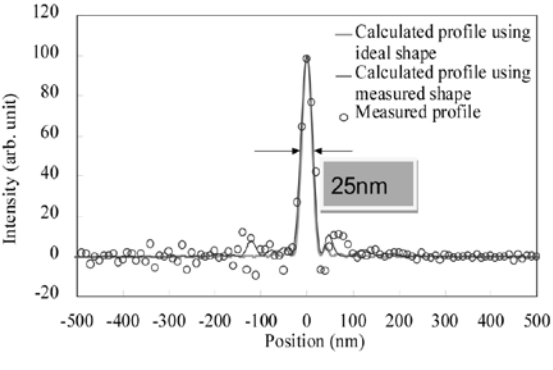

Fig. Focused X-ray beam profiles of the size of 25nm

O13-1

SR-XRF analysis of fluid-inclusions in cloudy diamonds from Koffiefontein, South-Africa

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The study of fluid inclusions within diamonds from different locations around the world gives important information on subduction processes (e. g. of oceanic lithosphere material) and the diamond growth. For this, cloudy diamonds from Koffiefontein and Finsch mines were studied systematically at the European Synchrotron Radiation Facility (ESRF) at the beamlines ID18F and ID22. In addition, XANES measurements (at HASYLAB beamline L) and Raman Spectroscopy (at JWG University) were performed on the same inclusion suite to complete the identification of the inclusions.

To avoid the loss of information when separating the solid part of the inclusion from the diamond host and releasing the gas and/or fluid content, dedicated measurement techniques must be applied to study these fluid inclusions "in-situ". In this work, the experiment performed at ID22 to investigate very tiny fluid inclusions in a specially prepared Koffiefontein diamond (Kf07-4) is demonstrated. The application of the confocal XRF method appears to be essential to unambiguously retrieve information from within the diamond needle on the trace element and sub-micron level. In such way, the distribution of elements such as Cl, Br, K, Ca, Ti, Mn, Fe, Ni and Cu could be studied in great detail. The extreme in-homogenous distribution of these elements in a single diamond was surprising. And whether this distribution indicates immiscibility during entrapment of the fluid phase or subsequent separation into a solid, fluid and probably gas phase during uplift of the diamond host remains speculative at the moment and is a matter of our ongoing measurements.

These studies should also provide a standard reference for future investigations on fluid inclusions entrapped in "superdeep" diamonds from Kankan (Guinea) and Juina (Brazil).

O13-2

Applications of the remote operation of PIXE and Micro-PIXE measurements

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Fast internet connections that are available today worldwide are opening new possibilities in the research and education using accelerator based analytical techniques. Our newly developed accelerator computer control and recent improvements in sample positioning and data acquisition systems enabled a long distance access to experiments performed at accelerator including different aspects of the application of PIXE technique. At the Laboratory for ion beam interactions of the Ruđer Bošković Institute, PIXE is applied at three different beamlines. These are a) the broad beam PIXE vacuum chamber with automatic sample changer, b) the external beam PIXE system with computer controlled sample stage for large objects and c) the proton microprobe facility. As each of these systems is equipped with a dedicated software and hardware for remote operation, PIXE measurements can be entirely or partially performed from distant locations.

These capabilities have been shown of particular importance for sensitive microPIXE measurements (e.g. in biomedical applications) when the typical measurement time needed for low concentrated elements can be achieved only by overnight measurements. This aspect is also important in collaborative work when the samples have been sent by experimenter that is not personally present during the measurements on site. In both cases possibility to be connected to the ongoing measurement for collaborators from distance locations is of great value. And finally we will show that this possibility can be easily used for the long distance learning by access to accelerator operation console and subsequent analysis using PIXE and RBS techniques.

O13-3

Micro-XRF from Carbon upwards with a laboratory x-ray source

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Micro X-ray fluorescence analysis (µ-XRF) is widely used for sample analysis in the µm-scale. However, for the analysis of low Z elements ($Z<14$) the challenge lies in a very sophisticated experimental set-up. Of particular importance is an efficient excitation from the source and a good attainable detection of the low energy photons emitted from the light elements in the sample.

Sample examination under medium vacuum conditions is essential to avoid undesired effects, which would normally occur in air, such as air scattering of the primary beam, existence of Ar K-lines and absorption of the fluorescence radiation. A preferential excitation source is an intensive low-energy photon source, like a Cr anode 1900 W point focus from a LFF diffraction x-ray tube, which was used in the work presented.

In order to achieve a micro-spot on the sample (spot size 40µm) a polycapillary (XOS) is used. The detector is a horizontally mounted Peltier cooled SDD with a 300nm ultra thin window (MOXTEK), offering an adequate high efficiency to reach even down to carbon. The shaped output signal is collected via ADC in a multichannel analyzer and stored as spectrum of the individually examined pixels. The vacuum chamber with a 8µm Kapton entrance window is closest coupled to a 300 µm Be window of the x-ray tube. The capillary is mounted inside the chamber on an x-z micro stage to obtain optimal alignment with respect to the x-ray tube. The sample is fixed on a frame, which can be moved 25 x 25 mm² horizontally and vertically by two computer-controlled x-z micro stages. An additional translation stage allows adjusting the sample surface in the focus of the polycapillary. The sample surface is observed through a microscope with a CCD camera.

The following investigations have been performed, utilizing the aforementioned set-up and will be presented as (1) scans across a pattern, that was applied on a plexiglass reflector by ink jet picodroplets containing Sc; (2) analysis of the spatial distribution of a 1 µl Na(F) sample on a Kapton foil; and (3) the elemental distribution of light elements in a slice of human bone.

Prospects for future improvements of the set-up and its applications will be presented (see also poster S. Smolek et al).

O13-4

3D analysis of biological samples by confocal µXRF

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The confocal setup consists of x-ray lenses in the excitation as well as in the detection channel. In this configuration, a micro volume defined by the overlap of the foci of both x-ray lenses is analyzed. Scanning this micro volume through the sample, 1-3 dimensional studies can be performed.

For the confocal setup, we used a commercial glass monocapillary in the excitation channel and a monolithic half polycapillary in the detection channel. The polycapillary was home-made by means of drawing of multibundles of glass capillaries in a heating furnace. The experiment was carried out at the D09B beamline of the Synchrotron Light National Laboratory (Laboratório Nacional de Luz Síncrotron, LNLS) using white beam. A silicon drift x-ray detector of 150 eV resolution at 5.9 keV was used for detection of fluorescent photons.

A model for a theoretical description of the x-ray fluorescent intensity registered by a confocal µXRF was introduced by Malzer and Kanngieβer in 2005 [1]. These authors showed that the scan of the x-ray fluorescent intensity is the spatial convolution of the sensitivity and the x-ray fluorescence emission rate to the detector. In a previous work we showed that the convolution theorem can simplify the calibration and quantification process in confocal µXRF [2]. In the present work, we applied these ideas to analyze samples of aquatic plants and a sample of tooth by confocal µXRF. We showed that confocal µXRF can be successfully applied to help the study of the effects of water bioremediation on aquatic plants. We also showed that confocal µXRF can be used to make topological studies of teeth.

[1] W. Malzer, B. Kanngieβer. Spectrochim. Acta, B60 (2005) 1334-1341.

[2] R.D. Pérez, H.J. Sánchez, C.A. Pérez, M. Rubio, in preparation.

O13-5

X-ray Fluorecenece Analysis of Liquid/Solid Samples

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We have applied X-ray fluorescence (XRF) analysis for the direct measurement of solutions and the solid surface of the samples in the solution [1,2]. A glass guide tube, which was attached to an X-ray tube, was inserted into the solution. The solid surface in the solution was irradiated by the primary X-rays. The X-ray fluorescence was detected through another glass tube by the energy dispersive X-ray detector. The glass tubes for X-ray irradiation and X-ray detection were combined; therefore, it was easy to approach this XRF probe to the surface of the sample.

The quantitative analysis of the method was evaluated by using standard solutions. The lower detection limits for solution samples were in the range of ppm order. The XRF spectra changed depending on the distance between the XRF probe and the solid surface in the solution. Usually, the XRF spectrum includes the information of both the solution and the solid sample. However, by subtracting the contribution from the solution, the XRF spectrum of the solid surface in the solution could be obtained. We have also applied the XRF analysis using a needle-type collimator [3] to know the concentration distribution of elements in the solution.

[1] K. Tsutsumimoto, K. Tsuji, Proposal of XRF analysis for Solid/Liquid Interfaces and Monitoring Chemical Plating Processes, BUNSEKI KAGAKU, **56** (2007) 499-504.

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O13-6

Micro-beam X-ray fluorescence analysis of individual particles

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Micro-beam x-ray fluorescence spectrometry is one of the basic method of elemental analysis of minute samples, especially individual particles and grains. Several methods of correction for absorption and particle shape effects in micro-beam x-ray fluorescence analysis were investigated experimentally and with the use of Monte-Carlo simulation. A fast energy-dispersive, silicon drift detector was used to measure the primary x-ray beam transmitted through the sample. The absorption factors were calculated using the data acquired with the SDD. The possibility of using the coherently and incoherently scattered primary radiation for determining the mass of individual particles was examined. The proposed methods were validated with the use of glass micro-spheres of known composition.

Synchrotron radiation x-ray fluorescence confocal imaging is among the methods, which are able to provide three-dimensional, quantitative information on the elemental distribution in the probed sample volume with trace level detection limits. The confocal X-ray fluorescence microscope was applied for 3D micro-XRF analysis of microscopic inclusions in mineral grains. Intensities correlation method was applied for determining the concentrations of major and minor elements in mineral grains.

I14

Nanoparticles observed under X-ray grazing incidence

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Particles, especially the smallest are nowadays of primordial interest. They are used in many disciplines and in several applications in biology, medicine, biochemistry, pharmacy, material sciences and also in conservation sciences. Man is continuously producing nanoparticles. Laser printers, copy machines, Diesel fuel driven cars, Pt-Pa-Rh catalyst converters built-in in cars, laser applications in medicine and technology, lasers used for LIBS (Laser Induced Breakdown Spectrometry) and several other applications produce nanoparticles. They are in terms of their diameter located in the range below one micrometer. Single members of the finest fractions, those below 100 nm, are difficult to characterize via conventional methods of chemical analysis or microscopy if their morphology and/or composition should not be altered during measurements.

An approach to the chemical characterization as well as some hints about the morphology of very fine fractions of nanoparticles can be deduced from experiments using X-ray grazing incidence techniques (TXRF, Total Reflection X-ray Fluorescence and XSW, X-ray Standing Waves). Some theoretical aspects will be discussed in detail. Results of modelling and simulation will be compared with the experimental data obtained from XSW experiments performed at DELTA synchrotron facility. Advantages and drawbacks will be shown for metallic nanoparticle characterization using TXRF and XSW. The power of X-ray methods for these purposes will be compared with those obtained by other technique

O14-1

Reference-free TXRF analysis of semiconductor surfaces with synchrotron radiation

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Total-reflection X-ray fluorescence (TXRF) analysis is a well-established method to monitor lowest level contamination on semiconductor surfaces. Even light elements on a wafer surface can be excited effectively when using high-flux synchrotron radiation in the soft X-ray range. To meet current industrial requirements in non-destructive semiconductor analysis, the Physikalisch-Technische Bundesanstalt (PTB) operates dedicated instrumentation for analyzing light element contamination on wafer pieces as well as on 200 mm and 300 mm silicon wafer surfaces. This instrumentation [1] is also suited for grazing incidence X-ray fluorescence analysis (GIXRF) and conventional energy-dispersive X-ray fluorescence (EDXRF) analysis of buried and surface nanolayered structures, respectively. The most prominent features are a high vacuum load-lock combined with an equipment front end module (EFEM) and a UHV irradiation chamber with an electrostatic chuck (ESC) mounted on an 8-axis manipulator. Here, the entire surface of a 200 mm or a 300 mm wafer can be scanned by monochromatized radiation provided by the plane grating monochromator beamline (PGM) for undulator radiation in the PTB laboratory at the electron storage ring BESSY II. This beamline provides high spectral purity and high photon flux in the range of 78 eV to 1.86 keV. In addition, absolutely calibrated photodiodes and Si(Li) detectors are used to monitor the exciting radiant power respectively the fluorescence and scattered radiation [2]. Furthermore, the footprint of the excitation radiation at the wafer surface is well known due to beam profile recordings by a CCD during special operation conditions at BESSY II that allow for drastically reduced electron beam currents. Thus all the requirements of completely reference-free quantitation of TXRF analysis are fulfilled and will be presented.

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O14-2

Grazing incidence X-Ray fluorescence characterisation of ultra shallow junctions in the ANNA consortium

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Dopant profiling in ultra shallow junctions in Si and other semiconductor materials, is a very current problem in applied physics and is well known to the scientific community involved in the characterization, design, fabrication as well as simulation of processes and devices in microelectronics [1].

Grazing Incidence X-Ray Fluorescence Analysis (GI-XRF) is known for its capability of performing qualitative and quantitative elemental analysis of surfaces, near surface layers, thin films [2]. For the characterisation of ion implants in silicon wafers it has been shown that it can give quantitative information on the total retained fluence and on the depth profile shape [3].

A perspective will be given of its use for the characterisation of Ultra Shallow Junctions within the ANNA project [www.anna-i3.org], an Analytical Network for Nanotechnology funded by the European Commission under the Framework Programme 6.

The results of laboratory measurements obtained on arsenic implanted silicon wafers with a self-developed chamber (Mo Kα excitation, As Kα fluorescence recorded) at the Atominstitut are presented.

A novel evaluation approach based on the coupling of Secondary Ion Mass Spectroscopy (SIMS) maesured profiles and GI-XRF developed at the Fondazione Bruno Kessler will be outlined and discussed. In this approach the deeper part of the SIMS profile is assumed to be accurate whereas the near surface part (where SIMS is known to have quantification weaknesses) is adjusted using the information obtained from GI-XRF measurements.

Employing monochromatized undulator radiation at the electron storage ring BESSY II, the PTB conducted GI-XRF measurements on As implanted 200 mm silicon wafers at 1540 eV in order to reveal the implantation profile. A routine is currently developed to calculate and fit this depth profile for the implanted element using an IMD simulation [4] of the standing wave field inside the silicon wafer. These measurements are also planned for B implanted wafers.

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O14-3

Trace element analysis and zinc speciation in size-fractionated aerosol samples using SR-TXRF and XANES

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The health effects of aerosol depend on the size distribution and the chemical composition of the particles. Heavy metals of anthropogenic origin are connected to the fine ($PM_{2.5}$) and ultrafine (PM_1) aerosol fraction. The composition and speciation of aerosols can be variable in time, due to the time-dependence of anthropogenic sources as well as meteorological conditions. Synchrotron-radiation total-reflection X-ray fluorescence (SR-TXRF) provides very high sensitivity for aerosol characterization. X-ray absorption near-edge structure (XANES) spectrometry in conjunction with TXRF detection can deliver speciation information on heavy metals in aerosol particles collected directly on the reflector surface. The suitability for SR-TXRF for elemental analysis and XANES for zinc speciation in size-fractionated aerosols from a short sampling period is presented.

Atmospheric aerosol samples were collected at different urban and rural, continental and marine locations using a 7-stage May cascade impactor having the opportunity of sampling on Si wafers with high temporal and size resolution. The measurements were performed at HASYLAB Beamline L using the TXRF vacuum chamber. For TXRF, the energy of the synchrotron radiation was tuned to 18.4 keV using the NiC multilayer monochromator. For TXRF-XANES at the Zn K-edge, a Si(111) monochromator was used. The vertical dimension of the beam was set to 0.5 mm for both cases. Cr standards having a known mass in dimensions identical to the deposited aerosol particles could be used for calculating the elemental composition.

For TXRF elemental analysis, detection limits of transition metals in the pg/m^3 range could be reached for a 20-min sampling time in the 0.5-1 μm aerosol fraction. Information on Zn speciation could be obtained from air concentration of Zn as low as 100 pg/m^3. The size distribution of the elemental composition as well as the Zn speciation was found to be in accordance with the origin of the aerosol samples.

O14-4

TXRF cation analysis by anionic membrane collection

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A new method for the determination of metal cations by anion selective membranes is presented. The anion selective membranes were composed of polyvinyl chloride (PVC) as a matrix, Aliquat-336 as anionic extractant, dibutyl phthalate as plasticizer and various ligands as complexing agents [1]. These membranes were capable of capturing cationic metals such as Co, Ni, Mn, Fe, Cu, Zn in solutions that had excess of anionic ligands (cyanides etc). The membranes produced on the surfaces of quartz reflectors; they were put in the centre of the reflectors as a ~3 mm diameter liquid spot, they were dried and they were immersed in water solutions containing various concentrations of metals. By the end of the equilibration time, the reflectors were left to dry and they were analyzed by Total reflection X-Ray Fluorescence (TXRF). The effects of various experimental parameters (pH, equilibration time, metal speciation, competitive cations, and different complexing ligands) were tested. Minimum detection limits of the order of 1-10 ppb (or even lower) were achieved.

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O14-5

Application of high-resolution grazing emission x-ray fluorescence (GEXRF) spectroscopy for detction of low level impurities on Si-wafer.

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The production of ultra clean silicon wafers is one of the most important issues for Si-based microelectronic technology. Application of the TXRF method combined with intense synchrotron sources offers presently the best possibilities for measuring very low concentration impurities on Si wafer surfaces. Using the synchrotron x-ray beams the TXRF sensitivity on the level of 10^8 atoms/cm^2 was achieved [1] at optimized conditions. However, the synchrotron radiation based TXRF technique, which employs the grazing incident geometry, cannot benefit from the available micro-focused synchrotron radiation beams for performing high-resolution 2D mapping of impurities on Si wafer surfaces. Moreover, in standard TXRF arrangements low-resolution semiconductor silicon detectors are usually used, which limits in some cases the elemental resolution capabilities and results in poorer detection limits due to the low-energy tailing of semiconductor x-ray line profiles. Therefore, further development of new direct techniques to measure the metallic impurities on Si wafers is still a challenging question.

We report on application of the grazing-emission x-ray fluorescence (GEXRF) method [2, 3] to measure the x-ray emission from metallic impurities on Si-wafer. The GEXRF technique was combined with intense synchrotron radiation beam and high-resolution x-ray detection by employing a von Hamos-type spectrometer. In order to determine the detection limits for the GEXRF method, the K-, L- and M x-rays of several elements, having x-ray energies in the range between 1.7 keV and 7 keV, were measured. From the measured x-ray spectra the GEXRF detection limits on the level of 10^{12} atoms/cm^2 were obtained. By means of the GEXRF technique the composition, density and thickness of the layers can be deduced by measuring the intensity evolution around grazing exit angle. Differences between the bulk, film-like and particle-like layers were clearly observed. Additionally, to test the 2D-mapping capabilities of the GEXRF method a 1D-scan employing 25 μm beam size was performed using Si wafer with periodic Cr layer.

The further improvement of detection limits for the GXRF technique can be achieved by applying the vapor phase decomposition (VPD) preconcentration technique. Since a spot of x-ray synchrotron beam is very small (1mm^2) thus the VPD enhancement factor can be up to five orders of magnitude. Therefore, a combination of the high-resolution GEXRF method with the VPD technique can lead to the detection limits on the level of 10^7 atoms/cm^2.

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O14-6

A novel approach for chlorine determination in acidic medium by total reflection X-ray fluorescence

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Determination of chlorine at trace levels in different matrices is of importance in biological, environmental, medical, nuclear and industrial technology. During total reflection X-ray fluorescence (TXRF) determination of chlorine in acidic solutions there is appreciable loss of chlorine when the sample is heated on quartz sample support for sample preparation [1]. This results in lower recovery of chlorine from nuclear materials e.g. UO_2, ThO_2 and PuO_2 etc. where major matrix is removed using solvent extraction after dissolution in nitric acid [2]. Silver nitrate has been successfully applied as a stabilizer for iodine determination by TXRF [3]. In present work, an indirect novel method of chlorine determination by TXRF has been developed. The method involves addition of a known excess amount of $AgNO_3$ solution (than that required for chlorine precipitation as AgCl) to the analyte solution and determination of the excess (unused) Ag in the filtrate by TXRF using Cd as internal standard. The TXRF spectra were recorded using an ATOMIKA TXRF spectrometer with W continuum excitation at 50 kV and 38 mA. Amount of Ag present in filtrate was determined by using Ag Kα and Cd Kα line intensities of analyte and internal standard respectively. Concentration of chlorine in original solution was calculated from the amount of Ag consumed in AgCl precipitation. The method has been found to have a precision (1σ RSD) and accuracy better than 16% for the samples having chlorine concentration in the range of 15 to 60 μg/mL. The method gives satisfactory results in HNO_3 medium of acidity up to 4.5 M and is thus suited for the determination of chlorine in nuclear materials after their dissolution and separation of major matrices: thorium, uranium or plutonium using tri-n-butyl phosphate. Experiments conducted by using synthetic mixtures of standard uranium and NaCl solutions have shown encouraging results by this methodology.

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Abstracts
Poster Session A

PA-1

Analytical characterization of the ground layer in paint section of Rubens' paintings at "El Prado" National Museum

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"El Prado" National Museum collection has several pieces of Rubens artwork, some of which were painted in Spain during his last two stays at Spanish Royal Court. However, his other paintings come from Ambers, Belgium, where he usually used to work. He always used the painting style of his time; such as reddish ochre grounds from natural colored earths, which have a complex chemical composition.

At present, a multidisciplinary project is being developed in order to clearly identify the origin of several of Rubens undated paintings at "El Prado" Museum. The first step of this project is to carry out a detailed study on two of his paintings of unknown origin. The data gathered in this study will be compared with the data obtained from the previously used materials.

The estratigraphic cross-sectional micro samples have been studied by Scanning Electron Microscopy (SEM), High Resolution Transmission Electron Microscopy (HRTEM), and Light Microscopy (LM). Furthermore, a detailed analytical study by Energy Dispersive X-ray Spectroscopy (EDS) was carried out.

Results of the well dated canvas entitled "*El duque de Lerma"* (1609) (Ambers) will be presented. Thin samples obtained by cross-sectional method were embedded in an epoxy resin. Special care must be taken in order to keep the micro sample unaltered.

Numerous qualitative and semi-quantitative microanalyses by EDS have been performed in order to locate the pigments and additives used by the artist. These results show the main and secondary components, such as different types of feldspars and micas, mixed with very pure iron oxides/hydroxides, silice (quarz and opal), titanium oxides, calcite and dolomite.

PA-2

SR micro-XRD, SR micro-XRF and SR micro-XANES analyses on degraded Cadmium Sulphide paint samples

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The paintings of the end of the 19th-C and the beginning of the 20th-C form an interesting field of research as numerous new pigments were developed by the emerging chemical industry at that time. These new painting materials often outclassed the traditional pigments with regards to colouring intensity, purity, cost price, covering power etc. However, not all of these modern pigments appeared to be chemically stable on the long term. This seems for instance the case for cadmium yellow, a cadmium sulphide compound invented by Stromey in 1818 and commercialized around the middle of the 19th-C. Fading of the yellow colour and loss of adhesion has been reported by several authors, but the exact deterioration process remains a point of discussion. Both in the Royal Museum of Fine Arts of Antwerp and in the Kroeller-Mueller Museum, degraded cadmium yellow was found on paintings of the Belgian avant-garde artist James Ensor (1860-1949). Under the microscope, the surface of the yellow paint looks dull and flaky; it also displays cavities, has become brittle and lacks cohesion. However, the most striking feature is the formation of whitish, semi-transparent protrusions on the surface. The chemical characterization of both the white globules and the overall degradation process is obviously of great interest/concern to conservators as it is a warning signal for ongoing transformations.

The conservators of both museums supplied scrapings/samples of the surface of the paint containing white globules and some yellow paint. The materials were examined at the ESRF by means of micro-XRD at beam line ESRF-ID18F and micro-XRF and micro-XANES at ID21. The collected XRD spectra and maps show the distribution of cadmium sulfate hydrate ($CdSO_4.H_2O$), otavite ($CdCO_3$) and greenockite (CdS) throughout an assembly of grains isolated from one of the paint scrapings. Greenockite and otavite was identified in the non-degraded, yellow areas. By contrast, the whitish/transparent grains are rich of $CdSO_4.H_2O$. On the basis of these findings, the major mechanism for colour change of the yellow CdS could be identified, i.e.: $CdS + 2O_2 + H_2O \rightarrow CdSO_4.H_2O$. The XANES and XRF maps collected at ESRF-ID21 confirmed this hypothesis and allowed us also to obtain information on the depth of the oxidation front.

PA-3

EDXRF coupled with vis-RS to study iron-gall inks: laboratory tests and *in situ* analysis on Palladio's drawings

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Different kinds of inks used in drawings, engravings and manuscripts can be usually distinguished by elemental analyses. In the case of ancient iron-gall inks, also diverse batches produced in different periods can be recognized because of some differences in composition. Non invasive methodologies like PIXE [1] and micro-ED-XRF [2] have been successfully used with this aim on manuscripts of Galileo, Goethe and Mozart.

In this work we show the possibility to use a portable ED-XRF spectrometer without capillary x-ray optics to study drawings, which limits the analyses to broader traced lines (about 3 mm). The different kinds of drawing patterns (single lines, cross-hatchings, liquid shadings of different intensity) suggests the need to use a preliminary clustering of the investigated points that can be performed on the basis of colorimetric results achieved by visible Reflectance Spectrometry (vis-RS).

The method has been tested on laboratory test samples with different kinds of iron-gall ink, then applied in situ to study sixteen drawings of architecture by Andrea Palladio (1508-1580) belonging to the Pinacoteca Civica di Vicenza (Italy).

A discussion of the method and results is provided.

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PA-4

Analysis of pigments on paintings from two churches in Dubrovnik

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Eight paintings located in two churches in Dubrovnik have been systematically analyzed by using portable XRF system, proton microprobe, optical and UV microscopy techniques, with the aim to compare the use of pigments by an author or authors of the paintings.

Four of investigated paintings, all located in church of "st. Blaise", represent one evangelist. The other four analyzed paintings, located in the church of "Lady of Carmen", are very similar to the first four paintings. They represent the same four evangelists as the first four paintings from the other church. Since they also look quite similar to the first set of paintings, there is a common understanding that all these paintings originate from the same period and that they were painted by the same author(s).

In our analysis we compared pigments of the four evangelists paintings from church of "st. Blaise" with the pigments of the four evangelists paintings from church of "Lady of Carmen". In order to make comparison easier, micro-samples for the analysis were taken from similar positions on each of two similar evangelist paintings from two churches. The work presented here is focused on analysis of pigments by x-ray spectroscopy methods, which is just one aspect of the larger project which will investigate these paintings in more detail with the final goal to investigate their attributions to Mattia Preti.

PA-5

Monitoring the process of gilding, tarnishing and restoration of 21st centry daguerreotypes by wavelength-dispersive X-ray fluorescence spectrometry

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Work announced to the world in 1839 by Louis J. M. Daguerre and Joseph Nicéphore Niépce resulted in the earliest form of photography known as daguerreotyping. In the daguerreotype process a polished silver plate is exposed to halogen vapor (I, Br, Cl or a combination thereof) to make the surface light sensitive. It is then exposed in a camera to form a latent image. The modified silver halide surface is then developed by exposing it to mercury vapor and the image fixed by treatment with Na_2SO_3 (hyposulfite of soda). Toning and strengthening of the image is achieved by treating the silver surface with a solution of gold chloride. The image is susceptible to tarnishing when exposed to air and preservation of the image performed by housing in a tightly sealed case with a protective cover glass. The brass mats of such housings are a catalyst to tarnishing on the images. As such, restoration of tarnished, yet delicate and irreplaceable images has become an area of active research. This study presents the use of wavelength-dispersive X-ray fluorescence spectrometry (WDXRF) on modern daguerreotypes to monitor the photographic development process as well as the tarnishing and restoration of daguerreotypes. The WDXRF system equipped with LiF(200), PET and OVO-55 analyzing crystals provides a means to estimate the relative surface content of various elements including the light elements, sulfur and the halides. The photographic plate composed of a copper backing and a silver surface, provides an adequately thick layer of silver as to attenuate any copper signal from the backing (in comparison to inherent system Cu contamination) while allowing for signal normalization to the silver X-ray(s).

PA-6

Computed radiography of XIX century Brazilian paintings

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Four paintings of some of the most representative Brazilian artists from the XIX century were characterized using Computed Radiography. The analyzed paintings were: “The Model at Rest” (Almeida Junior, 1882, 100 x 130 cm); “Bad News” (Rodolfo Amoedo, 1895, 100 x 74 cm); “Redemption of Can” (Modesto Brocos, 1895, 199 x 166 cm) and “Inside the Atelier” (Rafael Frederico, 1898, 20.5 x 40.5 cm).

Radiographic techniques have been used in paintings to reveal the extent of old damages sometimes concealed by past restoration; the successive phases of the artist creation (preparatory drawing, underpainting and changes of design); the nature of the support; the canvas weave; presence of lead pigments; crackings and detachments of ink; losses of support; etc.

The experimental setup consisted of an Oxford X-ray source, operating at 35 kV and 200 μA, placed at 85 cm from the painting, a GE CR 50P Portable Computed Radiography Scanner and a Fuji Imaging Plate detector. The IP detector (35 x 43 cm) was fixed behind the canvas to perform each radiograph. The images were revealed by introducing the exposed IP in the scanner, which also erased the film after the image processing.

The radiographic images revealed that the paintings were in a relatively good state of conservation – most of them had been restored during the XX century. Small regions of losses could be observed and also some details like: the canvas weave, the wooden support, the nails used to fix the fabric on the wood, the use of lead white, the characteristic brushing technique of the artists and some changes in the design. These results – together with the EDXRF analyses - have been used to create a database about the XIX century collection of the National Museum of Fine Arts, in order to assist restorators, conservators, researchers and students.

XRF and PIXE analysis of the wooden polychrome altars from the northern Croatian region

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The aim of this work was the investigation of pigments from five wooden polychrome altars from parochial churches in northern Croatia. All altars stem from the famous sculptor's workshop of Frantz Straub, which was active in the 1760s. Three of these altars from the parochial church of the *Blessed Virgin Mary* in *Kloštar Ivanić* have been recently restored in the *Croatian Conservation Institute*. The two other studied altars were the main altar from the parochial church in *Pakrac* and the altar from *Velika Ludina*. Being important objects for the national cultural heritage an extensive research on the painted wooden objects was undertaken as a part of the conservation-restoration process. Among still unresolved questions was whether the Straub workshop had its own standard collaborating painter(s), or the altars were left on the intended places unpainted, leaving the work of painting to local artists. Paints in the palette of each painter have its own characteristic pigments combination and this 'fingerprint' is even more individualized by trace, impurity elements in pigments and binders, which are dependent on geographic source of the material, technology of purification, etc.

To address this problem, an extensive preliminary in-situ pigment investigation was done using a portable X-ray fluorescence device (XRF). XRF is a non-destructive, fast and relatively simple analytical method for multi elemental analysis. In its portable version, used here, it is also a non-invasive method, which is of particular importance when working on precious artifacts. It reduced sampling (and related damage to the artifacts) to a minimum. XRF analysis yielded positive identification of most pigments used.

Only the problems which could not be resolved by this method (organic materials, pigment layer cross-sections, binders, etc.) were further analyzed using additional off-site lab methods, primarily micro-PIXE (proton induced X-ray emission) at the nuclear microprobe of the Rudjer Boskovic accelerator facility, as well as thin-layer chromatography (TLC) and Fourier-transform infrared spectroscopy (FTIR). The opportunity to research 5 artifacts built by a single outstanding workshop provided us with new insights into its ways of manufacturing altars, its style and technologies it used.

PA-8

Homogeneity study of modern bronzes for artistic castings using PIXE and PLP

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Metal casting is the most efficient way of shaping metals both for industrial purposes, as well as in art modeling. However, when casting an art model in metal, focus is on shape and form, and quality of a cast is often neglected. Therefore, artistic casts may vary in composition and structure, and often exhibit poor homogeneity. Inhomogeneity in composition decreases mechanical properties of a cast alloy, and also has a negative affect on corrosion resistance of alloy due to formation of anodic and cathodic places. These can lead to very dangerous local (galvanic) corrosion.

Modern bronzes, cast in typical art foundries today, often show a high degree of inhomogeneity and various compositions due to many different casting methods in use and because of often very unrefined temperature control systems in processes of melting and solidification.

In this work, we have studied several specimens of cast statuary bronzes and compared the results with the results obtained from the industrial standard bronze cast. In order to examine distribution of Sn as a major alloying element and Zn, Pb and Fe as trace elements larger area line scans were performed using PIXE (proton induced X-ray emission). Furthermore, the PIXE elemental maps allowed calculation of the homogeneity factor. The areas which have showed large scale inhomogeneities were subsequently examined by the means of PLP (potentiodynamic linear polarization) measurements, which were able to confirmed higher potential appearance of galvanic corrosion for those regions.

PA-9

Contribution of tin compounds to protective properties of patina layers on statuary bronzes

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Outdoor bronze statues are usually exposed to aggressive environmental conditions thus covered with patina layers containing various constituents. Influence of sulfates is indicated as most important for creating patina layers under urban conditions.

Majority of corrosion products in patina were identified as copper products but several studies have indicated the presence of tin compounds within naturally formed patinas on bronzes in atmospheric environments.

In the present work, contribution of these tin-containing compounds to the protectiveness of a patina layer on statuary bronze (CuSn6) have been investigated.

Artificial patina layers have been formed on bronze samples in 15mM Na_2SO_4 solution by immersion. The Cu/Sn ratio in patina layer was monitored versus immersion time using PIXE (proton induced X-ray emission) and the correlation between immersion time and Cu/Sn ratio was determined.

The protective properties of patina layer have been determined by the method of electrochemical impedance spectroscopy. To avoid the contribution of increasing thickness of patina layer to corrosion resistance due to increased immersion time, the referent set of pure copper samples was immersed in the same solution as CuSn6 samples and measured at same time.

These measurements helped establish correlation between protective properties of patina layer and Cu/Sn ratio in patina layer, and gain better understanding of bronze corrosion in neutral aqueous solutions.

PA-10

Physicochemical investigation of late Bronze Age artifacts using EDXRF Spectrometry

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The region of Vršačko Gorje is exeptional for its large concentracion of hoards with metal artifacts because it was the crossroad for the trade routs and conection between the most important metalurgical centres from late Bronze Age situated between rivers Sava and Danube and Transilvania as a major source of copper. This hoards consist usualy of varios objects and besides the fragments of bronze artifacts, very often the ingots of pure copper can be found. A main goal of this investigatons was to reveal informations regarding used metalurgical processes in weapon manufacturing (knives, daggers and spears) in that period, origin source of raw materials and trading routes for final products.

Physicochemical investigation process was divided in two phases. First, undestructive analysis of all artifacts was performed using EDXRF spectrometry with radioisotope excitation sources ^{109}Cd and ^{241}Am and Si(Li) semiconductor detector. All the artifacts was cleaned from surface corrosion layer on the investigated area. With this results we have a good insight in the composition of the analyzed artifacts. All the artifacts was made from bronze with average copper content of 93% and average tin content of 6% with arsenic, antimony, lead, iron, silver, zinc and nickel as minor or trace elements. On the other side analysis of the ingots showed that they are made of almost pure copper with average content of 97% and with no traces of tin, lead and antimony. All these results confirmed that the manufacturing process involved melting and mixing recycled bronze and pure copper ingots for making suitable material for weapon production.

PA-11

Analysis of the enamel of Benvenuto Cellini's "Saliera" using XRF, confocal XRF and SEM/EDX

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Before re-exhibiting Benevenuto Cellini's "Saliera" in the permanent exhibitions of the Kunsthistorisches Museum (KHM) it has to be restored. For this purpose the compositions of its gold alloy and especially of the differently coloured enamels present were studied by non-destructive X-ray Fluorescence Analysis (XRF). Using XRF for the investigation of the enamel is a delicate matter, as the analysis in air leads to absorption of the x-ray radiation of the light fractions in the matrix - mostly sodium, one of the main components. To solve this problem a portable prototype XRF-instrument equipped with a compact vacuum chamber [1-3] to reduce absorption in the excitation and fluorescence radiation path could be used due to a co-operation with the International Atomic Energy Agency (IAEA), Seibersdorf Laboratories, and the Atomic Institute of the Austrian Universities (ATI).

For reasons of comparison some minute enamel chips – already detached from the "Saliera" – were analysed by Scanning Electron Microscopy with Energy Dispersive X-Ray Detection (SEM/EDX). Additionally, the elemental distribution of one of these minute enamel chips was verified by confocal XRF performed at the Seibersdorf Laboratories of the IAEA. A clear insight into the inhomogeneous character of the enamel chips could be gained. Hence, some differences in the quantitative results of XRF versus SEM/EDX investigations can be explained.

Although it was possible to perform semi-quantitative analysis on the enamels of the "Saliera" using XRF, it became evident during the measurements that some improvements concerning the shape of the measuring head, and therefore the vacuum chamber, as well as some technical improvements could lead to better results and easier accessibility of the different parts of the "Saliera" and comparable objects. Therefore, a new research project funded by the FWF (Austrian Science Fond) building an enhanced version of the vacuum chamber equipped instrument has just started.

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PA-12

Chemical and structural features of the Neolithic pottery from Alba Iulia-Lumea Noua (Romania) archaeological settlement

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The paper focuses on the investigation of the Neolithic pottery discovered at "Alba Iulia-Lumea Noua" archaeological settlement, in the middle basin of the Mures River (Romania) in order to achieve information about the possible provenance and manufacturing technique used for their production. Four samples of raw clays originating from different natural deposits situated in the surroundings of the site have also been analyzed. A multianalytical approach was adopted; chemical, mineralogical, microstructural and petrographic features of the ceramic bodies were determined by X-ray fluorescence, X-ray diffraction and optical microscopy, respectively. Chemical composition of the slips and painting materials was identified by SEM-EDS analysis.

The petrographic examination of the thin-sections allowed the individuation of two different types of ceramic bodies, the primary distinction being related with the presence or absence of different types of bioclasts. In spite of this, most of the artefacts can be retained of local provenance.

The mineral phases of the ceramic bodies seem to indicate two ranges of firing temperature; samples with high contents of illite were fired between 600-800°C, while the samples with low quantity of illite at higher temperature.

SEM-EDS and mineralogical analysis of the coatings and decorations showed that the slips were obtained with specific raw materials, consisting very probably of carbonatic clays with high content of illite. At the "leather hardness" state the surface was polished and painted using iron-rich materials.

The comparison between the chemical composition of the potsherds and of the raw clays does not show any overlap when major and minor elements are considered, probably because of the textural and compositional variability of the raw materials.

PA-13

PIXE characterization of particle modified consolidant applied to quarried limestones

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The aim of this work is to evaluate the consolidation performance on different types of Croatian limestones that were used for monuments in the past. The fresh quarry samples have been consolidated with Particle Modified Consolidants (PMC) consisted of a silicate matrix (Conservare OH-100) and colloidal alumina particles (Al_2O_3). This composite has been chosen on the basis of a bibliographic research aimed to better protection from salt crystallization damage [1]. The application by capillary rise has been taken under laboratory conditions [2]. Different stone types show different behaviours towards consolidation. Knowledge of consolidant distribution within the porous stones is important in definition of more appropriate consolidant for each particular case.

The evaluation of consolidation effect in the samples has been carried out by the study of the depth profiles and elemental distribution of silicon and aluminium. Analysis was performed by external beam millibeam as well as with in vacuum microbeam PIXE spectroscopy. Additionally, the modification of the stone structure induced by consolidation treatment has been examined by optical and electronic microscopy. The differences between fresh and strengthen stone samples are discussed. The results obtained in this investigation are significant because of their contribution to better understanding of consolidation process in the stone.

This work may have important implication for specific conservation works: the palace of Dioklecianus in Split, the cathedrals in Trogir and Šibenik, and the Arena (Roman amphitheatre) in Pula.

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PA-14

Ban Chiang pottery from archaeological site of Thailand: study of firing technique in ancient periods

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The pottery shards excavated from the Ban Chiang archaeological site-UNESCO world heritage, Thailand, are best known for their beautiful designs painted in red by ancient villagers made. The pottery assemblages are spanned from pre-Metal, Bronze to Iron Age. With the aim of exploring the firing techniques used for pottery production in ancient periods, X-ray absorption spectroscopy (XANES and EXAFS) were used to measure Fe^{2+} and Fe^{3+} distribution in pottery and local coordination environment of Fe atoms. Measurements were carried out at BL8 of the National Synchrotron Research Center (NSRC), Thailand. Furthermore, a range of analytical techniques, including XRD, XRF, IR, DTA and TGA were also used for examination to get more information. Fe K-edge absorption spectra of the mixture's standard iron compound and the red-clay ceramics fired under control conditions allow us to determine the ferric/ferrous ratio and firing temperature of pottery shards. The results revealed that the Pre-metal Age pottery was likely produced under reducing atmosphere at temperature 1200 ^{o}C, while the Bronze and Iron Ages were produced under partial reducing condition at temperature between 700 and 900 ^{o}C.

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PA-15

Micro-X-ray fluorescence and 3D confocal Micro-X-ray fluorescence analysis of chinese ancient cultural heritages

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Polycapillary X-ray optics can focus the X-ray beam produced from X-ray sources into micro levels by external total reflected method [1].In this paper, the setups of micro-X-ray fluorescence (MXRF) and 3D confocal micro-XRF and their applications of analysis for the Chinese ancient cultural heritages in our Lab were reported. The micro-XRF system was consisted of a rotating anode X-ray generator, glass polycapillary X-ray optics, Si-PIN detector, XYZθ sample stage, CCD camera and associated electronics and a piece of ancient porcelain made in Ming Dynasty decorated with blue-and-white glaze (AD 1368–1344),Jun porcelain and Ru porcelain made in Song Dynasty(AD 960–1276) were analysis by this instrument. 3D confocal micro-XRF system was comprised of a low-power MCBM 50 X-ray tube combined with focused polycapillary optics (FWHM = 39 μm, at 17.4 keV) manufactured by our Lab. A Peltier cooled Si-PIN diode detector equipped with a polycapillary half optics (FWHM = 30.9μm, at 17.4KeV) in front of Be windows of Si detector. The two lenses are situated perpendicular to each other in one plane, in such a way that the intersections of the two focus spots form a confocal volume. Only fluorescent signals generated in this volume will reach the detector. The depth analysis and elemental mappings in a certain depth of Chinese ancient bronze plate made in Warring States (B.C.770-476) and “Heqigu”bronze mirror smelted in Eastern Han (A.D.25-220) were analysis by this system. The characteristics and results of analysis of Chinese ancient cultural heritages by micro-XRF and 3D confocal micro-XRF were reported in this paper, also.

(Endnotes)

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PA-16

XRF analysis of two terracota polychromated sculptures by Pietro Torrigiano

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The name of the sculptor Pietro Torrigiano was very well known already in the 16th century, when he made most of his important works. Artists as Giorgio Vasari or Benvenuto Cellini wrote about him in their books. He got his artistic education in the heart of the Renaissance Italy, in the Academia of Florence, where he studied under the custody of Bertoldo di Giovanni, together with Michelangelo. His restless spirit made him travel around Europe, working for noble families, courts and the catholic church. In 1522 he came to Seville where he carried out his latest, but majestic artworks. Two of them, made around 1525 by order of Spanish Hieronymus for their monastery, are exposed today in the Museum of Fine Arts of Seville: *San Jerónimo* (Saint Hieronymus) and *Virgen de Belén* (Virgin of Nativity).

Both sculptures were analysed by the non-destructive technique of X-ray fluorescence. The equipment used has an X-ray tube of 30 kV with anode of W and one SDD detector with energy resolution of 140 eV. By this technique, used directly *in situ* in the exposition room, the support and the pigments were analysed.

The results of the first artwork, *San Jerónimo*, show a great part of modern materials applied, such as titan-zinc white (denoted by the elements Ti and Zn) or lithopone (Ba, Zn). The sculpture was restored almost entirely. Its base and the upper part of the cross are new. The original polychromation, that can still be detected in some areas, show the use of lead white (Pb), yellow and red ochre (Ca, Fe), cinnabar (Hg) and umbra (Mn, Fe). The raw material is terracotta (Mg, Al, Si, K, Ca, Mn, Fe), used as well in the *Virgen de Belén* sculpture. The spectra of the figure of the Virgin and child are different as those of the bench under them, which reveals that it is not original and it was added later. Also in this sculpture modern pigments were found (titan-zinc white, lithopone, cadmium red) that reveal restoration interventions. The pigments applied are white lead, red ochre, cinnabar, blue azurite, some copper based green pigment, umbra and an organic black pigment. Also the presence of tin-lead yellow was detected. Some parts of the blue Virgin's coat are gilded.

PA-17

Possibility of punctual XRF analysis for archaelogical pottery classification

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The determination of elemental composition of archaeological pottery, with particular attention to trace elements, allows the classification of the samples on the basis of row clay provenance, applying multivariate analysis to the resulting data. XRF analysis is an appropriate tool if it is possible to grind ceramics and analyze a sample which is representative of the object. If we deal with particularly well preserved objects, we are often not allowed to sampling them. Moreover, also moving these objects from museum should be unfeasible.

The aim of this work is to evaluate if a punctual XRF analysis on integral objects is adequate to classify row material provenance even if ceramics is not an homogeneous material. We start from the consideration that, in order to have a good classification through multivariate analysis, is enough that different measurements on the same object give raise to the same grouping [1]. So we considered for each sample several measurement points in polished areas and verified in which cases it is possible to obtain equivalent quantitative results.

The test was conduct on a large set of samples of "depurate" Etruscan pottery and sun-dried (but not fired) pottery from Indonesia. The results were compared with those obtained with different analytical techniques. The limits and necessary working conditions are discussed.

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PA-18

Wires and granulation in gold jewellery pastiches

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The morphology and the elemental composition of granulation and wires used in the decoration of ancient gold jewellery items provide information on the goldsmith's manufacture techniques. The aim of this work is to evaluate how far ancient goldwork can be authentified by coupling exam of these decoration elements with analysis of their gold alloys, measured by different analytical techniques.

Granulation welded to gold sheets was produced by jewellers of EC programme AUTHENTICO [1] with several techniques and gold alloys. The morphology of both the granules and the joining regions was examined at low (binocular) and high (SEM) magnification. Gold jewellery items either attributed to the Etruscans or produced in the 19th century in the Etruscan tradition were examined at low and high magnification and compared to features. These objects were also analysed by PIXE with a 3 MeV proton and by SEM-EDX with an Oxford Link ISIS system. We could show that exam is in some cases sufficient to authenticate the objects while in the other cases the determination of the composition of the alloys was required. Results by PIXE and SEM-EDX were compared.

[1] STRP CT-044480: Authentication methodologies for metal artefacts based on material composition and manufacturing techniques.

PA-19

The use of EDXRF in gold alloys analysis: Instrumental set-up and evaluation

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In this work, we use a conventional low-cost EDXRF instrumentation to evaluate the performances of this instrumentation for the analysis of different gold alloys. The potential of X-ray instrumentation for the analysis of precious metals and gold assaying routine had been recently pointed out [1]-[2].

Some different certified standards of gold alloys were analyzed at different instrumental conditions in order to determine the accuracy and precision. In the work we use up to four different primary filters and four different focal spots, modifying the surface of analysis. The combined use of a motorized X-Y-Z stage and reduced irradiation area allows us to also determine the homogeneity of gold alloys.

The results exhibit the usefulness of EDXRF for the analysis of gold alloys al the levels of accuracy required by the official regulations in gold assaying, giving additional information about the nature and content of gold-accompanying metals

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PA-20

TXRF and underwater archaeology: revealing the liquid into the bottle

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Each The knowledge of archaeological objects in terms of chemical composition and or physical properties is mandatory for better understanding technologies used in the past and preservation and conservation procedures to be used in the future. These studies permits to answer questions concerned with the history of civilization by using and developing scientific methods namely physic chemistry, biology, etc. The tools that archaeometry field needs to achieve successfully results are in the mostly analytical techniques.

In this paper, the applicability of TXRF as a powerful analytical tool to discover the composition of a liquid inside a bottle found in the HMS Swift, a British warship which sank off Patagonia in 1770 is demonstrated. This bottle was found in the stern of the ship, inside a wooden box and together with assorted elements which are preliminarily interpreted as personal belongings of one or more officers. It still had a cork stopper in place and it was filled with a grey dispersion. In order to characterize the dispersion found in the bottle, a microsample was submitted for TXRF determination. The collected spectrum clearly showed the presence of Cl and Hg signals which were quantified using Compton peak as internal standard. After quantification, results perfectly match with Hg_2Cl_2 compound which was usually used as bactericide at those times.

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PA-21

SEM-EDX analysis of black-appearing Roman glass

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Artifacts of deeply colored, black-appearing glass were rather popular during the Roman era, in the form of jewels or tableware. The aim of this work is that of determining whether compositional changes, i.e. modifications in technology and raw materials, did occur in the period considered (2nd century BC-4th century AD), by analyzing a large number of samples originating from various locations in Europe and in the Levant.

176 samples of deeply colored glass were embedded into acrylic resin, which was mechanically ground and polished in order to obtain flat surfaces of unaltered glass. The samples were then analyzed with SEM-EDX; quantitative analysis was performed by using a standard-less ZAF-model. Further analyses are in progress, included the trace element analysis via LA-ICP-MS.

The composition of the glass has proven to be that of typical Syro-Levantine Roman glass, produced by mean of sand and natron in primary workshops in the Levant. The characteristic black-appearing coloration is the result of the presence of elevated levels of iron (intense green) or manganese (intense purple). Two ways of obtaining the dark green hue are identified: this was achieved either by using quartz-bearing sand that also contained various minerals (and hence containing a certain percentage of iron), or by adding iron ore to the colorless glass. While the first method is encountered with samples dated before 150 AD, the second procedure was used from that period onwards in European objects, possibly a manifestation of increased glass-working knowledge in the secondary workshops.

Non-destructive, depth resolved Investigation of corrosion layers of historical glass objects by 3D micro X-Ray fuorescence analysis

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The investigation of diffusion processes can give insights into the aging mechanisms of glass artefacts. In order to obtain concentration profiles of mobile elements, like potassium and calcium, the method of choice should be non-destructive. Our first results demonstrate the usefulness of the 3D micro X-ray fluorescence spectroscopy (3D Micro-XRF) measurements for this kind of investigations [1].

"Reverse painting on glass" comprises a special technique of preparation: glass plates were directly painted with oil- or resin-containing colors. Due to the fact that acidic materials cause glass corrosion it is assumed that certain binding media may initiate corrosion processes beginning at the interface glass/binding material. This leads to "loss of adhesion" inside of reverse-glass paintings, eventually destroying completely the decoration of the glass objects.

Measurements were carried out on a reverse-glass painting from the 19th century. The painting shows strong corrosion at several sites. In order to characterize the dissemination of the corrosion process we studied the composition of the glass material depending on the distance to the interface glass/binding material within the glass. Measurements have been carried out at the mySpot beamline of the Berlin synchrotron BESSY.

We could demonstrate that a corrosion layer has formed between paint and glass matrix. Lead and mercury ions migrate into the glass matrix originating from the paint layer (lead white and cinnabar dispersed in oil) whereas lighter elements such as manganese decrease in the corrosion zone.

[1] B. Kanngießer, I. Mantouvalou, W. Malzer, T. Wolff, O. Hahn, J. Anal. At. Spectrom., DOI 10.1039/B717286A (2008) - in press

PA-23

Nondestructive on site analyses of Islamic glass in Egypt by using a portable X-ray Fluorescence spectrometer

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When analyzing a large number of archaeological objects in a country like Egypt, where it is strictly prohibited to take any artifacts to overseas, on site analyses by using a portable XRF are quite effective. We have developed and brought portable XRF spectrometers, OURSTEX 100FA series to the Mission's research facilities in Egypt. Adopting Moxtek AP3.3 polymer window for the SDD detector allowed us to quantify the light elements like Na and Mg from 2006. This study focuses in particular on Islamic glass excavated in the Raya (8-12th centuries, Director; M. Kawatoko), one of the important port cities of Red Sea for the East-West maritime trade. Results of more than 800 samples obtained from a three-year research are summarized.

In the Early Islamic period (eighth to ninth century), the glass based on the natron as a soda source was mainly produced. Among this type of glass, Egyptian natron glass objects with high content of Ti, Fe and Zr were characterized in more detail based on the lime content. Meanwhile, the glass vessels with low content of Ti, Fe and Zr, and high Ca/Sr ratio seem to be imported from the Syro=Palestine region. From the ninth century, gradual transition from the natron glass to the plant-ash glass was observed based on their Mg and K levels. The newly developed XRF for the light elements made it possible to distinguish them clearly. Furthermore, it was found that the glass vessels with high MgO/CaO ratio (> 0.45, proportion by wt%) consisted mainly of colorless cut glass. Our compositional and archaeological insights suggest the possibility that these colorless vessels were produced in the Mesopotamian region. By adopting a portable XRF for on site analyses of archaeological samples, multielemental information from a large number of excavated objects were obtained.

PA-24

A quantification approach for portable μ-XRF spectrometers

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In μ-XRF analysis a polycappilary X-ray lens is usually utilized in the excitation channel to collect very efficiently, propagate and focus down to few tens of micrometers the exciting X-ray beam radiation. On the other hand, the X-ray lens introduces major difficulties in quantification, since its transmission efficiency being highly dependent on the transmitted X-ray energy results to a significant and not easily predicted modification of the energy distribution of the primary tube spectrum. Direct and indirect methods have been proposed towards an analytical description of the lens transmission efficiency [1-2].

In the present paper we propose a different analytical approach that provides an analytical description of the lens transmission efficiency. A theoretical FPA model was developed based on Ebel's description for the tube emission spectrum [3] and on a transmission efficiency expressed as polynomial of 5th degree versus energy. Measured and theoretically predicted characteristic K- or L- line intensities emitted by a large set of pure single element or compound targets (1.5 – 25 keV), with infinite or very small thickness were compared through X^2 minimization procedure with fitted parameters the coefficients of the transmission efficiency function. For the measurements a μ-XRF set-up consisting of a Rh microfocus X-ray tube operated at 50kV, a polycapillary X-ray lens and a Si-drift X-ray detector was used. The agreement between theoretical and experimental elemental intensities at the convergence minimum was equal or better than 10%. The developed FPA model was next validated in reproducing concentrations of ten NIST and BAM SRM glasses with deviations less than 10%-15%.

The proposed analytical approach has the advantage that does not require any removal of the X-ray lens from the μ-XRF setup configuration and it can be adapted in commercial μ-XRF spectrometers supporting a FPA methodology towards quantification in μ-XRF analysis.

[1] T. Sun and X. Ding, X-Ray Spectrom., 35 (2006) 120-124

[2] R. Padilla, P.Van Espen, A. Abrahantes, K. Janssens, X-Ray Spectrom. 34 (2005) 19-27

[3] H. Ebel, X-Ray Spectrom. 28, (1999) 255-266.

PA-25

Extended calibration procedure for the determination of micro-XRF excitation spectra

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Quantitative XRF based on fundamental parameters requires an accurate knowledge of the excitation spectrum. In case of a conventional setup this spectrum is given by the x-ray-tube-spectrum and can be calculated. [1]. The use of polycapillary optics in micro XRF spectrometers changes the spectral distribution of the excitation radiation. For that reason it is necessary to get access to the transmission function of the used optic.

Several authors have described experimental methods to determine the transmission of polycapillary optics for example with pinhole- or knife-edge-scans or with scatter measurements (e.g. [2]). In all these procedures it is necessary to remove the optic from the source to measure a pure tube spectrum as reference for the determination of the transmission function.

Due to the fact, that many commercial spectrometers are not designed for removing the optic from the x-ray-tube, those methods are often not possible. Furthermore the transmission depends on the current adjustment of the lens. It may also change for different tube-operation-voltages. For that reasons a pure transmission curve, measured under specific conditions, is not the correct function to determine the actual excitation spectrum.

To overcome these problems a new calibration procedure has been developed, which allows the user to determine the lens-transmission, without changing the experimental setup. The result of that calibration is the product of the geometrical factor and the transmission values for different energies. Fitting those results with a suitable function, delivers a relative transmission curve, that can be used to solve the Sherman equations.

The results are compared with experimental determined transmission functions of the used optic. The quality of the determined excitation spectrum is verified on the one hand, by a conventional calibration with different standards and on the other hand by comparing calculated concentration of measured standards with certified values.

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PA-26

Intelligent computational infrastructure for XRF-based investigations

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The aim of the research is to develop a number of computational technologies and corresponding software to support interdisciplinary natural science investigations. The following problems are under consideration:

- Consolidation of instrumental and analytical software in a distributed software environment, supporting automatic data transformation.
- High performance computational resources usage, such as GRIDs.
- Developing intelligent subsystems in the software allowing automation of some aspects of creative activity of analysts, such as experiment and analysis planning, XRF appliance control, data analysis on their quantitative characteristics, e.g., on the base of expert systems.
- Resultant data description, namely, automatic creation of self-describing electronically reusable hypertext tagged parts of scientific reports, self-adopting user interfaces of the software.

The above mentioned problems connected with increasing the precision of element concentration determination in samples, automatic analytic techniques synthesis, and analytic process control and planning, reducing human intervention during exploration, automatic resultant data processing and visualization, and consolidation various stages of an interdisciplinary science investigation in one virtual distributed investigation process.

Some pioneering applications and technologies have been developed, such as follows. Intelligent application, based on expert system technologies, for an appliance control and experiment planning, including automatic certified reference materials choose, system of calibration equation construction based on possible logical analysis of reciprocal line overlaps. A special microformat is been developing for data description, which allows to describe resultant data in scientific reports presented in well-known Internet hypertext format (HTML); microformat technology is a kind of Semantic Web technologies, a nowadays Internet development direction. An approach to construct user interface for modularized analytical software has been proposed, an example of the interface has been developed; the interface allows user to view the research plan in various detail degree and generate corresponding repots.

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PA-27

Thin film samples as reference samples for micro XRF

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An ideal reference sample for the calibration of the sensitivity of micro-XRF set-ups has negligible absorption of exciting and fluorescent radiation, high degree of uniformity and homogeneity and emits a multitude of non overlapping x-ray fluorescence lines over a broad spectral range with suitable intensity. Free standing thin films (FSTF) can meet these requirements; unfortunately after the discontinuation of NIST SRM 1832/1833 suitable reference materials are no longer commercially available. Therefore a project was started to develop FTSF into functional reference materials and first test samples have been produced by stacking thin metal films using PVD at AXO Dresden. As support we used “Ultralene” foil and recently Si_3N_4 membranes. The deposition technique assures very homogeneous layers and a large degree of flexibility regarding the choice of elements and mass densities.

The samples were characterized by ICP-OES at the University of Hamburg and by micro-XRF at Hasylab and ANKA. The ICP-OES measurements on eight sample foils show a very good reproducibility of the elemental depositions. The statistical evaluation of micro-XRF mapping data, obtained with beam sizes of 1.5µm to 100µm and beam energies up to 26 keV, limited mass deposition heterogeneities to below 1% RMS for most elements even at 1.5µm resolution. Very recently Si_3N_4 membranes have been tested as supports, since they can withstand very high radiation intensities. First XRF measurements indicate that these samples are equivalent in terms of homogeneity with the polymer foil based samples.

First applications of these FTSF aimed at assessment of absolute lower detection limit and characterization of depth resolution and sensitivity of confocal set-ups.

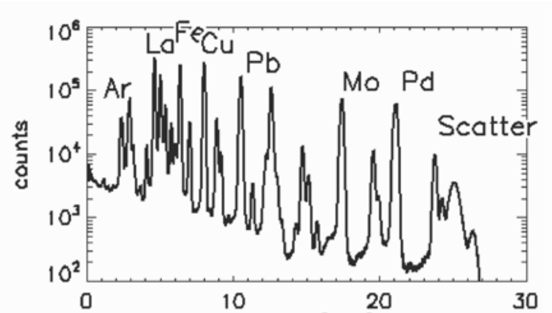

Fig. Micro-XRF measurements of sample sf1 (beam size 5 µm, 26 keV excitation energy, sum spectrum).

PA-28

X-ray fluorescence enhancement induced by photo-electrons secondary excitation

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Well established values for the X-ray fundamental parameters are very important but not enough for an accurate reference-free x-ray fluorescence quantification analysis. Secondary ionization processes following photon induced primary ionizations in matter may contribute significantly to the detected fluorescence radiation introducing significant errors in XRF quantitative analysis, if not taken into account properly.

In the present work, the relative enhancement to the primary fluorescence intensity from ionizations induced by secondary photo-electrons is studied both experimentally and theoretically. Several targets of Mg, Al and Si with few micrometers thickness and a wide range of exciting monoenergetic X-ray beams (2-30keV) were utilized in the study. Measurements have been performed in the PTB Laboratory and at the BAMline wave-length shifter at the synchrotron storage ring BESSY II with a fully characterized experimental setup of the PTB, consisting of a calibrated Si(Li) detector, calibrated photodiodes and a well known geometry with calibrated diaphragms. Experimental values of the relative enhancement to the fluorescence intensity due to photoelectrons were determined with low uncertainty. Additionally, intensive Monte Carlo theoretical calculations for all the experimental cases have been accomplished. The simulation codes have been developed implementing both Geant4 [1] and Penelope2006 [2] toolkits. The crucial performance of the databases for electrons ionization cross sections have been tested and evaluated for both codes using CASINO simulation tool for electron trajectory [3]. The powerful computer cluster “zeus” at the Institute of Nuclear Physics (over 60 Xeon® processors) hosted the long time simulation runs (up to 20 billions events per exciting energy). Experimental measurements and simulations are compared and discussed.

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PA-29

New XRF software packages for the application of the fundamental algorithm in practice

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Newly developed XRF software allows chemical composition calculations using the Fundamental Algorithm in X-Ray Fluorescence (XRF) analysis. It was designed by an XRF analyst, for XRF analysts, having in mind their day-to-day routine XRF analysis. Three different software packages are available: CiROU, CiLT and CiREG, each one using the same user-friendly Windows-based interface. The CiROU and CiLT packages allow the XRF analyst in particular to select analytes, calculate the X-ray tube spectra and theoretical influence coefficients, calibrate, read files of measured intensities, calculate net intensities and sample compositions, and print a report. The CiREG package does all the same thing, except by using empirical influence coefficients.

CiROU is applicable to samples of any composition with the utmost accuracy that can be obtained from a Fundamental-Parameters method. Its unique calibration procedure further adds to the accuracy by eliminating the bias between theory and experimental data. In addition to its unsurpassed accuracy, CiROU is faster than any other sophisticated program for XRF analysis.

CiLT uses the Lachance-Traill algorithm with theoretical constant influence coefficients. Consequently it is limited to a smaller range of compositions (0 – 10%). It is the optimal program to use with fused discs. In this case, CiLT takes into account the ratio sample/flux and the composition of the flux. Another fine feature of CiLT is its capability to manage with accuracy the loss of volatile components during the preparation of fused discs. No matter that the fused disc is prepared with the burned sample, or the original one, no matter if the LOI is known or not, CiLT can calculate in all the cases the sample composition with accuracy.

CiREG uses the Lachance-Traill algorithm with empirical constant influence coefficients, which are calculated by regression analysis. This program has been written for application to non-homogeneous materials that cannot be analyzed from fundamental principles. Surface, particle size and mineralogical effects are compensated for by comparing the unknowns to a large number of standards similar to them and prepared in the same way.

PA-30

Measurements and Monte Carlo calculations of X-ray fluorescence Kα/Kβ ratios for layered specimens

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The quantitative X-ray fluorescence analysis of an untreated specimen can be inaccurate due to possible depth inhomogeneous distribution of elements. As has been already shown in [1], so called depth heterogeneity can be recognized by means of Kα/Kβ ratios of all elements identified in a specimen. The principle of the proposed technique lies in the different attenuation coefficients of the Kα and Kβ lines. If an element is present at some depth in the specimen, its characteristic radiation has to penetrate a thick layer of the matrix, and the characteristic X-ray intensities can be significantly changed.

This contribution shows how the Kα/Kβ ratios depend on depth distribution of elements. The experiments were performed for specimens made of various thick substrates covered with one or two intermediate thick mono-elemental layers (Ti, Fe, Ni, and Cu). The Kα/Kβ ratios of elements present in a substrate and in layers were measured and then compared with the ratios obtained with the Monte Carlo computer code MCNPX [2]. Good correspondence between the experimental and the calculated values was achieved. The results demonstrate also the influence of inter-layer enhancement effect due to secondary emission of characteristic X-rays.

It has been demonstrated that Monte Carlo simulations with the code MCNPX make it possible to predict the Kα/Kβ ratios for arbitrary chosen distribution of elements in a specimen. The code can be applied to estimate the depth distribution of elements in a layered sample and for measurements of coating thicknesses, etc.

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PA-31

An algorithm to for calculation of atomic density factors used in facilitating calculation of x-ray production cross sections from raw data

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A method is developed for calculating density factors for various crystal structures which can be easily incorporated into computer software designed to calculate x-ray production cross sections from raw data, such as x-ray counts extracted from spectral data. The advantage of this algorithm is that it will aid in the calculation of x-ray production cross sections from data acquired experimentally, by allowing the atom density of crystalline substances to be determined from readily obtained parameters. This method is then used to calculate various density factors for FCC, BCC, diamond cubic, HCP, and ionic structures. These density factors can then be used to find x-ray production cross sections.

PA-32

Simulation of environmental aerosol loaded filters for ED-XRF analysis by partial least squares

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Environmental pollution is a problem of global concern. Its quantitative analysis requires the use of certified reference materials (CRM) for quality control. This has remained a difficult analytical problem due to unavailability of such CRMs in required amounts and lifetime. Analysis of this pollution poses even a greater challenge due to its multivariate nature. Laboratory reference material (LRM) was simulated for this purpose. This work details methodology of making such LRMs, spectral acquisition and resolution, quantification, accuracy, precision and range. The robustness of partial least squares (PLS) as an alternative quantitative procedure was constructed for energy dispersive X-ray fluorescence (EDXRF) analysis. EDXRF spectra were acquired directly and used to build a training set based on the total fluorescence spectrum after normalization using principle component regression (PCR). Both standard solutions and analytical-grade salts were used to make a homogenous mixture that was deposited onto 0.45μm membrane filters, dried in ambient air at standard room conditions of temperature and pressure, and then analyzed by radioisotope-excited EDXRF spectrometry. Two analytical methods were used and compared. Unlike Fundamental Parameter Method (FPM), the heavy metal (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Hg and Pb) loadings acquired via PLS demonstrates the comparative advantage and potential for fast, non-invasive, and accurate EDXRF analysis of trace metals in environmental aerosols. Homogeneity between filter loadings was evaluated using relative standard deviation at an average of 5%. The PLS procedure including validation and prediction was done using Statgraphics Centurion XV and Unscrambler® 8.0 software.

PA-33

Standardless material identification

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A new technique has been developed to identify unknown samples or materials utilizing only pre-calculated spectra. This provides a more universal and flexible approach than the traditional methods based on measured spectra of reference samples.

For practical analysis there are several advantages with the new method. No inventory of a large base of standard reference materials is needed. The meaning of “material” can be extended to a “class of material” which covers predefined concentration ranges. Coated alloys and multi layered samples can be included which are defined by related thickness ranges. For practical application, the class of material has to be defined only by element concentration and/or thickness ranges – there are no other requirements. After having performed a theoretical calculation of the spectra according to their “class of material” definition any measured spectrum of an unknown sample can be specified as “IN” or “OUT” with respect to the defined “class of material”. The respective data files which include all the necessary information to identify an unknown material can be exported to another instrument without any further setup and calibration.

This identification tool can be used for any application and is especially helpful when otherwise no standards are available. We will present practical examples for RoHS and precious metal analyses. The method will also assist the user to identify the correct measurement application which can then be used to make a full quantitative analysis.

PA-34

Micro distribution of biologically important metals in primary invasive ductal carcinoma of breast

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A micro beam synchrotron x-ray fluorescence (μSRXRF) technique was used to determine the localisation of metals in primary invasive ductal carcinoma of breast. The work was carried out at two facilities, namely the Hamburger Synchrotronstrahlungslabor at Deutsches Elektronen-Synchrotron, DESY, Germany and ANKA, Forschungszentrum, Karlsruhe, Germany. A number of samples were examined which were formalin fixed tissues arranged as micro arrays of 1.0mm diameter and 10μm thickness. Maps of the elements Ca, Fe, Cu and Zn, which are of physiological importance, are presented. The distribution of these metals was obtained at approximately 18μm spatial resolution at DESY and approximately 3μm at ANKA. The distributions are compared with light transmission images of adjacent sections that are H and E stained to reveal the location of the cancer cell clusters. Correlations were found between these reference images and the elemental distributions indicating an increase in all element concentrations in the tumour regions of all samples, with the exception of Fe, which in some cases showed a reverse of this trend. On average over all samples the percentage difference from the normal tissue elemental concentrations are Ca ≈ 67%, Cu ≈ 64% and Zn ≈ 145%. Micro X-ray absorption near edge structure (μXANES) spectroscopy was used to estimate the oxidation state of Cu in normal and tumour regions. Tumour regions were found to have a higher fraction of Cu^+ compared to the normal samples.

PA-35

Biological study using X-Ray microfluorescence images

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The bone structures consist essentially of a protein and hydroxyapatite. Trace elements are found in both mineral and organic phases, although their role in normal bone function and in bone pathology is not fully established. In this context, the knowledge of major and trace elements is very significant to elucidate some important questions that remain unanswered or are controversial about bone alterations such as aging process.

Several kinds of imaging techniques can be useful to access morphology and the minerals present in osteoporotic bones. In this work, Synchrotron Radiation by X-Ray Microfluorescence was used as an X-Ray imaging technique to investigate bone structures. Therefore, this research aims to improve the knowledge about some aspects of bone quality and its relationship with bone strength.

The measurements were performed at the Brazilian Synchrotron Light National Laboratory on the XRF beam line. This line is equipped with an HPGe detector with a resolution of 150 eV at 5.9 keV, a white beam, and the sample holder is placed at 45° in relation to the detector and the incident beam. The beam is focused by a fine conical capillary which provides X-Ray microbeam of 20 μm diameter. To perform the experiment, the samples were placed in a mylar adhesive tape, positioned in the experimental set up. The spectra were acquired in 10 s and 200 s to perform 2D images and single profiles respectively. No sample preparation was required and the experiment was performed in vertebrae and femur bone sites (in several positions) with 150 μm of thickness approximately. It was also measured NIST Standard Reference Material (bone ash and bone meal – SRM 1400 and SRM 1486) in order to evaluate our experimental method. The sample holder has complete translational capacity and all the stages are fully remote controlled. The XRF images were acquired over a range area equal to 0.87 mm^2 approximately which corresponds to a matrix equal to 30x30 $points^2$ respectively.

The results showed that the elemental distributions in bone zones in microns order were very helpful to understand those functions in such structures. Although Ca and P are the main component of bone as hidroxyapatite, other elements, such as S, K, Cu, Zn and strontium were also found in all the investigated bone sites. X-Ray microfluorescence images and profiles by synchrotron radiation can be an efficient and a non destructive technique to evaluate the distribution of minerals in bone samples and useful to provide information about the differences found between vertebrae and femurs sites. Using this methodology we show that the bone quality can and must be evaluating not only by the architecture of the bones but also to take into account the concentration and the distribution of chemical elements which have important contribution on bone strength, such as Sr and Zn, specially to demonstrate alterations in bone morphology in the aging and osteoporosis processes.

PA-36

SR-XRF analysis of trace amounts of Pt in gold alloys

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Pt provides important information on the origin and provenance of ancient gold. Among the few analytical techniques available to non-invasively measure low contents of Pt in gold [1], SR-XRF fulfils all the necessary requirements.

In our first attempt we used excitation energy at the PtL_3-edge (11.564keV) taking into account the resonant Raman scattering [2]. The MDL was estimated to 20ppm. In order to improve the MDL and avoid the difficult quantification process, we made new developments of both the analytical SR-XRF set-up and the quantitative calculation procedure with excitation energy at the PtK-edge [3]. The MDL was estimated to 40-90ppm using the PtKβ1 line, but the unknown thickness of small and thin gold items is a significant source of error for quantitative analysis.

The aim of this work is to present the most recent developments of the determination of Pt with excitation energy at the PtL-edge and a Si SDD detector accepting higher count rate. At the chosen energy of 11.58keV we could reach a MDL of 3.1ppm.

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PA-37

Absolute determination of cross sections for resonant Raman scattering on silicon carbide

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Reference-free total-reflection x-ray fluorescence analysis for the quantification of surface contamination requires the accurate knowledge of all experimental values as well as of the fundamental parameters involved [1]. Besides the fundamental parameters of the contaminants also the parameters of the substrate affect the result. To reduce the impact of tabulated data with unknown or estimated relative uncertainties the resonant Raman scattering of X-rays in the vicinity of the K absorption edge of silicon carbide has been studied. The investigation was carried out at the plane grating monochromator beamline for undulator radiation of the PTB laboratory at BESSY II in Berlin.

For the investigation a silicon carbide wafer was thinned to a thickness of about 10 µm to allow for transmission measurements to determine the absorption correction factor for the fluorescence measurements. Cross sections were determined absolutely for the energy range below the silicon K absorption edge of incident photons with small relative uncertainties employing calibrated instrumentation avoiding any reference samples. The experimentally determined values for this silicon compound are compared to the values determined for pure silicon [2].

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PA-38

A study of low energy Kα X – Ray satellites of Phosphorous and its compounds

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Low energy K_α X – Ray spectra of Phosphorous, Magnesium Phosphate, Potassium Phosphate, Zinc Phosphate and Cobalt Phosphate generated by photon excitation are studied by a wave length dispersive spectrometer (Philips 2404) using PET plane crystal. The energies of the observed low energy X -ray satellites are measured. Comparing these energies with the Semi – Empirical Auger - Electron energies[1], the X – ray satellites have been identified as KLL RAE[2] (Radiative Auger Emission) Peaks. These lines are ascribed KL_3L_3, KL_2L_3, $KL_2L_{2,}$ and $KL_1L_{2\text{-}3}$ transitions. The integrated KLL RAE intensity is measured in phosphorous and its compounds and analyzed for chemical effects. Aberg's theoretical value of integrated KLL Relative intensity of Phosphorus based on SCF (Self Consistent Field) calculations is in better agreement with the experimental value compared to the Scofield's[3] theoretical value based on Hartee – Fock formalism.

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PA-39

A novel multi-purpose PIXE induced XRF chamber

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The development and implementation of a multi-purpose scattering chamber at the Demokritos Tandem 5 MV TN accelerator is presented. The set-up combines effectively particle and photon interactions with matter and aims to fundamental and applied research topics such as: Sub-keV X-ray fluorescence spectrometry, X-ray Resonant Raman scattering [1], study of the PIXE continuum polarization properties [2] and the successful treatment of interference problems that usually appear in conventional XRF and PIXE techniques [3]. The PIXRF scattering chamber utilizing multiple primary target – sample rotatable holders and selectable absorber foils for the modification of the primary exciting radiation allows the accurate and reproducible production of particle-induced, almost monochromatic and background free X-ray beams of discrete set of energies, enabling in a reliable manner complementary PIXE-induced and (externally performed) SR-induced XRF studies of identical samples. With the additional use of an ultra–thin window X-ray detector (600 nm polymer window) having a transmission of about 40% for carbon and oxygen K-lines, low energy particle-induced X-rays can provide unique possibilities for X-ray spectrometric studies in the low or sub-keV energy region.

A suitable integrated C++ software has been developed including appropriate data bases to account for: i) the K-shell, L-subshell and M-subshell heavy ions ionization cross sections (up to 5 MeV/amu) for all the elements of the periodic table ii) K and L – sub-shell fluorescence cross sections, iii) stopping power of heavy ions in matter and iv) mass attenuation coefficients of X-rays in matter. By this way, integrated simulations of the PIXE induced XRF intensities, can be carried out in order the experimental parameters (heavy ion type, kinetic energy, primary target, absorbers etc.) to be optimized.

First experimental results are presented and discussed revealing the potential of the novel experimental apparatus.

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PA-40

On the accuracy of L-shell ionization cross sections II. The choice between experimental or thoretical

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In the PIXE analytical technique the fundamental parameter approach is frequently used. Therefore the physical quantities of excitation, decay and transport parameters need to be included and knowledge of their accuracy is required. However, the scatter of these experimental data is huge [1,2].

Beyond that a strange practice is used, where the data are averaged, outliers are discarded and this average is considered. Basic statistics and simple logic dictate that this method is related to human behavior. The proper method is to find and eliminate the reason of the scatter or if this is not possible incorporate it into the analysis. If we have ten data points with significantly larger scatter than the error bars that are claimed then we cannot average to find the best value. Averaging nine bad data with one good datum will generally result in a poor value. Therefore good measurements are required.

An alternative is to use the theoretical data. However the data generated by present theoretical approaches used in PIXE is not expected to be an accurate representation and with the support of experimental data we will present that it is inherently incapable of yielding the needed cross sections.

Beyond that it is worth to note that even these experimental data are biased by the tendency to get good agreement with “theory”. There is a need for unbiased data, and we will present some elements for consideration.

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PA-41

PIXE protocols for cluster analysis of archeological samples: the funny filter case

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Ion Beam Analysis techniques were developed and utilized for applications in the domain of archeology at the accelerator laboratory of the Lebanese Atomic Energy Commission. In order to have accurate and relatively fast measurements for analysis studies of archeological objects, mainly ceramics, different experimental protocols were tested and established, using “Proton Induced X-ray Emission” technique. The first experimental protocol was done using two runs at 1 MeV and 3 MeV. The second one was more advantageous since it is time consuming by using just one run at 3 MeV with a pinhole filter as x-ray absorber. Hence, a classification study based on the elemental composition and on multivariate statistical techniques could be performed for provenance studies of archeological objects. The performed protocols were applied and checked on standard reference materials such as DRN, BEN from Geo-standard and SRM-679 brick clay from NIST.

PA-42

PIXE identification of fine and coarse particles of aerosol samples from Beirut

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Beirut is a cross road for several meteorological phenomena during the year, thus the transport of pollution over the different seasons and storm episodes was studied, by simultaneous sampling of PM10 and PM2.5. The collection of fine and coarse particles on Teflon filters was carried out once a month, for a period of 24 hours, during a whole year between February 2004 and January 2005, using a dichotomous sampler. The characterization of the elemental content of the two fraction mode, fine and coarse particles, were analyzed using proton induced X-ray emission (PIXE). The use of 75 µm of Kapton filter, as x-ray absorber, with a 3 MeV proton beam delivered by the 1.7 MV Tandem-Pelletron accelerator of the LAEC facility, allowed the simultaneous determination of Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn and Pb. Furthermore, PIXE study and the calculation of the enrichment factor showed the differentiation, of pollution sources, between anthropogenic versus natural emissions. Finally, the results of PIXE analysis of the NIST SRM 2783 will be showed.

PA-43

In-situ observation of chemical state change of sulfur in solid targets during MeV-proton irradiation

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Change of fine structures of the K X-ray spectra for sulfur compound targets during MeV proton irradiation was observed in-situ using a high-resolution X-ray spectrograph. Six standard samples of sulfur with different chemical states (elemental sulfur, MoS_2, Na_2SO_3, $(NH_4)_2SO_4$, Na_2SO_4, and $Na_2S_2O_3$) were prepared for this measurement. The proton beam current and the beam spot diameter were 50-70 nA and 9 mm^2, respectively.

We found that the sulfur Kα line energy for sulfite became higher with the increase of the proton dose. After the irradiation of 90 μC protons, the Kα energy for sulfite was nearly equal to that for sulfate. This result indicates that the most of the S^{4+} on the surface of the target has changed into S^{6+} through the irradiation. For lower doses, we could determine the ratio of S^{6+} from the spectral shape. On the other hand, no significant change was observed in the Kα peak for other compounds. During the measurements, the loss of sulfur atoms was monitored by measuring the Kα X-ray yield by a Si(Li) detector. The relation between beam current and the rate of the chemical state change is also discussed.

PA-44

Approximate solution for the fraction of backscattered electrons using invariant imbedding method.

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Electron Probe Microanalysis (EPMA) is a widely used technique for material characterization. Is based on detection of the characteristic X-ray radiation emited by a sample when a electron beam, with energies ranges from 2 to 50 kev, impinges on it. The beam-sample interaction generate backscattering electrons, secundary electrons, absorbed electrons and a complex X-ray spectrum. During 50 years, EPMA has been applied in order to obtain the chemical composition of samples starting from analysis of microvolumes (1μm3).

Quantitative analysis of solid samples with EPMA requires correction procedures of the experimental data. Therefore, information about the physical processes involves in the scattering, as much of inpinging electrons as X-ray photons, is needed. Although these processes have been studied during many years, most of correction procedures are based on empirical or semi-empirical aproximations.

In this work, an aproximated analytic method used for calculate the fraction of backscattered electrons in EPMA, is reported. The fractions are calculated in function of the initial energy of the electron beam and the atomic number Z of the target.

Starting from Invariant Embedding Method applied to a "states ladder model" (used to represent the energy lost of the electrons in the sample [1,2]), the theoretical expressions for the fraction of backscattered electrons are obtained. A previous reported model was restricted to electron movements in an one-dimensional (1D) space.

The current proposal is an improvement of the mentioned previous model. By mean of a new aproximation method that simplify the calculations, theoretical expressions for a 3D model are obtained[3]. In this work this new method is applied to a 1D model, and comparisons with experimental data and the 3D model are made and exposed.

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PA-45

EPMA determination of modes of gold and silver occurrence in lithochemical stream sediments exemplified by the Ducat gold-silver deposit in northeastern Russia

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The EPMA technique has been elaborated to measure the composition of stream sediments containing silver and gold. This technique made good use for identification of the modes of gold and silver occurrence in loose sediments of litho-chemical stream sediments.

In search of gold-silver deposits application of qualitative and quantitative characteristics of ore elements at some deposits should be supplemented with additional criteria to make prospecting more effective. We order to use the modes of occurrence of mineralization indicator elements – gold and silver – as an additional criterion for searching.

Dependence of silver and gold intensities on beam power densities was chosen as the criterion for selecting optimum conditions of analysis. Stability of sediments was determined. It found that the beam power densities >2.55 $\mu W^{*}\mu m^{-2}$ are unacceptable for silver-containing samples. The quality of available results complies with the "applied geochemistry" category of performance (category 2).

This technique is applicable in prospecting as the criteria for a perspective evaluation of geochemical anomalies ascertained with litho-chemical stream sediments.

The modes of silver and gold were studied in alluvial sediments of litho-chemical stream sediments. The larger part of gold is available as micro-inclusions and micro-impurities in the oxides and hydro-oxides of iron and manganese. It is established that mineral and element compositions of primary ore of Dukat gold-silver deposit are very much similar to those of gold and silver-containing loose sediments and minerals from litho-chemical streams of the same deposit.

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PA-46

Investigation of phase composition of metallurgical silicon by EPMA

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Production of metallurgical silicon with insignificant impurities is important for its application as the base material for solar elements.

The samples of metallurgical silicon obtained by traditional technology contain some impurities, e.g. Fe 0.4, Al 0.3, Ca 0.4 wt. %. The goal of this study was to define the element and phase compositions of inclusions for developing the methods aimed at reducing abundances of impurities in silicon.

The investigation of metallurgical silicon samples by the electron microprobe (Superprobe–8200) defined fine inter-metallic silicon-containing inclusions (silicides) and nonmetallic. The silicides are small-sized (2 -50 μm) and occur on the boundaries between silicon grains. Their composition is very heterogeneous, that is evident on the inclusion images acquired in back-scattered electrons and X-Rays. The data of quantitative analysis point out that silicides are composed of silicon, aluminium and iron. The chemical composition of silicides is defined as adequate to the following phases in metallurgical silicon: Al_5Fe_2, (Fe,Ti)Si(Al), $FeSi_2$(Al) and AlFeSi. The nonmetallic inclusions are round-shaped, their size reaches 300 μm, and they consist of $CaSiO_3$, SiO_2 and SiC. The data obtained agree with the results of x-ray phase analysis and metallographic investigations.

The further purification of refined silicon provided multi-crystalline silicon, received by directed crystallization. The investigation of multi-crystalline silicon shows that it consists of pure silicon crystals with the thin fibers of silicides present between silicon grains. These inclusions are very few; their size is smaller than that in metallurgical silicon.

It has been eventually inferred that a single crystallization is not sufficient for production of truly pure multi- crystalline silicon from refined metallurgical silicon.

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PA-47

X-Ray and electron emission during transporting of slow energy electrons through glass capillary optics

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The transmission of ions through dielectric capillaries has attracted considerable attention during recent years [1-3]. As a result of experimental and theoretical studies performed, it was demonstrated that high transmission coefficient ions through a dielectric channel is explained by electrification of channel walls in the course of ions motion, followed by self-organization of a beam–wall charge system, i.e. a charge is generated, at which there are no more collisions of ions with the wall and no more changes in the charge distribution. We believe, that it is of interest to investigate the mechanism of transporting of electrons through glass capillaries.

In this work we investigate the transmission of electrons with the energy from 1 keV to 10 keV through the glass tube, polycapillaries and tapered glass capillary. The experiment was conducted using a chamber designed for electron and X-Ray spectroscopy measurements. Glass poly-capillaries were fabricated by M.A. Kumakhov, Institute for Roentgen Optics.

The main results of the experiment are:

The transmission coefficient of electrons decreases with the increase of incident electron beam current.

The transmission coefficient of electrons decreases with the increase of the time of measurement.

Electron energy at the exit of glass tube differs by several percent from energy of incident electrons, i.e. the most part of electrons moves without collisions with the wall of the tube.

From the X-ray spectrum at the exit of the glass tube follows that the part of the electrons ionize the atoms of the wall during collision with the walls.

The results of the measurements indicate that the transporting of the electrons through the glass capillary is related with electrical charge-up and discharge on the bulk and on the surface of the capillary due to incident electrons.

This work has been supported by INTAS Grant No. № 06-1000012-8972

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PA-48

X-ray detection system for PIXE measurements based on a SDD coupled to polycapillary optics

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Silicon Drift Detectors (SDDs) offer higher performance than conventional silicon detectors traditionally used in X-ray spectroscopy applications, thanks to their very low output capacitance (of the order of 100 fF) independent of the active area.

In order to fully exploit in PIXE the superior performance of SDDs especially for the detection of low- and medium-energy X-rays, avoiding the negative effects of backscattered particles, we developed a custom spectrometer based on a 10 mm^2 chip with a thermoelectric Peltier cooler and home-designed front-end electronics, coupled to a weakly focusing polycapillary lens. Thanks to the latter, a large collection efficiency for X rays can be achieved, while backscattered particles are prevented from reaching the detector.

This work describes the detector + lens assembly and reports the results of first tests carried out at an external beam line of the LABEC laboratory in Florence. Excellent energy resolution is achieved under real operating conditions in a PIXE run (measured FWHM at 1 keV is 81 eV with a count-rate of 500 cps), and the line shapes are also very good (FW1/10M over FWHM ratio is 2.1). These preliminary tests also helped to point out some aspects worth to be investigated, in order to profit fully from such a good performance of the spectrometer.

PA-49

Sim-IBA - computer software for simulation of PIXE and RBS spectra and elemental mapping

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A new expert system Sim-IBA is developed to provide simulation and semi-quantitative analysis tool to ion beam community. One of the main features of this program is to simulate PIXE and RBS spectra for any sample composition and experimental conditions. The program also provides simulation of line spectra as well as elemental maps of an arbitrary, user defined, 3D sample composition. The expert system is based on previous work of one of the authors (1) but its functionality, features and data base is now significantly upgraded. Through a modern and functional GUI the program allows the user to define a wide variety of experimental parameters, e.g. energy and species of incident ions (protons, deuterons and helium), detection geometry, characteristics of detectors and filters for both PIXE and RBS channels. User can define excitation geometry as well as 3D elemental composition of the sample and simulate PIXE line spectra as well as elemental maps on pixel by pixel basis. By using parameterization of the latest database the code is very efficient and calculates elemental maps of a complex sample composition in only several seconds. It is our belief that Sim-IBA is an excellent teaching tool for students/researchers with no experience in PIXE/RBS techniques. Secondly, it is of immense help in planning an experiment and choosing the optimal experimental conditions for various analytical problems that PIXE analyst encounter in contacts with various collaborators. Such expert system will give the user a possibility to run a simulated experiment for an unknown sample and test various settings/scenarios to achieve the optimal results without actually running the experiment. This could potentially save a lot of expensive machine time that would otherwise have been spent on trial and error experiments.

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PA-50

A methodology based on thickness dependent sample irradiation to evaluate the enhancement in K-shell ionization cross sections due to vacancies in the projectile.

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The interaction ion-atom is a physical phenomenon normally described by a semi classical model of two particle collision. The Plane Wave Born Approximation PWBA, and its derivative the ECPSSR model, have been good to describe collisions in which projectiles are low mass and energetic. At relative low projectile velocities and near symmetric collisions a very different quantum system is formed when the collision partners approach, the named Molecular Orbital system. In this transitory state, an orbital vacancy in the projectile can be transferred to the target atom by coupling of electronic orbital states. Experimental ionization cross sections attained with light ions impact and those for symmetric collisions present very different tendencies, and it is impossible to relate them by means of a scaling law. The growth observed in cross sections is attributed to 2p vacancies in the projectile transferred to 1s orbitals in the target. The total ionization of a target atom have been expressed as the sum of a direct ionization σ_d by impact with the projectile plus an ionization σ_S due to the mechanism of transfer vacancies from the projectile during the Molecular Orbital formation. A procedure is suggested here to evaluate the enhancement in ionization cross sections due to orbital vacancies in the projectile transferred to the target, consisting of the irradiation of a sequence of different thickness thin targets to monitor the K shell X-rays produced. According to a rate equation and to the production of K X-rays in target, it is expected to get a threshold thickness in which the enhancement reaches a maximum.

Abstracts
Poster Session B

PB-1

Large area silicon drift detectors

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Silicon Drift Detectors (SDDs) are commercially available for more than 10 years. They are widely used in XRF, TXRF, electron microprobe analysis systems and synchrotron applications.

The big benefit of SDDs compared to other x-ray detectors as Si(Li)s or pin-diodes is the spectroscopic performance principally being independent of the sensitive area. As there is a growing demand for larger detector areas, KETEK has developed SDDs with active areas up to 100 mm².

We will present spectroscopic measurements of SDDs with areas varying from 10 to 100 mm². Energy resolution below 130 eV for the Manganese Kα line and peak to background values of more than 10,000 will be shown for devices with active areas of 100 mm² when cooled down to -60°C. Count rate dependency of the energy resolution and the peak position is shown to be negligible up to count rates of 100,000 counts per second.

Temperature dependent measurements of the energy resolution will be shown for different detector areas. We will present improved cooling techniques for KETEK VITUS modules which allow detector temperatures down to -50°C at an ambient temperature of +20°C. Energy resolutions below 135 eV for 100 mm² SDDs and 130 eV for 30 mm² devices at -50°C are achieved.

PB-2

Enhance detection sensitivity of micro X-ray Fluorescence by using advanced X-ray optic chain

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Both polycapillary X-ray optics and doubly curved crystal (DCC) optics have been widely used in X-ray analytical instruments and a variety of research applications. A polycapillary optic is a broad-band optic that consists of up to millions of small channels that are precisely curved to a designed profile to efficiently transmit X-rays by multiple external total reflections off the inner surface of each individual capillary channel. The optic collects a large solid angle of X-rays from a divergent X-ray source and redirects them to either a parallel beam of a focused beam. A focusing polycapillary optic can generate a focal spot less than 10μm while delivering an X-ray intensity equivalent to a pinhole collimator of millimeters in diameter, making it an inevitable tool to use for many applications. A doubly curved crystal (DCC) optic, on the other hand, is a diffractive X-ray optic that collects X-rays from a divergent X-ray source and redirects a narrow band of them by diffraction to form a focused, monochromatic beam. The two optic technologies have their own characteristics and advantages, but also have their limitations. We will report in this paper the use of a DCC-polycapillary optic chain to achieve a monochromatic beam with the focal spot size less than 10μm and the use of such configuration for micro X-ray fluorescence applications. The performance will be compared with that of other technologies to demonstrate the capability of the innovative approach in achieving higher detection sensitivity, higher measurement precision and other analysis benefits.

PB-3

Ultratrace total reflection X-ray fluorescence (TXRF) analysis of platinum group elements applying nickel sulfide melt enrichment

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The analysis of platinum group elements (PGE) is of high importance in many application fields. In most industrial applications, e.g. PGE for catalytic processes, concentration ranges are in the high mg/kg up to wt.-% range. For these samples common X-ray fluorescence (XRF) methods offer an adequate solution.

In other application fields, in which PGE are processed (mining/exploration, medicine, pharmacy, automotive catalysts), element concentations are in the low mg/kg or even µg/kg range. Those samples require digestion procedures and subsequent analysis by means of TXRF or atomic spectroscopy.

However, for many samples even a digestion is not sufficient, either the accuracy of this procedure is insufficient or the concentrations of the PGE are in the low µg/kg or even ng/kg range.

In this presentation a procedure for the PGE enrichment by melting the samples after addition of nickel sulfide is described. Measurement data derived by TXRF analysis are compared with results from inductively coupled plasma mass spectrometry (ICP-MS). On the basis of these measurements the benefits and limitations of the TXRF method are evaluated.

PB-4

Improvements of the low-energy performance of a micro-focus X-ray source for XRF analysis with the SEM

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XRF with a scanning electron microscope (SEM) is a valuable completion of the analytical capabilities of SEMs [1]. A small and compact micro-focus X-ray source such as iMOXS [2] is mounted to the microscope chamber, and the X-ray spectra are monitored with the conventional EDS system.

Modern SEMs are characterized by large specimen chambers to enable the implementation of several analytical methods like EBSD, FIB, WDS, etc. The consequence of such a large specimen chamber is the large clearance between the X-ray tube outside the chamber and the specimen inside. The distance between the input focus of the X-ray optics with its position on the tube target and the output focus on the specimen ranges between 30 and 40 cm.

Up to now the X-ray tubes used for the micro-focus X-ray sources have thick beryllium windows. The poly-capillary optics has its transmission and gain maximum at photon energies around 10 keV. They drop down in both low and high energy ranges [3]. L-radiation from a Mo or Rh target will be strongly attenuated. The excitation of fluorescence in the soft X-ray range becomes very ineffective.

A new micro-focus X-ray source was developed. It is characterised by lower self-absorption in the tube target, thin beryllium windows and an X-ray optics having a large distance between its foci and the maximum of transmission at about 5 keV. Thus K-line fluorescence of light elements becomes effectively excited by the L-radiation from Mo or Rh targets. We have determined a detection limit of about 1 mass-% for sodium oxide in glass.

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PB-5

Development of the analyzer for thickness and trace elements in multilayer using multi excitation sources

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The X-ray fluorescence (XRF) analysis is a very suitable technique for the estimation of the thickness of layers in the plating and multilayer on the Si wafer[1]. Recently, it is required to analyze not only the thickness of layer but also trace elements in the layer. Then, the WDXRF and EDXRF with some X-ray tubes were put on the market. However, these analyzers are large size and expensive.

In this research, the table-top EDXRF analyzer has been developed for measurement of the layer thickness at small area and trace element analysis in the layer. For satisfaction of the analyzer performance, the background must be reduced to improve the Lower Limit Detection (LLD). In addition, the X-ray source is selected which has high excitation efficiency for wide range elements.

In this report, a multi targets X-ray tube is developed which has three target materials, namely, Cr, W, and Rh, on the anode, To select a target, the area that is bombarded by electron should be changed depending on the target materials by different electron source in same X-ray tube. The operating power of the tube is set to 50 watts (50 kV, 1 mA), and it is cooled by forced air convection. The diameter of the focal spot is 50 μm. The spot size on the sample is 50 μm as minimum limited by the collimator. The monochromatic X-ray beam is archived by selection of the filters. The filters were set each three filters, on which between X-ray tube and sample as primary filters, and between sample and detector as secondary filters. The Silicon Drift Detector (SDD) with high P/B ratio is selected for the improvement of the LLD.

This analyzer has following advantages: (1) wide range elements can be measured with high efficiency due to applied a multi targets X-ray tube, (2) the LLD can be improved by quasi-monochromatic excitation source with selection of the optimal filters, (3) the analytical accuracy of layer thickness can be improved because matrix correction is easy by using quasi-monochromatic excitation source and the fundamental parameter method is used, (4) it can be measured that not only thickness information but also the elemental information of layer itself and trace elements in the layer.

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PB-6

Short soft X-Ray sources

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It is demonstrated that laser-induced plasma is a very efficient generator of soft X-ray that has a high interest for applications in lithograph, sequencing of DNA and living cell studies [1]. In this work, a fast Faraday cup (FC) equipped by an X-ray filter is utilised to diagnostic the X-rays. The plasma was generated by a KrF excimer operating at 248 nm and 23 ns. The laser energies utilized were 40, 80 and 120 mJ and the laser spot was approximately 0.01 cm^2. The metal target utilised were made of Cu, Si and Ta.

Fig. 1 shows the experimental apparatus. The X-rays, provided by the laser-plasma, strikes the internal walls of the chamber and the FC collector and electrons of different energy are emitted. The cup signals can be positive or negative depending on bias polarity and electron energy. A collimator was placed in front of the cup because the electron emission from the chamber walls does not favour a good diagnostic of the X radiation. To characterize the X-rays, we suppressed the electron emitted from the cup collector by polarising the cup at a trapping positive voltage. The electron currents decrease as the trapping voltage increases. Measurements of the X-rays energy were done by means of a filter of 0.2 μm thin deposited on 1 μm C3H6. Comparing the X-rays percentage reduction with the attenuation coefficient of the filter we calculated the X-rays energy. The X-rays energy was less than 200 eV. The obtained results are comparable with the ones found by the FC.

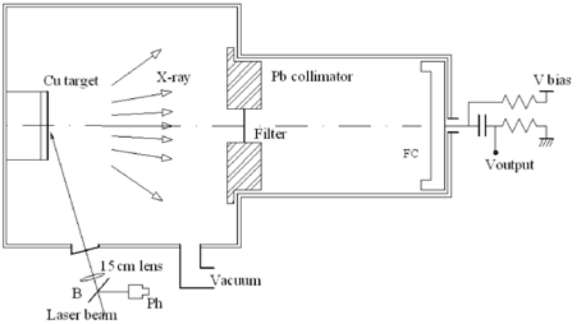

Fig. 1: Experimental set-up. B: beam splitter; Ph: photodiode; FC: Faraday cup.

[1] T. Yorkey, J. Brase, J. Trebes, S. Lane, J. Gray, Proc. SPIE v. 1345 (1991) 255 – 259.

PB-7

Development of laboratory µ-XRF spectrometer using multi monochromatic X-Ray sources

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X-ray fluorescence (XRF) analysis is a suitable technique for elemental analysis in non-destructive measurement. Recently, small area analysis by using the XRF technique has gained popularity. The synchrotron radiation source is responsible for the increase in the popularity of µ-XRF analysis. However, most people find it difficult to gain access to the synchrotron radiation facility. On the other hand, the laboratory µ-XRF spectrometers with the capillary lens optics had been developed[1]. The capillary lens can focused X-rays but it cannot monochromatize. Then the background of measurement spectra are higher than using monochromatic X-rays as excitation source.

In this study, a µ-XRF spectrometer has been developed for use in laboratories, with which multi monochromatic X-rays as excitation sources. To enable the use of this system, it is necessary to satisfy the following two conditions: (1) the excitation source must be optional for efficient excitation of the sample and (2) the X-rays must be focused. An X-ray tube with multi excitation sources has also been developed[2]. In this tube, there are three targets, namely, Cr, W, and Rh, on the anode, and each target can be excited sequentially without changing focal spot position. An Einzel lens is applied as the electron gun. The operating power of the tube is set to 50 watts (50 kV, 1 mA), and it is cooled by forced air convection. The diameter of the focal spot is 10 µm. As the optics for focusing of X-rays, Johansson type Doubly Curved Crystal (DCC) which is Si(111) crystal has been made. A DCC has Johansson focusing geometry along horizontal direction and Von Hamos geometry along vertical direction. Then the effective area of diffraction is almost all surface of crystal. In addition, the focusing efficiency is quite good as compared with Johann geometry. Therefore, the focus size becomes smaller and intensity gain becomes higher.

A system composed of an X-ray tube and DCC optics is used to perform the small particle analysis. In this report, some estimation results of the µ-XRF system and capabilities of the system are discussed.

[1] D. A. Carpenter, *X-Ray Spectrom.*, 18 (1989) 253-257.

[2] S. Maeo, T. Utaka, T. Kubota, K. Taniguchi, *Adv. X-Ray Chem. Anal., Japan*, 38 (2007) 165 - 174.

PB-8

Usability of industrial grade Si wafers for x-ray optical instruments

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Si wafers are produced by semiconductor industry in large amounts and with very good quality. Due to their extremely low surface microroughness, other PSD properties and low cost, Si wafers are of high interest as X-ray mirrors for laboratory instruments and for X-ray space telescopes. The work summarizes the study of industrial Si wafers done for the purpose up to now. It includes measurements of wafer properties relevant to X-ray optics and to X-ray mirrors manufacturing processes. Surface characterisation and multi instrument PSD analysis are of the main concern. Experimental Si-wafers data is compared to typical properties of optical glass currently used for the mirrors.

PB-9

Characterization of polycapillary halflenses in two directions

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Polycapillary halflenses are widely used to focus x-ray radiation onto a small spot. Additionally they can reduce the field of view of a detector when placed in front of one. In 3D micro X-ray fluorescence spectroscopy (3D Micro-XRF) with synchrotron radiation two polycapillary halflenses are used in a confocal geometry. Up to now characterization measurements have only been performed in the case of the lens focusing parallel radiation. Assumptions have been made, that in the other case, when isotropic radiation from a spot source is transported to a detector, the intensity distribution in the focal plane is Gaussian, as well [1]. In this presentation, we show for the first time measurements with an electron beam which confirm this assumption.

With a polycapillary halflens placed in front of an EDX-detector of a SEM it is possible to scan the sensitivity of the investigated optic in the focal plane. Measurements have been performed at the ZELMI in Berlin. The Gaussian form and symmetry of the sensitivity distribution have been verified, and the energy dependence of the FWHM has been analysed. Additional measurements without the lenses provide the possibility to determine the focal and the total spot transmission.

Furthermore the lenses have been characterized in the conventional focusing direction by knife-edge-scans with synchrotron radiation at BESSY II in Berlin. In this presentation the energy dependence of FWHM, focal and total spot transmission are compared for the different experimental methods. We show, that the spot size in the focal plane differs for the same lens, when used in the two different geometries.

[1] W. Malzer, B. Kanngießer, Spectrochim. Acta, Part B 2005, 60, 1334-1341.

PB-10

X-Ray capillary optics: status and perspective

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In this poster the principles of X-ray capillary optics are described and different types of capillary optical elements are considered. Especially, the main parameters of these optical elements such as intensity gain, focal spot size, beam divergence and others, are discussed in detail and experimental results for these parameters are presented. Also is analyzed further developments of capillary optics. They are described some examples of applications of these optics.

PB-11

New applications of capillary optics for XRF and XRD

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The varios application examples in micro X-ray fluorescencs analysis for determination of the two dimensional elemental distribution at sample surfaces as well as depth profiling are given. Finally, the usefullness of capillary optics for different diffractometric investigations is shown. Especially, examples for single crystal, polycrystal and powder diffraktometry also with high lateral resolution and real time diffraktometry are presented.

PB-12

Characterisation of the Multilayeroptic Astix 100

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Monochromatic excitation for x-ray fluorescence analysis has several advantages: it simplifies the quantification and, in some cases, it enhances the sensitivity of a spectrometer. Furthermore, for Micro-XRF monochromatizing properties have to be combined with focussing ones. The development of X-ray optics with monochromatizing properties and local spot sizes below 50 µm is very interresting for Micro-XRF [1].

Therefor we investigated a modified Montel multilayer optic Astix 100 produced by AXO DRESDEN GmbH. These multilayer optics are produced for their application in Micro-XRD, enlarging the anode spot size of the X-ray tube by a factor of 3. We used this optic in the demagnifying geometry, for the reduction of the spot size.

The multilayer optic was characterized by its spot size and its spot shape produced and its throughput. Results will be shown and discussed in view for use in Micro-XRF.

[1] B. Kanngießer, B. Beckhoff, J.Scheer, W. Swoboda, *Advances in X-Ray Analysis*, Vol. 37 (1994) 535-544

PB-13

Monochromatic X-beam for micro-beam EDXRF

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It is well known that a doubly curve crystal (DCC) optic can provide a monochromatic micro beam from a point x-ray source based on Bragg reflection. A compact x-ray source integrated with a focusing DCC optic, called X-beam, has been developed and continues to evolve for monochromatic micro XRF applications. In this paper, recent developments of DCC X-beams will be presented. Focusing geometries, beam profiles and spot sizes will be discussed for various beam energies. Each type of beam has a monochromatic energy of 5.4 keV, 8.0 keV, 17.5 keV or 22.2 keV. The beam spot size is in the range of 30μm to 200μm.

A DCC Mo K_α X-beam that provided a 70μm monochromatic beam with energy of 17.5 keV was used for energy-dispersive XRF applications. A silicon drifted detector was used to record the fluorescent spectra. Elemental maps of various samples at low level concentrations will be presented and discussed. Fe and Cu maps of mouse brain tissue with Alzheimer Disease (AD) are illustrated. This technique can be a valuable tool to assist AD clinical research.

PB-14

Comparative characterization of x-ray beams formed by complicated waveguide-resonance compositions

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X-ray optics devices functioned on base of the waveguide-resonance mechanism for X-ray flux propagation as opposited to conventional units destined for the radiation fluxes formation is characterized by a number of indisputable advantages. The devices form nanosize width beams of quasimonochromatic X-rays with an enhanced radiation density. Moreover, these devices are distinguished by very low attenuation of X-ray flux intensity in process of the radiation transportation [1]. But the simplest device construction – the planar X-ray waveguide-resonator (PXWR) has some user's imperfections. There are the noticeable angular divergence ($\Delta\varphi \sim 0.1^\circ$) and the low integral intensity magnitude of it's emergent beam. So, the chief task of X-ray waveguide-resonance optics development is the attack on these imperfections.

The work presents the space distribution intensity investigations for X-ray quasimonochromatic component of beams formed by some specific design PXWRs. Data of these investigations were compared with ones obtained for slit-cut beam former systems and for planar monocapillars at the same conditions of X-ray source function. On base of the set results we discuss more effective approaches and methods for the waveguide-resonance structure modification. Some attention is devoted to technological peculiarities description of PXWR preparation. Main directions for the practical using of the elaborated waveguide-resonance constructions are assigned. There are forecasted principle tendencies to X-ray nanophotonics development on base of the planar waveguide-resonators.

[1] V.K. Egorov, E.V. Egorov. *Spectrochimica Acta*. B59 (2004) 1049-1069.

PB-15

The performance of picrofocus X-Ray tubes: The influence of X- Ray tube- settings

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Since microfocus x-ray tubes in combination with x- ray optics are more and more used lately, the stability and reliability of their anode spot has received a greater deal of importance.

This presentation shows the characterization of x-ray tubes by the use of two different methods to determine spot size and spot shape at the anode. Depending on the x-ray tube’s settings the results can differ vastly.

For the first method a knife-edge of a thin foil was being moved horizontally and vertically step by step through the x-ray beam. At each step a spectrum was gathered by an energy dispersive detector. According to the German Industrial Norm (DIN EN 12543-5) the second method consists of a lead sphere being placed in front of the x-ray tube into the beam. The resulting image is captured by a CCD camera.

The two methods are being exemplified by testing a microfocus x-ray tube. The differences and results between the two approaches are elaborated.

The results show clearly that it is inevitable to have a good characterization of the x- ray tube’s anode spot’s size in order to obtain a reliable experimental set up for Micro- XRF Analysis.

PB-16

Discharge of meta-stable nuclei during muon capture and realization of the high power monochromatic γ radiation source

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The problem of creation of the high power monochromatic γ radiation source is studied. The possible approach is based on the effect of discharge of meta-stable nuclei during negative muon capture. A negative muon captured by a meta-stable nucleus may accelerate the discharge of the latter by many orders of magnitude [1,2]. For a certain relation between the energy range of the nuclear and muonic levels the discharge may be followed by the ejection of a muon, which may then participate in the discharge of the other nuclei. We present the results of calculating (within QED energy approach [2]) characteristics for discharge of a nucleus with emission of γ quantum and further muon conversion, which initiates this discharge. The key features of the possible high power monochromatic γ radiation source are analyzed.

[1] V.I.Gol'dansky, V.S.Letokhov,JETP 67 (1974) 513-518; L.N.Ivanov, V.S. Letokhov JETP 70 (1976) 19-28.

[2] A.Glushkov, L.N.Ivanov, Phys.Lett.A 170 (1992) 31-36; A. Glushkov etal, Recent Advances in Theory of Phys. and Chem. Systems (Springer) 15 (2006) 301-318.

PB-17

Search of the optimal plasma parameters for X-ray lasing on the basis of modeling the elementary processes in a collisionally pumped plasma

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In recent years the X-ray laser problem has stimulated a great number of papers devoted to the development of theoretical methods for modeling the elementary processes in collisionally pumped plasma. The problem of diagnostics for the collisionally pumped plasma and search of the optimal plasma parameters of X-ray lasing are studied. We present the uniform energy approach, formally based on the QED for the calculation of electron collision strengths and rate coefficients for electron-collision excitation. The electron collision excitation cross-sections and rate coefficients for some Ne-like ions (Fe, Ba) are calculated. To test the results of calculations we compare them with other authors' calculations and with available experimental data. The most effective ions and transitions for producing lasing in the vacuum ultraviolet and soft X-ray region are found and analyzed.

[1] A.Glushkov etal, Int.J.Quant.Chem.104 (2005) 562-572; A.Glushkov, O. Khetselius, etal, Recent Advances in Theory of Phys. and Chem. Systems (Springer) 15 (2006) 285-300

PB-18

Generation of ultra-short X-ray pulses in cluster system during ionization by femto-second optical pulse

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We present the results of modeling generation of the atto-second X-ray pulses during ionization of atomic and cluster systems by femto-second optical laser pulse. The concrete data are received for the cluster Ar_{10} response, the molecular 2D H_2^+ response for different inter nuclear distances (R=2.5, 3.5, 7.4, 16a.u.) with smoothed Coulomb potential and atomic (H) response (spectral dependence) under ionization of the system by femto-second optical pulse. Our calculation show that the generation of the atto-second X-ray pulses in the cluster system is more effective and profitable (as minimum the 2-3 orders) than in similar molecular atomic one. The generation of the atto-second pulses in the molecular system is more profitable too (as minimum the 1-2 orders) than in similar atomic one. The last achievements in this field demonstrate a possibility of construction of the compact X-ray radiation sources.

[1] A. Glushkov, et al, Int.J.Quant.Chem. 99 (2004) 889-895; 104 (2005) 562-572.

PB-19

New measurements and observations on aged NaI detectors

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Although advanced high efficiency, high resolution low energy gamma ray detectors are today available, sodium iodide scintillation counters – i.e. NaI - are still used in medical and technological applications [1, 2]. Despite to almost fifty years of extensive investigations, a full description of phenomena originating spectrum features including aging and damaging effects is difficult to find in the open literature. In this work an experimental distribution resembling the K X ray fluorescence (K-XRF) of iodine is found and proved to interfere with both the K-escape and XRF peaks eventually allowed by when low energy incident photons are used. XRF investigations with different equipments and photon transport simulations are carried out in order to assess such unexpected distribution and to establish its nature. The hypothesis of a thin dead layer near the front surface induced by aging or degradation of the crystal is proved to explain the building up of such peaks. In addition, such peak can be exploited as an internal reference to assess the dead layer thickness and the relative loss of efficiency. Results by both experimental and simulation seem to strongly support such conclusions.

[1] S. Steenstrup et al. X ray Spectrometry 29 (2000) 249-252

[2] A. Tartari et al. Radiation Physics and Chemistry 61 (2001) 737-738

PB-20

X-Ray prism spectrometer for ultra-fast single pulse spectral measurements

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Energy dispersive X-ray prism spectrometer (EDXPS) for ultra-fast measurements and time-dependent investigations is proposed. A new compound mosaic construction of a refracting prism provides energy dispersion up to a theoretical limit. Physical requirements to a prism material, detection unit and processes of heat dissipation at high power radiation loads are considered. Dispersive properties of diamond and beryllium prisms were computer simulated. It was demonstrated that expected parameters of the European X-ray free-electron laser (XFEL) ensure EDXPS energy resolution of a few eV at E~10 keV. The technique provides unique opportunities for single pulse x-ray absorption spectroscopy in the femtosecond time domain.

Preliminary results of the EDXPS testing in laboratory conditions are presented. An optically polished diamond prism was used as a dispersive element. Broad band emission and absorption spectra were registered using scintillation counters and high resolution CCD matrix.

PB-21

2θ-resolution in synchrotron micro-XRPD: instrumental comparison at HASYLAB Beamline L

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The µ-XRPD (X-Ray Powder Diffraction) setup at HASYLAB Beamline L has been utilized successfully for the investigation of several materials [1]. Two important characteristics define the applicability of an XRPD setup: the detection limits (the lowest abundance of a phase diffracting with an intensity above the background noise) and the resolving power (the ability to distinguish reflections with a small scattering angle difference). The detection limits are determined by the primary X-ray beam intensity and the detector sensitivity. The resolving power can be expressed by the Full-Width-at-Half-Maximum (FWHM) of the diffraction peaks as a function of scattering angle 2θ. The contributions to the diffraction peak FWHM can be divided in two groups:

(a) sample induced broadening due to finite crystallite size, strain and defects

(b) instrumental broadening caused by the energy resolution ΔE/E and divergence of the primary X-ray beam, the point spread function (PSF) and number of pixels of the CCD area detector collecting two-dimensional diffraction patterns within a solid angle behind the sample.

At HASYLAB Beamline L two double multilayer monochromators (DMM) and a double crystal monochromator (DCM) are available, covering a ΔE/E range from 2 % to 0.02 %. A gain in energy resolution is obtained at the cost of a reduced X-ray flux. Depending on the needs of the experiment, it is useful to employ the appropriate balance between beam intensity and scattering angle resolution. Two case studies are presented, illustrating this: a study about the chemical forms in which heavy metals are present in polluted soil from the Val Basento district (Basilicata, Italy) and the speciation of uranium in DU particles in soil collected at Ceja Mountain (Kosovo).

[1] R. Terzano, M. Spagnuolo, B. Vekemans, W. De Nolf, K. Janssens, G. Falkenberg, S. Fiore and P. Ruggiero, Environmental Science & Technology, 41 (2007) 6762-6769

PB-22

High performance read-out electronics for Silicon Drift Detectors

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Semiconductor Drift Detectors (SDD) have nowadays reached a leading position as detectors for X-ray spectroscopy due to their outstanding performances in terms of energy-resolution and detection-rate. These performances can nevertheless be exploited at the best only with specifically and carefully designed readout electronics. We discuss here the critical aspects of the readout process and present the experimental results recently obtained with new circuits.

The SDD's performances are basically due to their very small output capacitance. The integration of the input JFET of the preamplifier directly on the detector maximizes the benefits of the low output capacitance [1]. The readout electronics here presented has been designed for SDDs with integrated JFET.

A pulse-reset preamplifier, with embedded the integrated JFET, was designed and tested. This solution allows keeping high values of the spectroscopic resolution also at very high count-rates. The noise associated to the anode discharge current can in fact be avoided. Moreover the gain stability is greatly improved by the feedback configuration. A hybrid version of this preamplifier and a four channel integrated CMOS (AMS 0.35 μm) version will be presented.

A VLSI CMOS 8 channel readout circuit, designed for large-scale applications [2], is also presented. It's composed of an analog and a digital section. The analog section is based on charge preamplifiers with selectable shaping times, baseline holder and peak stretcher. The digital section performs the signals management: queuing of events, pileup rejection, multiplexing of the analog outputs. It also provides a real time signal for timing purposes. The circuit is characterized by high peak stability and good spectroscopic resolution.

In order to fully exploit the detection rate performance of SDDs coupled with our readout electronics a novel 4 channels (extendible up to 48) acquisition and processing unit has been designed [3]. The on-board histogramming capability allows reaching count rates rate up to 1 Mcounts/s per channel.

[1] P.Lechner, S.Eckbauer, R.Hartmann, S.Krisch, D.Hauff, R.Richter, H.Soltau, L.Struder, C.Fiorini, E.Gatti, A.Longoni, M.Sampietro, Nucl. Instr. and Meth., A 377, 346-351, 1996.
[2] T. Frizzi, L. Bombelli, C. Fiorini, A. Longon, 2006 IEEE Nuclear Science Symposium Conference Record
[3] R.Alberti, S.Buzzetti, C.Fiorini, C.Guazzoni, T.Klatka, P.Lechner, A.Longoni, L.Struder, IEEE Trans on Nucl. Sci. Volume 54, Issue 3, June 2007, 751-757.

PB-23

The advantages of digital adaptive filtering in fast pulse processing

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Improving the productivity and performance of XRF is of great importance in determining elements in samples of various origin. The advantages of using adaptive matched filtering in digital pulse processing for the purpose of energy dispersive x-ray fluorescence analysis are demonstrated by comparing the instrumental performance achieved with that of conventional analog processing and other digital filtering methods. Due to the task complexity of matched filtering computation[1], an application-specific digital pulse processor was designed, based on fast, state of the art, field programmable gate arrays (FPGA). The performance of different pulse processing techniques was evaluated for two different detector types: SiLi and thermoelectrically cooled silicon drift detector (VITUS-SDD). The results clearly show that digital adaptive matched filtering can be as twice faster, compared to analog processing, without degrading the accuracy. It also has improved accuracy at same processing time, compared to other digital filtering methods[2].

[1] G. Georgiev, I. Peev, EXRS-2006, Adaptive Matched Filtering Of XRF Detector Signals.

[2] V. Radeka and N. Karlovac, Nucl. Instrum. Methods 52: 86–92, 1967.

PB-24

Modelling the response function of an EDS with a silicon detector

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A new physical model-based, analytical description of the response function of an energy dispersive X-ray spectrometer with a silicon detector (Si(Li) or SDD) is presented. It accounts for charge generation statistics, electronic noise, incomplete charge collection that gives rise to peak tailing, the escape effect, the fluorescence of the front contact or the dead layer, and hot photoelectrons that cause the shelf. Only five free parameters are necessary to describe the response function for any individual detector: the electronic noise, three parameters describing the shape of the charge collection efficiency beneath the front contact [1], [2] and the thickness of the front contact metal layer including any possible dead layer. The thickness of the front contact layer can be determined from the spectral sensitivity curve, the electronic noise from the line width or the zero-energy peak if available. The parameters describing the charge collection efficiency beneath the front contact can be obtained by fitting the model to a response function measured preferably close above the silicon K-edge where tailing is most pronounced. Once determined, this set of parameters can be used to calculate the response function for any photon energy in the range from 0.1 to 30 keV.

A free computer program has been written in MATLAB™. It enables the determination of an optimal set for the five parameters by fitting a measured spectrum for either purely monochromatic radiation or a K-series fluorescence spectrum from a 3d metal. As the direct analytical computation is fast, a (m,n) response matrix can be calculated to be used in an XRF quantisation program to convert the calculated fluorescence intensities of n fluorescence lines of a multi-element specimen to an m-channel spectrum to be directly compared to the measurement.

[1] S. Goto, Nucl. Instrum. Methods A, 333 (1993) 452 – 457.

[2] F. Scholze, M. Procop, X-Ray Spectrom. 30 (2001) 69 - 76

PB-25

Modular analytical X-Ray acquisition system (AXAS-M)

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The Analytical X-Ray Acquisition System (AXAS) is commercially available for more than five years as a compact analogue signal processing tool including all necessary power supplies, preamplifier and shaping amplifier in combination with a KETEK Vitus Silicon Drift Detectors (SDD) in one housing.

The new modular Analytical X-Ray Acquisition System (AXAS-M) consists of two parts M1 and M2. AXAS-M1 includes a thermal optimized and stabilized detector head in combination with a reset type preamplifier and KETEK Vitus SDD with active areas selectable from 10 to 100mm². Part M2 includes all necessary stabilized and well-defined filtered power supplies for biasing the detector and for powering the implemented thermoelectric cooler. Optional, signal processing either analogue or digital can be implemented in the M2. The signal processing can be chosen by either using an analogue shaping amplifier with an analogue-to-digital converter in combination with a multichannel analyzer or a brand new digital pulse processor for complete digital signal processing.

The big benefit of this unique system is that KETEK provides a complete chain starting from the detector to the complete signal processing and the connection to a host PC via USB interface. All parts are well optimized for operation with KETEK Vitus SDDs to achieve best possible performance. In addition, thermal stability is improved significantly by using a properly designed heat sink.

KETEK will present technical datasheets and spectroscopic results as well as the complete system itself. The AXAS-M therefore represents a complete spectroscopic system.

PB-26

Fast tomography for the study of time-dependent processes

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A new micro-computed tomography (µCT) equipment was installed and commissioned last year on the high-energy beamline HARWI II at Deutsches Elektronen Synchrotron. In this new end-station, two different detectors can be used, depending on the application. With one of them, high resolution analysis of static objects can be performed. The second detector is a fast camera that enables the acquisition of a whole tomogram in just a few seconds, in what is called process microtomography (PµCT). In contrast to “conventional” µCT, where the time needed to acquire a tomogram can take up to several hours, with PµCT we can decrease the scan time down to scales where the study of time-dependent processes is possible. We will employ this technique to examine a number of dynamic samples, such as liquid and multiphase flow in porous ceramics, and the propagation in the blood vessels of ferrofluids acting as drug carriers for cancer treatment.

First tests have been performed in order to investigate the loss of spatial resolution at reducing fast speeds. For this, a sequence of tomograms of a static porous ceramic sample has been acquired with scan times ranging from 424 to 5 seconds. For comparison, the same sample has also been analysed with conventional µCT (scan time 90 minutes) and set as reference. The different fast tomograms have been compared to the reference image, and the trade-off between resolution and scan speed established. These conclusions, together with the planned experiments for the next beam time at the synchrotron, will be presented.

PB-27

Tomography analysis of femoral bones from rats under osteoporosis preventive treatments

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X-ray microtomography analysis has been performed to complement the results achieved by nuclear microscopy in a study of femoral bones from rats under osteoporosis preventive treatments. With nuclear microscopy, a change in the concentration of certain elements suggested a change in bone density, but this was not conclusive. With X-ray tomography, the changes in density may be correlated to the changes in element distribution and concentration.

In order to study the influence of steroid supplementation on bone remodeling, the distribution and concentration profiles of a number of elements within bone samples were imaged by nuclear microscopy [1]. The relevance of trace elements in bone structure and remodeling was shown. In particular, the depletion of Fe, Zn and S could indicate a decrease in bone mass, as they are matrix constituents and/or promoters of bone formation. With nuclear microscopy, this mass reduction could not easily be identified, due to the fact that the mineral composition did not vary greatly.

To better evaluate the changes observed in the elemental composition of the bone after treatment, the density should also be investigated. For this, the same samples are being examined by X-ray tomography, a technique that permits the non-destructive examination of the inside of an object, getting as a result a 3D density map. Any change between bone resorption by osteoclasts and bone formation by osteoblasts causes an absolute reduction in the amount of bone in osteoporosis. With X-ray microtomography, it is possible to image this loss of bone mass and to correlate it to the previous results on elemental distribution. With these results, it is possible to better weight the benefits of steroid supplementation for osteoporosis treatment.

[1] M.D. Ynsa, F.J. Ager, L.C. Alves, M.A. Zubeldia, J.C. Millan, T. Pinheiro, Journal of Microscopy, 224 (2006) 298 – 305.

PB-28

Ni mapping in *Berkheya coddii* by Micro-PIXE and NEXAFS

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Near Edge X-ray Absorption Spectroscopy (NEXAFS) and scanning transmission x-ray microscope (STXM), installed at 11.0.2 line of the Advanced Light Source of Lawrence Berkeley National Laboratory, has been used for quantitative elemental mapping in leaves of *Berkheya coddii*, Ni-hyperaccumulating plant from South Africa. Specimens were prepared using cryofixation in high-pressure freezer and freeze-substitution with diethyl ether, followed by sectioning with ultramicrotome. Spectra and maps were processed using AXIS2000 software.

Comparative studies of the same specimens were performed with micro-PIXE and proton backscattering spectrometry (BS) using the nuclear microprobe at Materials Research Group, iThemba LABS. Quantitative maps of Ni and other elements as well as concentrations of elements from selected areas within maps were obtained using GeoPIXE software. Thickness of specimens and composition of major elements obtained from BS method were used for matrix corrections in PIXE maps and spectra.

STXM offers excellent lateral resolution of the order of 30 nm. Available energy range is 80 – 2100 eV with ΔE/E > 7500. Ni mapping was performed using Ni L_3 absorption edge. Predictably, the requirement of x-ray transmission through the specimen introduces strict limits on specimen thickness. This is a serious practical limitation in multielemental analysis where various x-ray energies must be used.

Micro-PIXE has inferior lateral resolution (3 µm x 3 µm) but is much more flexible as far as specimen thickness is concerned. Multielemental analysis and easy quantification make it a method of choice for study of elemental distribution in plants. However, STXM is needed for studies of the details of elemental distribution at intracellular level, and chemical mapping.

PB-29

A compact 3D Micro-XRF laboratory spectrometer for archeometric applications

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After having gained experience from the setup and applications of a 3D Micro-XRF tabletop setup [1], a new compact 3D Micro-XRF laboratory spectrometer was designed and developed for non-destructive investigations of cultural heritage for the laboratory of the Center for research and restoration of French museums. For the excitation a Rh micro focus x-ray tube is used while a SDD detector serves for X-ray detection. The confocal setup is realized with a polycapillary mini-lens in the excitation channel and a Poly-CCC in the detection channel forming a probing volume with a FWHM between 33 µm and 50 µm depending on the searched element. The specific feature of this setup is the measuring head with the solid mechanical fixation of the lenses and the ease of its alignment with respect to the X-ray tube and the detector. The lens in the excitation channel is completely fixed whereas a movement of the Poly-CCC in the detection channel is only possible perpendicular to the beam direction. This simplifies the adjustment of the confocal setup and minimizes the danger of misalignment during sample change.

Several characterization measurements were carried out on this spectrometer concerning the dependence of FWHM of the probing volume on energy and the stability and warming up of the x-ray tube.

First investigations were carried out on paint layer dummies. Using the 3D Micro-XRF laboratory spectrometer the course of several layers could be determined. Further applications on archaeological and art objects are in progress.

[1] B. Kanngießer, W. Malzer, A. F. Rodriguez and I Reiche, Spectrochimica Acta Part B, 2005, P 41-47

PB-30

Collimation of non-axial x-rays spectrum by means of steering ferrofluid - way of reducing geometrical faults in x-ray-pictures

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Issues relating to the incoherence of X-ray beams generated both by older type X-ray tubes and newer, multi-focal tubes with a spinning anode, have been presented in the paper. Collimators employing high-density metallic materials are used for practical reasons to overcome difficulties with focusing X-rays. A wholly new approach has been to use dynamic magnetorheological fluid, which serves both as a spectrum filter and most likely also as a refractor, to change the parameters of the diagnostic beam.

The objective was to find answers to the questions: (1) does the rotation of the ferrofluid in the magnetic field influence the spectrum and geometry of the X-ray beam? (2) does the presumptive change of the beam's spectrum and geometry in the ferrofluid reduce the geometrical deformations of the image as effectively as when passing through a metal collimator?

Scope of work: performing a series of X-ray shots of a metal object and recording their results on a "DIGORA" system matrix while maintaining a fixed distance away from the X-ray tube.

Three series of measurements were carried out employing constant parameters of time and emission: (1) NC no collimation; (2) MC through metal collimators ; (3) DC through a dynamic collimator using 4 different volumes of ferrofluid and a repeatable sequence of rotations.

The following were assessed: (1) R(m) Deformation (magnification) ratio of the image for all the collimation techniques; R(ec) Effective collimation ratio; (c) A(e) average energy per each 1mm^2 .

Results: (1) changing the rpm of the collimator with ferrofluid, as in the case of metal collimators, leads to a considerable fall in the magnification ratio of the object's images; (2) The effective collimation ratio R(ec) has a significantly better value in the ferrofluid than in the steel collimator; (3) The average energy A(e) in the cross-sections of the collimators is higher in the case of the ferrofluid.

PB-31

X ray scattering tissue characterization in microbeams based techniques

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High quality X ray scattering distribution were obtained from biological samples at two typical intervals of the momentum transfer variable $q=4\pi \sin(\theta/2)/\lambda$ nm^{-1}, i.e. $0.04 < q < 4.9$ nm-1 (Small Angle X ray Scattering, the SAXS regime) and $4.6 < q < 47.0$ nm-1 (Wide Angle X ray Scattering, the WAXS regime). θ is the scattering angle and λ the incident wavelenght. The measurements were performed at the ID02 beam line of the ESRF-Grenoble, France and intact excided samples of human skin, lung, white and grey cerebral matter were considered. The obtained diffraction patterns - which found interest in technological applications other than classical chemical structure investigations – were investigated in terms of their possible exploitation. Two techniques are particularly interested. First, pathological signatures based on the spectrometry of scattered X ray both in wave (WDXRS) or energy (EDXRD) dispersive modality [1]. Second, the X-ray micro-beam radiation therapy (MRT), a preclinical radiotherapy technique based on the use of arrays of X-ray microbeams with a mean energy in the hard X ray regime [2]. It is shown that the inclusion of the measured scattering distribution in the photon transport calculations induce not negligible effects in the dose deposited around the microbeams.

[1] SE Bohndiek et al. Phys Med Biol 53 (2008) 655-672

[2] M De Felici et al. Nucl Instrum Meth A580 (2007) 489-492

PB-32

Metals in aerosol particulate matter from the metropolitan zone of the valley of Mexico

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The impact of metal pollution in the Metropolitan zone of the Valley of Mexico was assesed by means of SEM-EDX (Scanning Electron Microscopy and Energy Dispersive X-ray Microanalysis) of particulatte matter (Total Suspended Matter, TSP and PM10) obtained with an automatic high volume sampler in an average flow rate of 1.5 m^3 min^{-1} for 24 hours in five monitoring stations of the National Network System, covering the four cardinal directions and the center zone. One of the most important group in which particles were classified was the metal group that acomplish the criteria to have a transition metal in concentration ≥ 20%. Metals were observed in all samples though with higher abundance, up to 46%, in Northwest (Tlanepantla) and Southest (Cerro de la Estrella) monitoring stations, in both TSP and PM10. Metals found were Ti, Cr, Mn, Ni, V, Sn, W, Co, Zr, La, Ce, Cu, Zn and Pb. Some of them have soil as their common source but others have and anthropogenic origin and some discussion about this subject its made.

[1] T. Martinez, J. Lartigue, P. Avila-Perez, L. Carapio, G. Zarazua, M. Navarrete, S. Tejeda, L. Cabrera. J. of Radioanalytical and Nuclear Chemistry, 273 (3), (2008)799-806.

PB-33

Identification of aerosol particle sources in semi-rural area of Kwabenya, near Accra, Ghana

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Aerosol particles from Kwabenya, near Accra, capital of Ghana, was sampled using a Gent sampler. The particles were segregated into two size fractions – fine (PM2.5) and coarse (PM10-2.5) - and were collected on Nuclepore polycarbonate membrane filters. EDXRF together with gravimetric and black carbon analysis (BC) were used to determine elemental, BC and mass concentrations in the two particle fractions. Principal component analysis (PCA) was applied to characterize possible sources of the aerosol particulate matter.

Over 26 elements were identified in the aerosol samples; however not all of them were used for the source assignments. The coarse particle fraction contained over 80% of the mass. The results show that the fine particle fraction in the aerosol has much higher contribution of black particles than the coarse particle fraction, a finding which is typical of all industrial areas world-wide.

Six source profiles could be identified on the basis of element analysis. There was very good agreement between the experimental particulate mass and the particulate mass as modeled on the basis of the principle component analysis .

PB-34

Determination of elements in PM_{10} by EDXRF in the air in 2006-2007 over Flanders, Belgium

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Flanders is a densely populated region in the North of Belgium. Residents of the region are exposed daily to ambient air pollution, arising mainly from industrial and traffic activities and domestic heating. To better understand the high PM_{10} concentrations in the region the Flemish Environment Agency (VMM) carried out the one year long Chemkar PM_{10} project from September 2006 to September 2007. Six sampling sites in the region of Flanders were chosen, namely: Aarschot (background site), Borgerhout (urban), Hasselt (suburban), Houtem (rural, about 10 km from the North Sea), Mechelen (suburban site), Zelzate (industrial zone).

As part of the Chemkar project PM_{10} was collected on two types of filter material every 6th day during 24 h with LVS automatic samplers at a flow rate of 2.3 m^3/h. The PM collected on Teflon (PALL Teflo) filter material was analyzed by the University of Antwerp (UA) with energy-dispersive X-ray fluorescence (EDXRF) and the PM collected on quartz filter material was subjected to ion chromatography (IC) analysis (also by UA).

The EDXRF spectrometer Epsilon 5 from PANalytical (Almelo, The Netherlands) was used. The spectrometer has a powerful X-ray tube, 3D polarizing geometry, up to 15 secondary targets and a high-resolution HPGe-detector. The conditions for EDXRF determination of 22 elements (Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Rh, Pd, Cd, Pt, Pb, Se) were optimized. Most of the detection limits of elements were found within 1-5 ng/m^3 range. Relatively high concentrations of some anthropogenic elements were detected. Soil fraction contribution in total PM_{10}, calculated on the basis of the EDXRF results was within the range of 6-14 % depending from sampling location.

According to a comparison of IC and EDXRF results, all total Cl was found in soluble form of Cl^-. 74% of total S was SO_4^{2-} for one sampling location, for other sampling sites all total S was found in the form of SO_4^{2-}.

PB-35

Study of the elemental concentration of air particulate matter by EDXRF method collected in Poland.

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The preliminary investigation of air particulate matter in Poland was conducted. All the sample collecting took place in a small city placed 25 km S/E from Warszawa in the Warszawa province, Poland. This city is a healthresort, all covered with forests. The NILU Filter holder System was used to collect the particulate matter on Nuclepore filters. The air particulate matter was divided into grainsize fractions. The samples were measured on the EDXRF spectrometer. Elemental concentrations were calculated using the AXIL program. Concentrations of particulate matter were below admissible values. Coarse fraction (> 8 μm) contained mainly soil derived elements like Ca, Ti, Fe. Pb and Br were derived equally by all collected fractions. Zn during the first two days of the campaign was mainly in coarse fraction but afterwards it changed into fine fraction. The measurement in various seasons will be continued.

PB-36

Analysis of urban and sub-urban fine particles ($PM_{2.5}$) collected in Ouagadougou, Burkina Faso

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Background measurements of CO, PM, NO_x, VOC and O_3 along with meteorological parameters was performed at two sites in Ouagadougou, Burkina Faso in December 2007. The aim was to determine the mass, black carbon (BC) and elemental concentrations in fine particles ($PM_{2.5}$) and their variations at the two sites. Ouagadougou is located in the hot arid steppe climate of the Sahel region at 12º20' N, 1º40' W. The weather situation in Ouagadougou during the field campaign was dominated by high pressure with variable cloudiness and no precipitation. Temperatures varied between 19 - 38 °C and wind speeds show a diurnal pattern with gusts of up to 6 m/s during daytime, while evenings and nights were generally calmer (≤ 3 m/s) with more stable atmospheric conditions.

Cyclones were used at both sites to collect $PM_{2.5}$. The inorganic analysis was done using EDXRF spectroscopy. Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, Br, Rb, Sr and Pb were identified and quantified in the samples. The mass concentration of the collected particles varied between 27 - 164 $\mu g/m^3$ while the BC varied between 1.3 and 8.2 $\mu g/m^3$. Iron attributed to half of the weight of the detected elements. Mean concentrations of Br and Pb was higher at the sub-urban site. The concentration of the other detected elements and the mass and BC content was higher in the urban site compared to the sub-urban site. The similar mass variation at both sites can be attributed to the soil dust present in the air most of the day. This was confirmed by comparing the elemental content on the particle samples with the elements on an analyzed soil sample.

The project was performed in collaboration with Directeur Diallo and his staff at Direction de la Meteorologie Nationale (DMN) in Ouagadougou, Burkina Faso whose help we acknowledge greatly. The project is financially supported by SIDA/sarec.

PB-37

Elemental content of aerosol particles in an underground tram station

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Particulate matter is an important air pollutant, especially in closed environments like a tunnel. The aim of this study was to determine the mass, black carbon and elemental concentrations of particulate matter of two size fractions at an underground tram station in Hammarkullen, Göteborg, Sweden. Samples were collected during June 2007 using a dichotomous virtual impactor separating the sampled aerosol particles into coarse (aerodynamic diameter between 2.5 and 10 μm) and fine fractions (below 2.5 μm). To minimize the possible influence of waiting passengers the platform for trams going towards the suburb Angered was chosen. The elemental analysis of the samples, collected on Teflon filters, was carried out using EDXRF spectroscopy resulting in concentrations of 13 elements in most of the samples. Data reduction was done by Principal Component Analysis (PCA) to identify possible sources for the elements in the particles.

Due to the tunnel environment the difference between the fine and coarse particle fractions was not as large as under normal ambient conditions. Likewise the influence of the local weather was not significant. Particle content from the tram traffic as well as from natural sources were identified, with Fe being the major element in both coarse and fine particles. Comparing the mass concentration of the measured aerosol particles to the corresponding ambient concentration measured at a monitoring station in downtown Göteborg shows a higher mass concentration in the tunnel. In some days the mass concentration was over the daily ambient air quality standard of 50 μg/m^3, but lower than the limits in the environmental work act, 5 mg/m^3.

This project has been carried out in cooperation between University of Gothenburg, Chalmers University of Technology, University of Lisbon, Gothenburg Environmental Protection Agency and Gothenburg Traffic and Public transport Authority. The kind support of all involved parts is highly appreciated.

PB-38

Trace elements in hourly ambient aerosol samples determined with synchrotron XRF

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Ambient aerosols were sampled with a rotating drum impactor (RDI) in different places in Switzerland in the winter of 2005/2006. RDIs allow for a size-segregated collection of particulate matter in the size ranges of 0.1 – 1 μm, 1 – 2.5 μm, and 2.5 – 10 μm. With sampling time of one or two hours, relatively little mass is deposited on the collecting substrate, a 1.8-μm Mylar foil. For the analysis of trace element concentrations, reasonable signal-to-noise and signal-to-background ratios were achieved with synchrotron-XRF[1,2], which was performed at PSI's synchrotron light source, SLS. However, the smaller size ranges typically exhibit an increasing amount of carbonaceous material not accessible with synchrotron-XRF.

The results showed remarkable differences in sample composition for the different size ranges. Zurich and Reiden, the sampling sites north of the Alps, show similar elemental distributions in the smaller size ranges. In the largest size range, Cl is conspicuous for Reiden, which is close to a freeway where road salt is regularly applied in winter. The intermediate and smallest ranges are dominated by S and K. South of the Alps, Cl is the dominant element in the largest size fraction, Fe in the intermediate fraction, and S and K equal each other in the smallest size fraction.

[1] N. Bukowiecki *et al.*, *Environmental Science and Technology* **39** (2005) 5754-5762

[2] N. Bukowiecki *et al.*, *Spectrochimica Acta Part B*, in preparation (2008)

PB-39

PIXE and XRF analysis of Suspended Particulates in an Urban Residential Area of Zagreb, Croatia.

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Knowledge of the elemental composition of airborne particulates is essential to identify potentially toxic components, enable pollution source profiling and apportionment, and augment the assessment of the effects of particulate matter on health and welfare [1]. Nevertheless, no single analytical method is suitable for measuring all chemical species of interest in airborne particulates. PIXE and XRF techniques [2,3] were consequently employed in an optimized manner to characterize a wide range of elements in suspended particulates collected from an urban residential area in Zagreb, Croatia, during summer and winter seasons. The PIXE quantitative technique, based on calibration done using micromatter standards, showed enhanced sensitivity for low Z elements at 2 MeV proton energy with a mylar filter of 24μm, for air filter analysis. The XRF spectrometer was also optimized by careful selection and combination of four secondary/polarizing excitation targets of Ti, Co, Mo, and Al_2O_3 Barkla polarizer. Validation of the quantitative methods of both techniques with the air filter standard SRM2783 gave good agreement in the results for most of the elements. Consequently, by focusing on the inherent strengths of the two respective techniques, the following elements were identified and quantified: Al, Si, S, Cl, K, Ca, Cr, Mn, Fe, Cu, Zn, Br, and Pb. A comparison was carried out on the elemental compositions of the suspended particulates in the different seasons, and between the two techniques.

[1] W. Zhao, and P. Hopke, Atmospheric Environment, 38 (2004) 5901.

[2] USEPA, Compendium Method IO-3.6, "Determination of Metals in Ambient Particulate Matter using Proton Induced X-ray Emission (PIXE) Spectroscopy" EPA/625/R-96/010a, June 1999)

[3] USEPA, Compendium Method IO-3.3, "Determination of Metals in Ambient Particulate Matter using X-ray Fluorescence (XRF) Spectroscopy" EPA/625/R-96/010a, June 1999

PB-40

Seasonal variations in particulate mass concentrations and elemental composition of urban aerosols in Zagreb, Croatia, using ED(P)XRF analysis

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Significant efforts in time, instrumentation, expertise, and money are required in aerosol sampling and data generation. It is therefore unfortunate to focus mainly on mass concentration measurements in air pollution studies. Subsequent and additional determination of the chemical composition of aerosol particles is needful, and of interest in deriving maximum information from collected aerosols [1]. Particle mass concentrations of suspended particulates in an urban residential area in Zagreb, Croatia, have been determined using the Gent air sampler at an average flow rate of 1 m^3/h. Twenty four hour samples were collected during the periods July – September 2007, and December 2007 – January 2008, and the mass concentrations for coarse and fine particle fractions have been determined and compared for the two seasons. This was followed by elemental composition analysis using energy dispersive polarized x-ray fluorescence (ED(P)XRF) spectrometry, with four secondary/polarizing excitation targets [2]. Also presented and compared, are the elemental concentration results of the following identified elements: Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Pb, and Br. This paper also discusses the seasonal influences on the particulate and elemental concentration levels.

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PB-41

Analysis of methyl bromide ozone depleting substance

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Methyl bromide (bromomethane, CH_3Br) is a wide application fumigant (e.g. in wood exporting; ISPM-15 regulation) and a soil sterilant. On the other hand methyl bromide is in the list of the ozone depletion substances [1] (bromine is much more dangerous for the ozone layer than chlorine).

During methyl bromide application as fumigant, it usually makes a thin layer on the sterilized surface. This layer can stay for many days (or even months) and its analysis is not easy with conventional methods of chemical analysis, especially if a fast and on site method is needed. Energy Dispersive X-Ray Fluorescence (EDXRF) cannot determine organic substances but it can easily analyze bromine. If the sterilized substrate (blank sample) does not contain high bromine content, bromine concentration can be attributed to methyl bromide. Analysis of thin layers is a quite accurate task in XRF analysis, if a suitable thin standard calibration has been used.

In the present work imported (from a non EU country) rubber samples that had been processed by methyl bromide fumigant, were analyzed for residual bromine. Radioisotope excitation and EDXRF analysis was used, with NIST and Micromatter thin target calibration; calibration assurance was confirmed by IAEA Interlaboratory test [2]. Blank rubber samples did not contain detectable bromine quantities, while analyzed samples contain significant amounts (of the order of 10 μg/cm^2) of methyl bromine; this amount was reduced as a function of time. The method can be easily used with an XRF mobile system for in situ analyses.

[1] http://www.epa.gov/Ozone/ods.html

PB-42

Determination of trace metal concentrations in waters of Nakivubo channel and Lake Victoria using Energy Dispersive X-ray Fluorescence Analysis

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In an effort to understand the pollution levels in waters of Nakivubo channel in Kampala, Uganda and Lake Victoria concentrations of Mn, Fe, Co, Cu, Zn and Pb were determined using convectional EDXRF and TXRF analysis.

Water samples were collected with a 1-litre Van Don sampler (code, 1077) and transferred into polyethylene containers that were stored in an ice cooled box. Five samples were obtained at each sampling site and were all stored at -21 ^{0}C until analysis. Filtration on cellulose filter gave a particulate deposit that was analyzed for trace metals on a convectional EDXRF spectrometer. Pre-concentration and evaporation at 50 ^{0}C were used for extraction of dissolved metal content that was analyzed on TXRF. Samples of the unfiltered water were treated with HNO_3 and H_20_2 in a process for extracting total trace metal content that was subsequently prepared and analyzed on TXRF. Spectra from the spectrometers were analyzed for the trace elements of interest and elemental quantification was achieved using Quantitative X-ray Analysis software from International Atomic Energy Agency.

The results showed high concentrations of particulate Fe and Mn, and relatively low Zn upstream the Nakivubo Channel. These were lower in the Lake Victoria waters. At the shores of Lake Victoria the dissolved Fe and Zn were higher than in the channel. The concentrations of Fe, Mn and Zn in Lake Victoria were below the USEPA maximum contamination limits of 0.3, 0.05 and 5 mg/L respectively. However, Fe at the mouth of Nakivubo Channel was high and in general the quantified total elemental concentrations increased upstream along the channel. This meant increased water pollution input upstream and along the channel.

US Environmental Protection Agency (EPA), www.epa.gov/osw/ visited on 23rd February 2008.
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PB-43

Analysis of major and trace elements content of mining waters by means of wavelength dispersive X-ray fluorescence of dried residues

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Analysis of trace heavy metals and major elements in aqueous solutions is becoming more important due to the increasing of environmental quality regulations. XRF techniques have been widely employed for the study and assessment of soil pollution. At many polluted sites, there are also concerns about heavy metal contamination of ground and surface stream water. The major drawback to the use of conventional XRF equipments (EDXRF and WDXRF) for water analysis raises in the detection limits that ranges in the $mg \cdot L^{-1}$ order. The common concentration of many pollutants is at $\mu g \cdot L^{-1}$ levels. To solve this situation several specimen preparation methodologies (precipitation, ion exchange, extraction and desiccation) were proposed [1]-[2].

In this work, we use a conventional WDXRF instrumentation to evaluate the content of a wide range of elements (20 different elements ranging from Na to Pb) in heavy metals polluted waters.

Samples were prepared by drying on a Prolene film producing a thin layer. Spectra were evaluated integrating the peak area instead of the commonly peak net intensity used in WDXRF. The limit of detection and sensitivities were calculated for all the elements using 3 different multielemental standard solutions. Limits of detection were improved respect to other studies obtaining limits of detection ranging from 0.005 to 0.1 $mg \cdot L^{-1}$.

Several mine water samples were analyzed and the results from the WDXRF method were compared with the results from Inductively Coupled Plasma spectrometry methods (ICP-MS and ICP-OES). The WDXRF results show a good agreement for the elements of $Z>20$ and some discrepancies in the elements with $Z=<20$.

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PB-44

XRF determination of metals in water using Polyurethane foams

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In this paper we propose a new high-performance technique of X-ray fluorescence (XRF) determination of metals (iron, cobalt, manganese, lead, and mercury) collected on polyurethane foam (PUF) discs using different chemical reagents (KSCN, PAN, and dithizone) in drinking and natural water. Analysis of PUF discs after the metal sorption from water was carried out by a portable wave-dispersive X-ray fluorescence spectrometer *Spectroscan* (Spectron). The mechanisms of metal sorption in the presence of KSCN, PAN and dithizone on PUF discs were studied and the optimal conditions for metal sorption were found. The combined sorption and XRF technique was checked using the method "added – found" and it was proved to give good results for determination of metal contents in water in the range of 10^{-2}-10 μg ml^{-1}. The technique developed is very simple, cheap and rather quick, does not demand complicated device and expensive chemicals and can be used for routine and field analyses and monitoring research. It allows to carry out simultaneous multielement analysis, does not need PUF discs to be colored and does not demand all the solution impurities to be masked or removed. We used our new combined sorption and XRF technique for determination of the contents of metals in drinking water from different sources and manufacturers, in Moscow tape water, in natural water from two Moscow rivers and several ponds, in winter and spring snow.

PB-45

WDXRS of minor and trace element contents in the soil of moscow's park

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Within recent years Moscow traffic increased greatly that made the ecological situation of the capital much worse. The topsoil is a strong absorber of many chemical elements keeping them in the surface, the most fertile layer. Thus, changes in the chemical contents of surface soil layer reflect adequately environmental cumulative alterations conditioned by the effect of both local and global factors. The aim of the present study was to determine concentrations of some chemical elements in topsoil samples of the Wooded Experimental Dacha (WED) belonged to the Moscow Agricultural Academy (MAA) using wave dispersive X-ray fluorescent spectroscopy (WDXRS). A simultaneous analysis of sub-samples of the CRM IAEA Soil-7 reference material was used to estimate the method reproducibility and the accuracy of the obtained results.

Contents of As, Ba, Br, Co, Cr, Cu, Fe, Mn, Mo, Nb, Ni, Pb, Rb, Sr, Th, Ti, V, U, Y, Zn, and Zr were measured using ARF-6 Analyzer (Ag-, Mo-tube) and SPM-25 Quantometer (Rh-tube). Measurements of 100s duration were carried out twice. The $K_{\alpha1}$-lines were used to register intensities of characteristic X-ray of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Rb, Sr, Y, Zr, Nb, Mo, Ba and $L_{\beta1}$-lines - Pb, Th, and U. The sample matrix effect was account by noncoherent scattered K_{α}-line of the X-ray tube.

The total contents of all investigated chemical elements in the topsoil of WED of MAA were in the range characteristic for “norm” or “clean” soil and do not exceed Russian environmental quality standards. For example, mean concentration of Pb equal 17.9 mg/kg (range 12.5-24.8 mg/kg) is under Russian environmental standard limit (32 mg/kg) and more less than Pb level in park soil of many cities of West Europe and North America.

PB-46

Application of a portable EDXRF spectrometer for in-situ measurement of pollutants in over-bank sediments of Mati River (Northern Albania)

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The recent interest in assessment of environmental pollution has created a growing need for in-situ analysis of a variety of pollutants in samples of different kind. Field portable EDXRF instruments offer great possibilities in this kind of activities.

The measuring head of the portable EDXRF spectrometer assembled at our laboratory includes a Peltier-cooled Si-PIN X-ray detector (XR-100CR, AMPTEK INC., USA) and a Cd-109 disc source (740 MBq) mounted in an orthogonal geometry. The spectrum acquisition system consists of the power supply and amplifier (PX2CR), Pocket MCA 8000A and palmtop computer (HP200LX). The spectrometer allows the multielement analysis of soil and sediment samples with acceptable analytical parameters. The calculated detection limits vary from about 2500 ppm for K to about 25 ppm for Cu and up to about 5 ppm for the elements from Rb to Zr. The precision for major elements is generally better than 5%, while for most of the minor and trace analyzed elements its values are within 10%. Generally a good agreement is observed between the measured and recommended concentrations of standard reference materials (SRM).

Overbank sediments of the Mati River are contaminated due to former Cu mining and metallurgical activities in the drainage basin. The concentrations of four major and twelve trace elements are determined by the in situ measurements of the different cross sections of overbank sediments. The results show that the main pollutants are Cu, Zn, As and Se which as confirmed by Factor Analysis are related with two main sources: copper metallurgy and copper ore processing plant. In the same time the results permitted not only the evaluation of the contamination but also the possibility to give an indication of the contamination history of the studied sediments.

PB-47

Determination of Mo, Nb, Zr, Y, Sr, Rb, U, Th, Pb in different rocks by X-ray fluorescence analysis

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Nowadays there are many techniques to determine Mo, Nb, Zr, Y, Sr, Rb, U, Th, and Pb in different rocks [1, 2]. During last 17 years we have accumulated the practical material on the application of XRF to the quantitative determination of contents of main and trace (C, F, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Mo, Ba, La, Ce, Pb, Th, U, W,) elements [3]. With progress in new technologies of substance study and development of analytical instruments of new generations the analytical studies are necessary in order to improve the techniques already existed for the quantitative determination of chemical compositions of different geological materials.

This report presents our technique for the quantitative determination of Mo, Nb, Zr, Y, Sr, Rb, U, Th, and Pb contents in different rocks using the S4 PIONEER automated X-ray spectrometer. The optimum parameters and measuring conditions were chosen for each element determined. For the accurate determination of contents of elements under analysis the contribution of foreign radiation to an experimental intensity of analytical line has been taken into account: for $\mathrm{MoK}_{\alpha1}$ – $\mathrm{ZrK}_{\beta1}$, for $\mathrm{ZrK}_{\alpha1}$ – $\mathrm{SrK}_{\beta1}$, for $\mathrm{YK}_{\alpha1}$ – $\mathrm{RbK}_{\beta1}$, for $\mathrm{NbK}_{\alpha1}$ – $\mathrm{YK}_{\beta1}$, for $\mathrm{UL}_{\alpha1}$ – $\mathrm{RbK}_{\alpha1}$, $\mathrm{SrK}_{\alpha1}$, for $\mathrm{ThL}_{\alpha1}$ – $\mathrm{RbK}_{1\alpha}$. To correct interelement effects the background standard method was used. When calculating Mo, Nb, Zr, Sr contents the incoherently scattered characteristic radiation of the X-ray tube anode was used as the standard. When calculating Y, Rb U, Th, and Pb contents the radiation intensity was used as the standard that was measured at the angular position $2\theta = 29^\circ$. We successfully used this angular position before.

When calculating the calibration characteristics the certified reference materials of rocks of different compositions were used. The ranges of determined contents were as follows (in ppm): Mo – 10-260, Nb – 3-380, Zr – 50-990, Y – 5-130, Sr – 5-3200, Rb – 11-1900, U – 2-63, Th – 2-130, and Pb – 5-490. The metrological studies were conducted to estimate the accuracy of results of analysis of elements determined. The values of the relative root-mean-square deviation of determination errors do not exceed the values of permissible root-mean-square deviations of the relative error of results of analysis made by the methods of I-III categories of the classification.

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PB-48

Application of High-Energy Polarised-Beam EDXRF for the study of metal burden in mining waste samples

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Environmental metal pollution as a result of abandoned mining activities is an acute problem nowadays. Although mineral resource extraction has been carried out for centuries, until the last several decades, relatively little attention has been given to minimise the metal dispersal around this areas coming from the indiscriminately dumping of mining waste. As a consequence, one of the challenges facing society today is the identification, evaluation and remediation of these old disused areas to protect public health and environment quality. These studies are heavily depending on observation and quantitative measurements of the amounts and distribution of metals, leading to the necessity of appropriate analytical methodologies.

The work presented is based on the application of High-Energy Polarised –Beam EDXRF spectrometry (HE-P-EDXRF) for the study of metal burden in the remains of different flotation ponds from an abandoned Pb-Zn mining area located in the northern part of Spain. A typical feature of these kinds of spoils is the high heavy metal content, mostly Pb and Zn (up to $g \cdot kg^{-1}$), but also the presence of other minor and trace metals associated with sulphide ores such as copper, iron, arsenic and cadmium (up to $mg \cdot kg^{-1}$) which are also of significance due to their high toxicity even at low concentrations. Additionally, for each mining waste sample, four different size fractions (<500μm, <250μm, <125μm and <63μm) were studied in order to assess the relationship between metal distribution and grain-size particles. It was found that lower size fraction contains higher metal concentrations that can dramatically influence the reactivity and mobility of metals and thus, the environmental impact.

PB-49

The seasonal variation of the elemental composition of particulate matter in Skopje, FYR of Macedonia

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Aerosol samples were collected at an urban background site in Skopje, FYR of Macedonia, during four measurement campaigns from December 2006 to October 2007. An impactor was used to collect aerosol particles in a $PM_{2.5}$ size fraction (total mass of particles with an equivalent aerodynamic diameter < 2.5 μm), and the samples were analysed for particulate mass, black carbon (BC) and seventeen elements (Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Pb). The 12 h average $PM_{2.5}$ concentrations varied in the range 10-140 $\mu g\ m^{-3}$ with the highest concentrations measured during wintertime pollution episodes and during the summer period. A statistical analysis of the dataset by means of factor analysis indicated large contributions to the aerosol from mineral dust (main observed tracers Si, K, Ca, Mn, Fe, Br), combustion sources (BC, S, Ni and Cu) and traffic (Pb, Zn). Combustions sources dominated during wintertime and were likely dominated by biomass burning and industrial activities within the city area. Mineral dust was observed throughout the year, but peaked during the unusually hot and dry summer of 2007. It is concluded that Skopje suffers from serious air pollution due to central and residential heating, the transport sector and industrial activities within the city. Topography and meteorological conditions aggravate the problems, and make the air quality comparable to the conditions in highly polluted mega-cities around the world.

PB-50

Design and development of an Energy-Dispersive X-ray Spectrometer: A tool for environmental research in Kenya

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Contribution of scientific research to local and international journals from Africa and indeed Kenya is weak in comparison to other regions. One of the main problems is the non-availability of reliable and affordable analytical instrumentation. Energy-Dispersive X-ray Fluorescence (EDXRF) analysis is a special analytical technique for trace elements in that it is economical and easy to use. Its analytical capacity has the advantage of having multi-elemental characteristics and satisfactory speed. Convectional EDXRF analysis is used in identifying toxic trace elements in the general environment, trace elements in airborne particles for source apportionment, investigation of micronutrients in different ecosystems and agriculture practices among other areas of scientific investigations.

A new EDXRF Spectrometer has been built and installed at the Institute of Nuclear Science and Technology, College of Architecture and Engineering, University of Nairobi. It is a new research tool that has improved local analytical detection limits of heavy metals in environmental and air pollution samples. A Siemens type D x-ray tube-stand was modified to facilitate x-ray irradiation of a Mo-secondary target. The target is a glued disk that was cut from a 1 mm thick Mo plate of 99.99 % purity. The fluoresced secondary x-rays propagate through three Ag collimators giving a near monochromatic Mo characteristic x-rays for sample excitation. The disk holder was designed to be easily removable, from the Al-measuring head, thus allowing the flexibility of carrying out experiments using different secondary targets. Air samples on Teflon filters and water samples on Cellulose filters were analyzed. The results were better than those obtained in previous spectrometer setups. The detection limits of trace elements improved by a factor of 10. The spectrometer is an extra facility for direct analysis of trace elements in air and other environmental samples.

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Abstracts
Poster Session C

PC-1

XRD and EDS investigations of metal matrix composites and syntactic foams

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Unidirectionally reinforced metal matrix composite blocks (MMCs), containing ~60 vol% carbon fibers were made by pressure infiltration technique. Two types of carbon fibers were applied; one had rather amorphous microstructure than other. X-ray diffraction (XRD) measurements were done to determine the quantity of intermetallic phase (Al_4C_3) in the interfacial zones. This is important because aluminium-carbide has strong influence on mechanical properties. XRD measurements showed that in carbon fiber reinforced metal matrix composites, which have higher quantity of amorphous carbon phase higher quantity of Al_4C_3 was formed. The crystallinity of carbon fibers was determined also by XRD method. When carbon fiber which contained higher quantity of amorphous phase was used, 18 times higher amount of Al_4C_3 produced.

Metal matrix syntactic foams filled with ceramic microballoons were produced by vacuum–pressure infiltration method. These cellular materials are closed cell foams, but they can be classified as MMC also. In the case of syntactic foams porosity – which is the main property of these materials – is generated by introducing hollow spheres (microballoons) into the matrix. In the syntactic foams different reactions can be happened between aluminum matrix and microballoons with high alumina and silicon content. The morphology and microchemical composition were investigated by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analysis, to clarify the kinetics of interphase reactions and the time–temperature dependence.

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PC-2

X-Ray diffraction studies on crystallography of Martensite in two Copper based shape memory alloys

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Shape memory effect is an unusually property exhibited by certain alloy systems, and the behaviour of shape memory alloys is evaluated on the basis of structural changes on the microscopic scale. The origin of shape memory effect is closely related to the changes in internal crystalline structure of materials caused by a phase transition, martensitic transition. This transition occurs on cooling from high temperature; and microstructural changes in microscopic scale govern this property.

Metastable beta-phases of noble metal copper based ternary alloys transform martensitically from the ordered structures to the layered structures on cooling from high temperatures. Martensitic transformations occur in a few steps with the cooperative movement of atoms less than interatomic distances by means of lattice invariant shears on a {110}-type plane of austenite matrix which is basal plane or stacking plane of martensite. Product phase in this transition has the unusual layered structures which consist of an array of close-packed planes with complicated stacking sequences called as 3R, 9R or 18R martensites depending on the stacking sequences on {110}- type planes of parent phase.

On the basis of austenite-martensite relation, it is experimentally determined that the basal plane of 9R (or 18R) martensites originates from one of the {110} -type planes of the parent phase, on which a homogenous shear occurs in two opposite directions with martensite formation. Furthermore, another step is hexagonal distortion of basal plane and at which atom sizes have important effect. The basal plane becomes ideal hexagon or distorted hexagon, respectively dependent on the equivalence or differences of atom sizes occupying the lattice sites.

Due to this distortion, the interplane distances of some plane pairs providing a special relation between miller indices become equal or different, and differences leads to disordering in martensite. In the present contribution, x-ray diffraction studies have been carried out on two copper based ternary alloys, which have the following alloy compositions in weight, respectively; Cu-26.1%Zn 4%Al and Cu-11%Al-6%Mn. X-ray powder diffraction profiles have been taken several times after post-quench heat treatments. These profiles reveal that peak locations of some diffracted planes change with ageing, and one can say that these changes lead to the disordering in crystal lattice of materials.

PC-3

X-ray study of composite materials based on montmorillonite organoclay

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Nanocomposites based on organoclay nanoparticles in the polymer or organic media draw much attention of researches due to their potential applications for the development of information record and storage devices, photonic crystals, opto-electronic equipment, etc. This work deals with the investigations of the nanocomposites based on montmorillonite modified with cetyltrimethylammonium bromide (CTAB) surfactant. The analysis of the results obtained by X-ray diffraction (small and medium angle ranges), IR-spectroscopy (400 – 4000 cm^{-1}, at the temperature range 100 – 400 K) and DSC methods is presented. The changes of the montmorillonite interlayer distances in the dependence on the sample preparation method, filler type and surrounding organic media are discussed. The nematic liquid crystal, 4-pentyl-4'-cyanobiphenyl (5CB) and glycol were used as fillers. The models for the CTAB molecule arrangements in the montmorillonite galleries are proposed and analyzed in the comparison way with other ionic surfactants containing longer alkyl chains. The possible mechanisms of the interface interactions between the solid particles and organic matrix are concluded from the IR-spectroscopy study. The phase transitions of bulk CTAB, CTAB-modified organoclay and the heterosystem of 5CB – CTAB-modified organoclay are investigated in the temperature range 100 – 400 K by the IR-spectroscopy and DSC methods. The possibility of the CTAB rotator phase display in the montmorillonite organoclay is demonstrated.

PC-4

Depth dependant nanolayer analysis of vertical sidewalls on structured wafers

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Complete cleans characterization plays an important role in today's semiconductor fabrication. This term summarizes investigations necessary to understand and improve cleaning processes, i.e. etch residue removal. Therefore, depth profiles as well as the chemical speciation of certain contaminants gain useful information.

Sidewall layers are of special interest but using most non-destructive analytical techniques they are only accessible with difficulties, e.g. ARXPS [1].The PTB developed an advanced alignment strategy to specify elemental depth profiling in sidewall layers on structured wafers by X-ray fluorescence analysis (XRF) [2]. Therefore total-reflection XRF (TXRF) [3] and grazing incidence XRF (GIXRF) techniques were combined employing monochromatized undulator radiation in the soft X-ray energy range. The investigated structures consisted of silicon bars with thicknesses in the µm and the nm range. On each sidewall a silicon nitride layer was deposited. Four different types regarding the bar thickness and density of these structures were examined. The developed alignment procedure consists of three main steps and allows for distinct excitation of sidewalls in the different structure types in order to provide information about depth dependant sidewall contamination, composition, layer thickness as well as chemical speciation. First results, obtained on these samples, demonstrate the potential of this technique.

The development of this alignment procedure enables measurements for cleans characterization and depth profiling on sidewall structures. The XRF methods used provide an enhanced information depth compared to ARXPS. Hence, layer systems with thicknesses of several 10 nm can be characterized.

However, there are requirements towards samples due to the size of the beam footprint: the structures must be of comparable dimensions to the ones presented here. Furthermore, it is necessary, that the structures are spread evenly across this field because the technique is based on the simultaneous excitation of multiple sidewalls.

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PC-5

Corrosion layers on steel and their XPS analysis

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This work is focused on the efficiency of corrosion inhibitors. Various types of corrosion layers were created for testing corrosion inhibitors. Steel samples (Czech Standard CSN 411373) were exposed to 6% $FeCl_3$ solution (by ASTM G48-03) for 1, 3, 5 and 7 days. Prepared corrosion layers were analyzed by XPS method on ESCA. Measured spectra describe surface conditions which are very important for following measuring of inhibitor's effectiveness. Surface properties markedly influence an inhibitory activity.

The inhibitors used in this study were triethoxy-3-(2-imidazolin-1-yl) propylsilane and T 440E, T 8529E (inhibitors used for industrial applications). Inhibiting effects were studied by the electrochemical method of measuring polarization curves (program Gamry instruments, software Framework 4/0). A steel electrode with total surface area of 2,2cm^2 was used as a working electrode and a second one as a reference and counter electrode for all electrochemical tests. The surface of the electrode was polished with 1500 silicon carbide paper and cleaned with ethanol. The electrodes were exposed in aggressive medium (S^{2-}, Cl^-, pH 3), simulating conditions in pipelines, with low concentration of oxygen. The measuring cell was irrigated with Argon during the experiment.

Electrochemical data were used to calculate corrosion efficiency. The results of measuring confirm a high efficiency of all corrosion inhibitors and usability as effective corrosion protection in pipelines. These experiments, mainly results of XPS analysis, are in order to know the effectiveness of these tested samples and to obtain a better understanding of the corrosion protection processes.

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PC-6

XPS investigations of nanoscale Ti-O-N films on silicon

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High surface sensitivity and excellent elemental sensitivity make X-ray photoelectron spectroscopy more and more popular because of growing interest in investigation of ultra-thin films for nanotechnology applications. When the film thickness doesn't exceed few nanometres, XPS allows to investigate film / substrate interface and reactions, which occur there as the result of thermal or radiation effects. Such investigations are essential in nanoelectronics where formation of undesirable bonds on the interfaces strongly influences on electric characteristics of obtained structures. The current work presents complex experimental study of ultra-thin (~5 nm) Ti, TiN, TiO_2 and TiN_xO_y films on silicon and Ti-O-N/Si interface with angle-resolved X-ray photoelectron spectroscopy. The films were grown by ion beam sputter deposition in controlled vacuum environment using cold cathode ion gun. Titanium foil of 99.99% purity was sputtered by argon ions with the 5 keV energy and 15 μA/cm^2 ion current density [1]. After deposition samples were transported from the preparation chamber to the analytical chamber without breaking vacuum. High-resolution XPS investigations were performed at the pressure of $5 \cdot 10^{-10}$ mbar with using of Mg-Kα X-ray radiation. The influence of substrate temperature during films formation and post deposition annealing on elemental composition and chemical state of obtained films and film/substrate interfaces were investigated.

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PC-7

Analysis of XPS spectra of metal oxides on corrosion surface

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Pitting and crevice corrosion are dangerous forms of localized corrosion. They result from a failure of passive film. Well-known examples include weld zones, surface deposits, rivets, and steam generator tubes.

Austenitic stainless steel 08CH18N10T was used for this study. The alloy had a composition about 20 % Cr, 10 % Ni, min. 0,5 % Ti. An autoclave simulating the secondary side of a steam generator was used at 300°C and 10 MPa, water solution, 100 mg/l NaCl and pH 10. Crevice sample was formed under Teflon block. Exposure samples showed different state and damage of surface. Samples were investigated by metallographic and microscopic methods.

Metal oxide films were identified from X-ray photoelectron spectroscopy (XPS) analysis. The XPS study was carried out using ESCAProbe P apparatus (Omicron Nanotechnology Ltd.) equipped with Al Kα (1486.6 eV) X-ray source with monochromator and hemispherical analyzer. The size of the analyzed area was approximately 1 mm^2. Ar ions (energy - 5 keV) were used for ion sputtering.

High resolution XPS spectra of metal surface where measured. The peak positions and peak shape of Fe 2p spectra were used to estimate Fe^{2+}/Fe^{3+} ratio on metal surface. Peak positions of Fe 2p, Cr 2p and Ni 2p depend on ionic states and determined chemical composition. The C 1s peaks of hydrocarbon were used for calibration of spectra.

The surface of the sample was examined on passive region, near pits, inside and outside crevice regions. Various compositions of metallic surfaces were determined. The XPS spectra of the surfaces were found useful for understanding the localized corrosion behavior.

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PC-8

Eu L_3 XANES investigations of the valence instability of $Eu_4Pd_{29}B_8$

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Intermetallic compounds containing Eu and other rare earth metals are subject of both experimental and theoretical interest since the oxidation state of these lanthanoides atoms can be influenced by chemical composition, temperature and pressure. In intermetallic Eu compounds, this may result in structural phase transitions as found for the mixed-valence phase Eu_4P_3 at 8 GPa [1] or a complete change from valence state Eu^{2+} to Eu^{3+} between ambient pressure and 9 GPa in $EuNi_2Ge_2$.[2]. Recently, the tendency to valence fluctuation observed experimentally for the perovskite-like $EuPd_3B_x$ phase were confirmed by theoretical calculations [3] and motivated us to investigate the valence stability of Eu in ternary phases of the system Eu-Pd-B.

The temperature dependent XANES studies of the new phase $Eu_4Pd_{29}B_8$ were recorded at the beamline A1 of Haslab at Desy. The spectra near the Eu L_3 edge at T = 5 K and 85 K show one dominant maximum reflecting the contribution of Eu with $4f^6$ (Eu^{3+}) configuration. Additionally, both low-temperature spectra reveal a shoulder on the rising edge of the white line that indicates a small contribution of the $4f^7$ (Eu^{2+}) state. This shoulder is significantly stronger in the spectra at room temperature and shows the increasing contribution of the $4f^7$ (Eu^{2+}) state at higher temperature. The comparison of the spectra at different temperatures indicates that the valence change of Eu takes place mainly in the temperature range 85 K < T < 293 K, but a complete $4f^6$ (Eu^{3+}) state is not reached down to T = 5 K. Magnetic susceptibility measurement shows an upturn below 55 K and a broad maximum at approx. 140 K. While the Curie law at lowest T (2 K < T < 40 K) corresponds to ≈ 7 % Eu^{2+} species, at highest T (400 K) the moment suggests the presence of nearly 50 % Eu^{2+} species.

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PC-9

Chemical speciation of unknown uranium ore and mine tailings particles with µ-XANES and µ-XRD methods

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Uranium as a necessary raw material for the nuclear fuel cycle is usually extracted from uranium ore. There exists only one uranium ore deposit in Hungary that is located in the south of the country at the foot of the Mecsek Mountains at the western border of the city of Pécs. A wide variety of uranium minerals exist in the Mecsek Mountains: uraninite, pitchblende, soddyite, autunite, liebigite, zippeite, uranopilite and clarkeite. Recognition of uranium species in U-rich particles from unknown uranium ore samples and unknown mine tailings particles was the aim of the investigations described in this work. The particles came from the ore and the mine tailings of the closed uranium mine.

Uranium particles were pre-selected with laboratory micro-XRF technique at KFKI AEKI. Mineral composition of the particles and the oxidation state of uranium in the particles was investigated at the micro-fluorescence beamline L at HASYLAB (Germany) using µ-XRD and µ-XANES. For simultaneous µ-XRF and µ-XRD, the energy of the synchrotron radiation was tuned to 21.0 keV. The diffraction images were recorded using a MarCCD camera. For µ-XANES UO_2, UO_3 and U_3O_8 particles were used as standards.

The chemical state of uranium in the mine tailings particles were 50–80 % in the less mobile U(IV) but many uranium minerals contain uranium in the U(VI) form. For the investigation of the oxidation state of uranium µ-XANES is a very efficient method. It can give us information one of the elements but sometimes this information is not sufficient. Micro-XRD was used as a complementary method for deriving the mineral composition of the particles, because many times uranium has the same oxidation state in the particles and more information needed.

PC-10

Structural characterization of Sulfur vulcanized natural rubber using X-ray Absorption Near-Edge Spectroscopy

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X-ray absorption near-edge spectroscopy (XANES) is an advantage technique based on synchrotron light application on chemical structure determination. At presented here, the chemical structures of sulfur contained in the vulcanized natural rubber (NR) by efficient vulcanization (EV), semi-EV, and conventional system (CV), were studied using XANES at beamline-8 equipped with Si 111 double crystal monochromator of the National Synchrotron Light Source Center (NSRC), Thailand. All samples were controlled of the thickness of rubber sheet and the vulcanization temperature. The XANES results have been illustrated the bonding of sulfur in the CV, EV and semi-EV system of the NR vulcanization as polysulfidic, monosulfidic, and both poly- and mono-sulfidic crosslinks, respectively.

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PC-11

Structure peculiarities of catalytically active gold nanoparticles by EXAFS and XANES spectroscopy

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It was shown recently that the Au particles of less than 5 nm in size supported onto various metal oxides exhibit the extraordinary high catalytic activity in some reactions.

A series of Au/δ−Al_2O_3 and Au/carbon catalysts prepared by the different procedures and differing in the mean Au particle diameter (d = 2-30 nm) was tested in CO oxidation. Gold particles for the model samples prepared by the deposition of metallic gold in UHV on Si(111) and Si(100) planes of single crystals. The AuL_{III} XAFS spectra were measured at 12 K, 296 K at the BM26 beamline of the ESRF (Grenoble, France) and at the VEPP-3 storage ring of the BINP (Novosibirsk, Russia) [1].

In spite of variation in the *d* value, the XANES spectra indicate no visible changes in electron states of Au and the absence of gold oxide species in all samples. Interatomic Au-Au bond length (R) and first–shell Au-Au coordination numbers (*N*) decrease and Debye-Waller factors increase from these samples to the samples containing the smallest Au particles with the average number of Au atoms equal to 100 - 200 atoms. The Debye-Waller factor for the most dispersed catalysts measured at 12K is about three times higher than that for the bulk gold, while this variation is only 10% at 296K. A gradual reduction of the Au-Au bond length (0.002-0.003nm) and variations in other microstructural parameters of Au nanoparticles are in line with an increase in their catalytic activity in CO oxidation.

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PC-12

EXAFS effects around K-edge in Lanthanum

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Total photon cross-sections in Lanthanum were determined at nine energies in the range of 30 keV-55 keV using secondary excitation method and deviations were observed near the absorption edges. Gamma photons of energy 59.54 keV from ^{241}Am radio active source were used to obtain characteristic X-rays of various energies from rare earth oxides Nd_2O_3, Sm_2O_3, Gd_2O_3 and Dy_2O_3. K_α and K_β X-rays thus obtained were used to determine photon cross-sections in La_2O_3. The experiments were carried out by employing a modified narrow beam geometry and a HpGe detector. The measured values of total photon cross-sections were used to deduce elemental cross-sections in Lanthanum. The experimental values were compared with those determined by other investigators[1, 2, 3] in the above energy range and also with theoretical values obtained by summing photo-electric cross-sections of Scofield[4], coherent scattering cross-sections of Hubbell and Overbo[5] and incoherent scattering cross-sections of Hubbell[6] etal. Deviations from theory were observed near the absorption edges. A deviation of about 23% was observed at an energy 686 eV away from the edge which indicates the existence of EXAFS effects around absorption edges.

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PC-13

Environmental analyses by TXRF - NEXAFS and IR-Spectroscopy: Speciation of Bromine in organics andcharacterization of the organic matrix

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Reference-free total-reflection X-ray fluorescence analysis (TXRF) [1] allows for the absolute determination of minute mass depositions on semiconductor surfaces. The use of tunable synchrotron radiation enables the speciation of compounds and functional groups by near-edge X-ray absorption (NEXAFS) spectroscopy. When combining reference-free TXRF and NEXAFS, a spectroscopic tool is formed capable to assess the bonding state of minor components in minute amounts of organics without any prior chemical pre-treatment or sample preparation, thus certainly preserving the chemical state of a trace component of interest: By a simple mechanical abrasive technique just a few ng of flame retardants (FR) [2] were deposited on a clean surface of a 200 mm silicon wafer. Initial results confirm the theoretical prediction and demonstrate the potential of the TXRF-NEXAFS method to successfully contribute to the elemental speciation, even of trace elements such as Br in FR.

In a case study involving the speciation of Br in various FR samples, Synchrotron-based IR spectroscopy in reflection mode was employed to characterize the organic matrix. The study also serves to assess the potential of this methodological coupling for the analysis of preparation-free deposition of nanoparticles such as aerosols in the field of environmental science. Trace component analysis reveals its importance in public control such as RoHS directive.

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PC-14

XAS on surfactant-based nanostructured V_2O_5 thin films: monitoring short and long range order from mesophase residual to crystalline network

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X-ray Absorption Spectroscopy (XAS) has been employed to characterize sol-gel derived surfactant-based nanostructured V_2O_5 thin films. The experimental data have been collected in Total Electron Yield mode on the GILDA BM08 beamline at ESRF, Grenoble, France.

In the XANES region, all samples show the characteristic pre-edge peak, with intensities comparable to that found in the orthorhombic V_2O_5 reference, suggesting an axial configuration very similar to the crystalline phase ($RO_A \approx 1.58$ Å, $RO_{Along} \approx 2.78$ Å). On the contrary, the near edge features depend on the different surfactant used (Brij®76, Tween-60 and Triton X-100), and show peculiar behavior suggesting differences in the symmetry of the equatorial oxygen atoms.

EXAFS analysis has shown a low temperature crystallization of the orthorhombic V_2O_5 phase. For all the annealing temperatures, even for samples heated at 250 °C, the VO_5 unit is detectable showing that the short range order is preserved even when the surfactants are present in the metal oxide network. Ordered VO_5 units are consistent with relatively low σ^2 values of the first shells of oxygen around the absorbing V_0 atom. Moreover, the possibility to extend the R-region of the fit up to 4.2 Å shows the good crystalline quality of the synthesized nanostructured thin films.

Slight discrepancies with the orthorhombic structure can be detected in the shells of the apical long V–O bond, linking adjacent vanadium oxide layers and on the nearest vanadium neighbors, located at $R_{V1} \approx 3$ Å. The discrepancies are eliminated by the thermal treatment, causing more order into the metal oxide framework. The final products (i.e. the high temperature samples) show EXAFS experimental $\chi(k)$ functions corresponding to those obtained in the commercial orthorhombic V_2O_5 powder.

PC-15

X-ray fluorescence determination of $FeO/Fe_2O_3^{total}$ ratio in rocks.

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Determination of chemical states of iron as Fe^{2+} and Fe^{3+} in rocks is of interest for geochemical, petrological and mineralogical research. Wet chemistry is the main technique to determine bivalent Fe. In 70s it was reported that ratio Fe^{2+}/Fe^{3+} in minerals can be ascertained by EPMA using the ratio of the X-ray intensities of Lβ and Lα lines [1]. Accuracy of EPMA determination of (Fe^{2+}/Fe^{total}) in amphiboles ranges from 6 to 20% [2]. In paper [3] it was recommended to define the chemical state of iron and some others elements using X-ray fluorescence with lines of K-series. The advantage of X-ray fluorescence technique is a low cost of preparation, as compared to wet chemistry.

In this work the possibility to estimate the ratio (FeO/Fe^{total}) in rocks using the K and L series of the x-ray florescent spectrum is studied. Measurements were carried out on a WDX Spectrometer S4 Pioneer (Bruker AXS). Accuracies of determination of (FeO/Fetotal) with the ratio of $K_{\beta5}/K_{\beta1,3}$ and L_β/L_α were compared through the samples of single mineral powdered fractions, e.g. garnet, pyroxene, ilmenite, amphibole and magnetite. It was found that the $K_{\beta5}/ K_{\beta1,3}$ ratio as an analytical signal, is preferable (using ratio L_β/L_α the correlation factor was less than 50%, with $K_{\beta5}/ K_{\beta1,3}$ it is over 80%).In the Table the relative standard deviations of FeO content determination for 46 reference standard materials of igneous rocks are shown for different range of (FeO/Fe^{total}) and different ranges of FeO content.

Range of FeO/Fe^{total}	Range of FeO,%	Number of samples	Relative standard deviation, %
>0.45	0,5-5,0	16	16.17
	5.0-20.0	19	5.51
<0.45	0,20-5.0	11	12.59

The accuracy of wet chemistry varies from 5 to 15%. As evident from Table, the X-ray fluorescence technique can ensure a comparable accuracy or a bit worse. However the XRF is adavntageous as it is express and has low cost of preparation; and it is can be used for routine analysis in geochemistry.

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PC-16

X-ray tracing study of crystall spectrometers for WDXRS application

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Construction of wavelength-dispersive crystal X-ray spectrometer, used in high resolution wavelength dispersion X-ray emission spectroscopy (WDXRS), may result in geometrical aberrations, such are systematic X-ray line shifts and changes of the X-ray line shape. Most of these aberrations can be reduced by a careful design of a crystal spectrometer, maintaining efficiency of the spectrometer as high as possible. Since experimental investigation of impact of WDX spectrometer design on aberrations is difficult, a numerical X-ray tracing procedure has been applied for this purpose, with output in the form of a 2-dimensional virtual X-ray intensity array on the detector surface or in the form of virtual X-ray energy spectrum.

PC-17

Spectrum modelling and influence on chemical state analysis using WDS-PIXE system

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The Tandem accelerator facility of the Ruđer Bošković Institute is equipped with high resolution wavelength dispersive spectrometer system (WDS) used for chemical state analysis by PIXE method. In our recently performed analysis of vanadium and titanium samples, the most important conclusions are derived from relative intensities and energies of the $K\beta_5$ and $K\beta''$ X-ray lines extracted from fitted $K\beta$ spectra [1]. In some cases results of analysis are very sensitive on the fitting procedures, especially on how they handle absorption K edge feature. In this work we report the influence of fit models on analysis of spectra and final interpretation of chemical states.

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PC-18

DLC layers on biocompatibile Ti alloys

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The principal materials for fabricating implants are usually metallic alloys, which have suitable mechanical and corrosion properties. Titanium and its alloys are widely used nowadays. In this work, we studied a thin layer appearing at the surface of samples of Ti and Ti alloys during electroerosion, which produce the high surface roughness suitable for good binding of material and tissue. The chemical composition of the carbon-based gradient layer was inhomogenious and the depth profiles of Ti, C and O in the layer were found by RBS. By Elastic Recoil Detection Analyses method the hydrogen content was analyzed [1]. The first estimation of layer thickness was about 0.5 μm, but during repeated measurement we have found it was inhomogeneous.

The layer thickness and composition was measured by both RBS method and Electron Probe X-ray Microanalysis (EPMA) and evaluated by suitable software [2]. Due to its high roughness, the reliability of ussual measurement by EPMA is low. Thus, the modified method using P/B ratio instead of X-ray intensities [3] was used for thickness and composition calculation. Simultaneously, the layer thickness was measured directly in SEM from cross-section samples approximately at the points of RBS and EPMA measurement. The results obtained by all the methods were in reasonable agreement.

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PC-19

Cement analysis for ASTM C114 by using bench-top WDXRF

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A newly developed bench-top WDXRF (Supermini) was applied to cement analysis for ASTM C114 qualification, which is a test method for chemical analysis of hydraulic cement. The equipment is a compact sequential spectrometer measurable from Fluorine to Uranium equipped with a new 200W Pd target X-ray tube and no cooling water is required.

The evaluation for the ASTM C114 was performed for both fused bead method and pressed powder pellet method. Empirical calibration curves for 13 components (CaO, SiO2, Al2O3, Fe2O3, SO3, MgO, K2O, TiO2, Na2O, P2O5, MnO, Cl and ZnO) were created by using NIST SRM's for cement. By using the theoretical alphas to correct for the matrix effect, accurate calibration curves could be obtained in both fused beads and pressed pellets even for Na2O. The results of duplicate sample analysis demonstrated the qualification for both of the differences between duplicates and the differences between the averages of duplicates from certified values. These results show that the spectrometer has adequate performance for both powder and fused bead method for cement analysis within affordable measuring time. This spectrometer can be used not only as backup system but also as master equipment instead of high power XRF in cement analysis.

PC-20

XRF application in the early prostate cancer diagnosis

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The method for prostate cancer diagnosis based on the measurement of zinc concentration in prostatic fluid was previously reported by us[1]. It was found that prostatic neoplasm resulted in sufficient about 25-fold decrease in zinc secretion in comparison with the normal level. At the same time, no changes in the Zn content were found for chronic prostatitis and adenoma as well. The EDXRF device with a Si(Li) detector and ^{109}Cd sources was particularly developed for precise determination of zinc concentration in the drop of prostatic fluid with volume in 20 µL only. The 10 min exposure made it possible to determine zinc in the most fluid specimens with a relative uncertainty no more than 5%.

In present study only this test for prostate cancer screening of 598 men, Obninsk residents, aged above 60 and without any pre-clinical manifestation of prostate diseases was used. Expressed prostatic fluid was conventionally obtained by digital rectal massage. The concentration under 100 mg/L was set as a limit for the selection of cancer risk group counted in 34 subjects. All of them were invited to the Department of Urology for more detailed examination under hospital conditions including common clinical, X-ray, ultrasonography and biopsy's morphology data. The probability of cancer cases in the risk group formed on the basis of zinc secretion results approached 30%. In the other words, the amount of wrongfully positive conclusions about 70% were at least not worse than PSA-test (prostate specific antigen test) data. However, the cost of EDXRF of Zn in prostatic fluid is much less and the method do not need in pierce the vein.

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PC-21

The skin barrier function: a micro-PIXE study

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Today, man is perpetually subjected to environmental exposures as sun, natural, urban or industrial pollutions and societal exposures. Skin is the main physiological barrier facing to these different stresses; however its response mechanisms are still not well understood. So, skin models are necessary to understand skin physiology and behaviour in normal conditions or under stress. Because of the large natural inter-individual variability and of some difficulties in obtaining human skin biopsies, we are working on the development and characterization of different skin models such as reconstructed epidermis in vitro, native pig skin and human keratinocyte cells. These models allow us to study the mechanisms involved in ion homeostasis in correlation with structural organisation and biological responses. We have undertaken the characterization of these models using a combination of original analytical and imaging techniques like micro-PIXE, epifluorescence and confocal microscopy. The aim is to evaluate the distribution of inorganic ions under normal or stress conditions, the transepidermal penetration of external agents, together with the cellular morphology to better understand the barrier function of the skin.

PC-22

Use of hydroxyapatite bone composites for the calibration of *in vivo* EDXRF-based systems for bone strontium quantification

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Various metals, most notably lead and strontium, have been quantified *in vivo* in human bone tissue using energy-dispersive X-ray fluorescence spectrometry-based systems. Calibration of these systems has tradiationally relied on the use of plaster of Paris (PoP) phantoms that are doped with the element of interest and calibration proceeds by the preparation of a standard calibration curve. For the *in vivo* quantification of bone strontium, calibration using the PoP method presents the significant challenge of strontium contamination (an inherent contaminate to calcium) and the required corrections due to calibration *via* a sulfate and not an apatite. This work presents the development and use of 'strontium-free' bone composites for the calibration of the *in vivo* EDXRF system, which allows for phantoms to be moulded easily into various geometries as needed, the purification of reactants ($CaCO_3$, $Ca(OH)_2$ and $CaHPO_4$) from strontium and the synthesis of continous phase carbonated or non-carbonated hydroxyapatite. The composite can be prepared easily and analytically with a short setting time and the setting liquid adjusted as to incorporate biological amounts of sodium, potassium, magnesium and other biologically relavant cations in the form of their respective hydroxides, if required. The method of phantom preparation described in this study ultimately results in a calibration curve for strontium with standards at concentrations that are lower than expected human bone strontium concentrations as well as a near 0 ppm phantom after purification of reactants using a 4,4'(5')-di-*t*-butylcyclohexano-18-crown-6 resin.

PC-23

Micro-PIXE and SEM study of endosseous implants surface and the implant material release in the surrounding bone tissue

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Titanium and its alloys are unambiguously considered as a preferred material for building bulk dental and orthopaedic implants. The debates about the implants surface treatment in view of possible metal release and eventual subsequently caused lateral effects however, are still opened. At present there is a number of developed implant surface treatment techniques which are based either on the implant surfaces roughening or appropriate implant surface coating in order to achieve a better osseointegration and to gain a shorter healing time as a consequence.

To evaluate the rate of the roughening procedure (and hence the effectiveness of bone anchorage) and to study the influence of the implant insertion on the surrounding tissue we have conducted a surface analysis of some commercially available dental implants. The tested implants have been made from a commercially pure titanium, roughened using different procedures such as: sand blasting (SB) with Al_2O_3, acid-etching, or a combination of both techniques. The titanium implants have been inserted in the tibia of New Zealand rabbits and after some period of insertion the animals have been sacrificed. A subject of interest has been also the implant material deposits on the interleave surface between the implant and the bone, as well as the implant material release in the surrounding bone tissue.

The study has been conducted using a microbeam-Particle-Induced X-ray Emission (micro-PIXE) technique and Scanning Electron Microscopy (SEM) analysis. The analyses were carried out using a proton microprobe set up of the 2 MeV Van de Graaf accelerator beam line at the National Laboratories of Legnaro, INFN and with the EDAX XRF-EDS of the University of Padua, (Italy). Maps of the elemental distribution drawn for the specific regions of interests have been studied.

The analysis of the elemental maps drawn using micro-PIXE as well as the analysis of the SEM images confirms the conclusions made in our previous investigations indicates that Ti released into the *peri*-implant tissues appears mainly as small-size debris. Analyses of the bone tissues in depth shows a presence of SB debris eventually drifted the implants through the harvesian canals of the compact bone structure.

PC-24

PIXE and PIGE assessment of *in vivo* elemental and physical changes of a composite from a dental filling

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Although successful in dentistry, composite fillings convey foreign elements in organism, degrade chemically and mechanically, and favor secondary caries formation. To reduce the latter, the new biomaterials release $F^–$ and Ca^{2+} ions. We analyzed by PIXE and PIGE such a composite removed surgically from an old dental filling of a patient's tooth and its elemental composition changes. The filling was sectioned centrally, and its outer and inner surfaces were examined comparatively, together with flat samples of the composites Ariston and Tetris Ceram (Ivoclar-Vivadent, Liechtenstein), Valux Plus and F2000 (3M Dental, USA) and of five Romanian products (Restacril). The specimens were irradiated at 45° with 3.0 MeV protons and PIXE spectra were collected with a HP Ge detector. PIGE spectra were recorded between 0 and 300 keV with the same detector at proton energies of 3.00, 3.20, 3.37 and 4.19 MeV.

The filling was identified as Tetric Ceram by similar concentrations of Ca, Fe, Sr, Zr, Ba, Yb and Hf. However, Ba and Yb were partly lost, and Cl and K were massively accumulated from saliva. PIGE showed an important decrease of F (110 and 197 keV) and the quasi-disappearance of Al (170.7 keV). The results suggest the partial dissolution of composite's particles of YbF_3 and of Ba aluminofluorosilicate glass, and to less extent of Ca fluorosilicate glass. The inner section's composition was similar to the outer surface's, pointing to the diffusion of $Cl^–$, K^+ deep inward and of $F^–$, Al^{3+}, Yb^{3+}, Ba^{2+} outward the filling. However, the ratio F(197)/F(110) was lowered outside and unchanged inside, suggesting some matrix physical structure alteration (non-uniformity) only at surface. Thus PIXE and PIGE showed that during the *in vivo* use of a dental composite chemically similar changes occur at surface and in bulk, but the surface is somewhat altered physically.

PC-25

Single detector PIGE and PIXE analysis of dental composites

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PIGE is widely used for analyzing light elements as a complementary method to PIXE. In particular, fluorine is analyzed by the 110 and 197 keV γ radiation from the $^{19}F(p, p'\gamma)^{19}F$ reaction at energies around 3 MeV. Fluorine helps the maturation and protection of teeth, and added in dental composites prevents secondary caries. We examined the feasibility of detecting fluorine by PIGE together with heavier elements by PIXE using protons and a single low energy HP Ge detector, a technique with the advantage of simplicity, and we tested it on F-rich dental composites. Flat samples of the composites Ariston and Tetric Ceram (Ivoclar-Vivadent, Liechtenstein), and reference materials including Teflon, NaF and metallic Al were analyzed. The samples were irradiated at 45° and at 3.0 MeV for PIXE, and for PIGE also at 3.20, 3.37 and 4.19 MeV, where the cross-section of F lines show maxima [1].

The composites evidenced mainly Ca, Zr, Ba, Yb and Hf by PIXE and F by PIGE. In addition, their PIGE spectra collected between 0 and 300 keV showed a line at ~171 keV, probably due to Al (170.68 keV). The PIGE detection limit for F was of ~0.2% with 3.0 MeV protons and of ~50 ppm with 4.19 MeV protons. However Al was best observed with 3.0 MeV protons. The cross-sections were material dependent. In the composites, F and Al arise as YbF_3, and Ca fluorosilicate glass and Ba fluoroaluminosilicate glass, respectively. As shown by the lower Ba and Al/F ratio, Ariston contained less of the latter glass than Tetric. The ratio F(198)/F(110) was slightly different in the composites, suggesting granularity differences. The results proved relevant for analyzing the dental composites, and encourage the technique's further development.

[1] A. Caciolli et al, NIM B 249 (2006) 98-100.

PC-26

A study by XRF and XRD of fossilized dinosaur bones from Spain

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We have addressed an XRF and XRD study on a collection of ca 30 Spanish dinosaur bone specimens referred to an age time range from 70 to 220 millions of years to investigate the fossilization in terms of physico-chemical properties. The fluorescence data show that the apatite of bones is containing the calcium and phosphorus elements and also strontium, which is expected for the case of herbivores. Further elements found at a significant level are iron, manganese and yttrium. The XRD patterns showed that a large fraction of the examined bones maintain an apatite-like structure, with the secondary presence of the calcite and quartz phases. In some cases we have also observed dolomite at varying level of concentration. The lattice parameters of the apatite phase appear to be subjected to changes on account of taphonomy and diagenetic processes involved. Also, the average domain size of the apatite phase roughly increases as a function of the age, with some noticeable outliers that deserve further discussion and interpretation.

PC-27

Elemental concentration in lead contaminated rat kidneys by EDXRF analysis

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There is a lack of knowledge about human and animal lead metabolism. However, it is known that kidney show substantially higher lead concentrations than other soft tissues, reflecting their importance in the lead excretation pathways [1]. It has been also determined that lead and lead compounds are reasonably anticipated to be human carcinogens based on limited evidence from studies in humans and sufficient evidence from animal studies (kidney tissue among others) [2].

Due to the many metabolic interactions among the different elements, it is important to study not only Pb, but also other elements which could be affected by toxicokinetic alterations.

In this study we have determined Pb, K, Ca, Fe, Cu, Zn and Br concentrations in exposed rat kidneys by Energy Dispersive X-ray Fluorescence (EDXRF) analysis [3]. The analysed samples belong to a group of adult *Wistar* rats (n=3) exposed to lead acetate since the fetal period and a control group (n=2) of the same sex and age. The obtained results show a steady level in exposed and control group animals for all detected elements except for Pb, where a strong increase was observed. All samples were analysed without any chemical treatment.

[1] L. Gehardsson, V. Englyst, N. G. Lundström, S. Sandberg, F. Steinwall, Journal of Trace Elements in Medicine and Biology, 9 (1995) 136 – 43.

[2] Agency for Toxic Substances and Diseases Registry's, US Department of Health and Human Services (2005).

[3] P. J. Custódio, M. L. Carvalho, F. Nunes, S. Pedroso, A. Campos, Journal of Trace Elements in Medicine and Biology, 19 (2005) 151 – 158.

PC-28

3D Micro-XRF under cryogenic conditions: A pilot experiment for elemental imaging in biological specimens

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For micro-XRF investigations of sections of biological and biomedical specimens it is mostly needed to section the samples physically with the risk to alter the sample structure and the chemical composition. In contrast, the 3D micro-XRF in combination with a cryo-fixation offers the possibility to scan arbitrary sites or sections of water-rich biological specimens without the need to cut them physically. To demonstrate the capabilities and prospects of this method a pilot experiment was carried out at the µSpot beamline of the synchrotron storage ring BESSY II. The spatial distribution of the trace elements Ca, Fe, Zn and Cu across virtual cross sections of the root of common duckweed was investigated with a resolution of around 20 µm and compared to a micrograph of a cross section of a root. Due to self-absorption in the specimen algorithms for absorption-correction had to be developed and were applied.

[1] B. Kanngießer, W. Malzer, M. Pagels, L. Lühl, G. Weseloh., Analytical and Bioanalytical Chemistry, 89 (2007): 1171-1176

PC-29

EDXRF Analysis of Thaumatococcus Danielli in Osun State of Nigeria

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Thaumatococcus danielli {*Marantaceae*} (Benn.) Benth. [Miraculous berry] is a multi-purpose perennial herb that is widely distributed in the tropical rainforest areas of West Africa. The leaves are simple, broad with slender stems connected underground to the perennial rhizomes. Farmers grow it in pockets within cocoa *(Theobroma cacao)* and kola *(Cola nitida)* plantations in South western Nigeria, Ghana and Cameroon. Propagation is mainly by rhizomes cuttings and occasionally by the seed. T. danielli plays very important roles in the rural economy generating income for the peasant farmers and traders. T. danielli is used mainly in three ways by the people. The leaves are used in food wrapping because of its very good flavour and its preservative ability; and roof thatching while the stem is locally used as straw in weaving mats and in making baskets, bags, hats, hand fans and other artistic works. Research has shown that the fruits of T.danielli contain low-calorie protein named "Thaumatin" which is about 2000 times as sweet as sucrose. The stems also can be processed to produce fibre industrially in addition to the industrial potential of Thaumatin. Thaumatin have been implicated to be suitable sweetener for diabetes patients. However, despite the great economic values, potentials and benefits of T. danielli, there is hardly any data on its elemental compositions. This work therefore presents the elemental composition of T. danielli plant's parts (leaves, stems, fruits (mesocarps), seeds and roots (rhizomes)) from six different towns in Osun State of Nigeria using Energy-Dispersive X-ray Fluorescence (EDXRF) spectrometry, and the EDXRF spectrometer facility at Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife, Nigeria supplied by AMPTEK INC., MA, USA. The results showed the detection of elements which include K, Ca, Fe, Mn, Sr, Zn, Pb, Br, and Cl at various concentrations. These very important novel results are presented and discussed.

PC-30

Why Lα:Lβ=1:1 in spite that the quantum mechanical intensity ratio is 2:1?

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In a typical EDXRF (energy dispersive X-ray fluorescence) spectrum, where the Lα intensity approximately equals to Lβ (Fig.1). Sometimes we observe spectra where Lβ is slightly stronger than Lα, depending on atomic number or spectrometer used. However, if you know quantum mechanics, after a tedious multiplet structure calculations including the spin-orbit interaction, the intensity ratio is expressed as $L\alpha_2$:$L\alpha_1$:$L\beta_1$ = 1:9:5. Since the observed Lα peak in EDXRF is composed of $L\alpha_1 + L\alpha_2$, thus Lα:Lβ = 10:5, or Lβ should be one half the intensity of Lα. In the present paper, we would like to show by experiments that the Lα to Lβ intensity ratio of various elements depends on (1) atomic number, (2) chemical state, (3) concentration, (4) X-ray tube voltage as well as target (Rh, W, …) for XRF, (5) electron acceleration potential for SEM, (6) EDX or WDX, (7) spectrometer resolution (slit used is fine or coarse for WDX), (8) filter, (9) detector counting efficiency, (10) grain size for powder or surface roughness for metal, and (11) solid or solution.

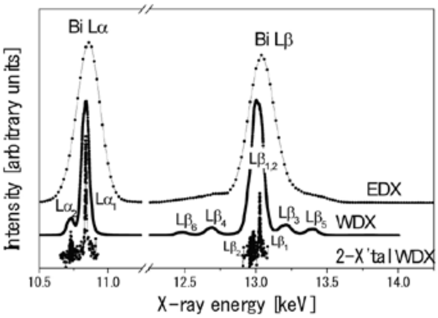

Fig.1 Spectrometer resolution dependent intensity difference.

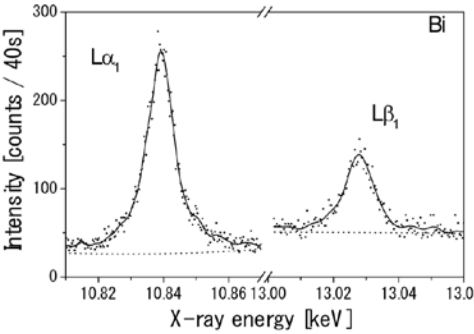

Fig.2 High resolution Bi Lα and Lβ measured by a double-crystal spectrometer.

PC-31

New approach for measuring fluorescence yields using tunable monochromatic radiation

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Most of the available experimental data concerning fluorescence yields have been determined more than forty years ago [1], and for low Z elements, the associated uncertainties are rather high. The lower Z, the lower ω_K, and the larger its associated uncertainty. For light elements, low ω_K means that the de-excitation process is preferentially done via an Auger transition, the X-ray photons being very few. To overcome the relative inefficiency of the X-ray emission for light elements resulting in large fluorescence yields uncertainties, Auger electrons counting should give better results.

Today, available experimental facilities, like monochromatic radiation (tunable X-ray source or synchrotron), improved semiconductor detectors should offer new perspectives of experimental measurements.

New experimental approaches are proposed, using the SOLEX facility [2] that produces a tunable monochromatic X-ray beam in the 1-20 keV range. SOLEX has recently been equipped with a new rotation system, thus the same monochromatic beam can be sent successively towards two different directions.

A first experiment reproduces a classical measurement system: the primary beam intensity is determined using a reference detector and then the same beam is sent under 45° incidence to the target whose fluorescence X-rays intensity is measured using another detector.

In a second step, there is no need for monitoring the primary since both the X-rays and Auger electrons are measured. However, acquiring a spectrum of emitted electrons as for photons is a challenging task. Experimental conditions are more demanding than for photons and detectors have to be carefully chosen. First experimental results and perspectives will be given as this experimental arrangement is conceived to be used on the metrology beam line of the SOLEIL synchrotron.

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[2] C. Bonnelle, P. Jonnard, J.-M. André, A. Avila, D. Laporte, H. Ringuenet, M.-C. Lépy, J. Plagnard, L. Ferreux, J. C. Protas, *Nuclear Instruments & Methods in Physics Research A*, **516** (2004) 594 – 601

PC-32

High-resolution X-ray analysis with multilayer gratings

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Periodic multilayers are nowadays widely used to perform x-ray analysis in the soft x-ray range (photon energy lower than 1 keV). However, they do not permit to obtain high-resolution spectra like natural or synthetic crystals. Thus, multilayers cannot manage some problems due to interferences between close x-ray lines. It has been shown and demonstrated experimentally [1] that patterning a grating within a multilayer structure leads to a diffractive optics having an improved resolving power.

We illustrate in this communication the use of a multilayer grating in the C K (around 280 eV) and Fe L (around 700 eV) emission ranges. In the C K range, we show that it is possible to separate the C K emission at the first diffraction order from the O K emission at the second order. We also show by comparing C K spectra from B_4C and cellulose that the shape of the emission band is sensitive to the chemical state of the carbon atom. In the Fe L range, the improved spectral resolution enables us to distinguish the Fe Lα and Lβ emissions (13 eV spin-orbit coupling). By using a sample made of a mix of LiF and an iron ore, we show that it is possible to easily resolve the Fe L and F K emissions. These examples demonstrate that an improved x-ray analysis can be obtained with multilayer gratings when there is the need to study samples having elements giving rise to close emission lines.

PANalytical is thanked for providing us with some analysed samples.

[1] R. Benbalagh, et al., Nucl. Instrum. Meth. Phys. Res. A**541**, 590 (2005).

PC-33

Post edge structure effects on mass attenuation coefficients

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The mass attenuation coefficient, [MAC], for any chemical compounds is usually estimated from the sum of the weighted contributions of the constituent elements, these contributions are additive and linear, a law known as Bragg's additivity law or the mixture rule is in common practice. The X-ray transmission, T, is defined as $T = I/I_0$, where I and I_0 are the observed intensities with and without absorber. This mixture rule ignores any changes in the atomic wave functions as a result of the molecular, chemical and crystalline environment and validity of the mixture rule is not well established in the soft and X-ray region and current methods of calculations are inaccurate at photon energies near any absorption edge and that experimental evidence of chemical effects is needed in particular close to absorption edges (Jackson and Hawkes, 1981, Jackson 1982, Saloman et al. 1988). Experimental results were presented by Deslattes (1969) Lakshminarayana et al. (1986), similarly, Kerur et al. (1993, 1994) have thoroughly studied photon cross sections at or near absorption edges and shown that deviations from the mixture rule occur as far as 1.2 keV above the edge, and also some 42 eV below the edge for transition elements.

In the present investigation, chromium compounds with purity 99.99% were chosen for the photon energy range from 5.895 to 14.439 keV to study the mixture rule. The X-ray spectrometer consisted of a Canberra make HPGe X-ray detector with a rated resolution of 200 eV at 5.898 keV and DSA-1000 stand alone system were used for measurements, all parameters of the X-ray spectrometer were set and the spectra was recorded and analyzed using Genie 2000 software. The long-time stability and linearity of the spectrometer were checked before data collection. Radioisotopes ^{55}Fe and ^{57}Co were used and both are electron capture source give their characteristic x-rays along with gamma rays, if present. The absorbers were prepared by blotting paper method (Kerur et al., 1993) so as to cover the transmission range $0.5 \le T \le 0.02$. The incident spectrum and the transmitted spectrum was obtained keeping the dummy and prepared blotting paper by gating the spectrometer at the area under photo peak. For each absorber, two to three times were measured on different area so as to cover whole area of the absorber. Finally, MAC was obtained by a least-squares method. For each specimen, MAC was determined two–three times to ensure a reproducibility within 2% for all samples. The measured values are compared with theoretical calculations. The disagreement between experiment and theory is larger than the experimental error when the incident photon energy is close to the K shell absorption edge. Further away from the edge the agreement between experiment and theory is within 3%. The breakdown of the mixture rule close to K absorption edges is discussed. *Acknowledgments:* One of the authors (BRK) is thankful to BRNS Office for providing the financial assistance to carry out the research project.

PC-34

Some cases of mineralogical effect due to the presence of crystals different from that one containing the fluorescent element

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Accordingly to Tertian and Claisse[1] "the mineralogical effect can be associated with variations in the fluorescence intensities of the order of 100% or more" and "presents serious problems to the analyst". However, references to this effect in the literature are very scarce. It is assumed to correspond to a diffraction phenomena originated into the crystal that contains the fluorescent element. Chandler et al[2] mention "the possibility of a well-aligned Bragg back-reflection, increasing the count rate of the upstream monitor detector", which was not quantified but ruled-out.

This paper describes some experiments by EDXRF where the mineralogical effect was evident by self-diffraction, and others that could only be explained by the influence of a crystal different than that one containing the fluorescent element. Results of the last ones show increases in the intensity of the Lα(Pb) higher than 50% when 10% Al was added to the matrix and higher than 100% in the intensity of Kα(Ca) with 10% K added. An analysis of the results is performed and the necessary conditions are proposed for 3 possible cases: enhancement by self-diffraction, enhancement by external diffraction and non-enhancement in spite of crystals presence. The variables considered are: fluorescent wavelength, inter-planar distance and the absorption coefficient.

[1] R. Tertian and F. Claisse, Principles of Quantitative X-Ray Analysis, Heyden & Sons Ltd. (1982), p. 311.

[2] C.T. Chandler et al, Radiation Physics and Chemistry, 61 (2001), 347-350

PC-35

On population dynamics of the atomic ensembles in a X-ray laser pulse: Optical bi-stability effect

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We consider the problem of interaction of the atomic ensembles with X-ray radiation. The results of numeric calculation of population kinetics of resonant levels for atoms in the X-ray laser pulse on the basis of the modified Bloch equations are presented [1]. Cited equations describe an interaction between two-level atoms ensemble and resonant radiation with an account of the atomic dipole-dipole interaction. It has been found a strengthen possibility of manifestation of the internal optical bi-stability effect special features in the temporary dynamics of populations for the atomic resonant levels under adiabatic slow changing the acting field intensity. The application of the cited effect in the nanoscience is discussed.

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PC-36

Study of the performance of two x-ray spectrometers in different matrix samples

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The aim of this work is to compare the features of two X-ray fluorescence spectrometers in order to evaluate their performances in different matrices.

Two non-commercial EDXRF spectrometers, a portable and a large dimension with tri-axial geometry one were tested using reference materials regarding different types of matrices.

Seven reference materials were analyzed, orchard leaves, (NBS-1571), clay (ISE-954), fish flesh (MA-A-2), animal blood (IAEA-A-13), bone meal (NIST-1486), 70% copper alloy (BCR-691) and 22ct gold alloy (Fischer).

The obtained results showed significant differences in the response of the two spectrometers for the different matrices.

Two case studies were also performed in order to appraise the performance of the spectrometers: two Portuguese coins from the XVIIIth and XIXth centuries and samples of animal tissues contaminated with lead.

PC-37

Construction and applications of the Cracow X-ray microprobe

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Since many years the IFJ PAN Institute in Cracow is using a nuclear microprobe to investigations in the field of biophysics, geology and materials science. Construction of an X-ray microprobe described in this presentation extended this research to interactions with focused beam of X-ray radiation.

As a source of X-ray an open type X-ray tube Hamamatsu L9191 with microfocusing down to about 1 µm spot is used. As exchangeable targets the Ti, Mo, Ag, and W were chosen. The microprobe will be used in the high resolution computer microtomography (CMT), to trace elements concentration analysis by µXRF and TXRF methods, and to radiation biology studies by irradiation of mammalian cells with targeted microfocused X-ray beam. In future also other measuring methods like SAXS or micro-crystallography are foreseen. The tube is emitting radiation into a cone of 120^0. When the formed beam, focused or parallel, is required, sets of elliptical or parabolic mirrors in the Kirkpatrick-Baez geometry are used. Low energy beam of 4.5 keV (Ti-K_α) used for the cell irradiations facility is focused by a pair of multi-layer mirrors produced by Rigaku (USA). Higher energies of 17.5 keV and 22.2 keV (Mo-K_α and Ag-K_α) in a stand for the µXRF and TXRF measurements are focused with the total reflection mirrors produced by Xradia (USA). Radiation of other energy ranges is used for the CMT only.

Details of the microprobe construction with special emphasis on the CMT method, its hardware, software, and the first experimental results will be presented.

PC-38

Micro X-ray Fluorescence Spectrometer with Low Power Tube for Light Element Analysis

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Micro X-ray Fluorescence (Micro-XRF) is a well established tool to determine the spatial distribution of major, minor and trace elements in a sample. It is widely used to investigate samples from different fields (biology, geology, life science, etc.). The method is non-destructive, requires little sample preparation and allows simultaneous multi-element detection.

Most available Micro-XRF spectrometers operate in air which does not allow the analysis of low-Z elements ($Z \leq 14$). To extend the analytical range down to light elements ($Z \geq 6$) a special micro-XRF spectrometer has been designed.

This system consists of an air cooled low power x-ray tube (50W) with molybdenum anode and a thin (70µm) exit window. An optional beam filter can be inserted to reduce spectral background. The beam is focused onto the sample using a polycapillary x-ray optics, offering a focal spot of about 30µm FWHM. Characteristic X-rays from the sample are detected by means of a Si(Li) detector with ultra thin window. An optical microscope attached to a high resolution CCD camera is used to control the measurement position. Sample positioning and scanning is performed using a motorised xyz sample stage.

The new spectrometer offers improved excitation and detection conditions, necessary for light element analysis. The thin window of the x-ray tube allows both, the molybdenum L-lines and K-lines to sufficiently excite the sample over a wide energy range. Detection of the low energetic characteristic radiation is possible due to the ultra thin window of the detector. To eliminate absorption of the exciting and fluorescent radiation in air the system operates under vacuum condition. Sample scanning is automated and controlled by specialized computer software developed for this spectrometer. Access to the spectrometer will be available for external users through the transnational programme of a running EC project (ANNA, www.i3-anna.org).

In this work the spectrometer design as well as first test measurements on different samples, such as artificially created elemental patterns of light elements and human bone will be presented.

PC-39

Portable TXRF spectrometer with a 40 kV X-ray tube

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A portable TXRF spectrometer with a Rh X-ray tube was designed and constructed. The size of the present spectrometer was similar to that of a portable TXRF spectrometer with a W X-ray tube presented in the previous papers [1, 2]. A maximum target voltage of the Rh X-ray tube was 40 kV, and it was four times as high as that of the W X-ray tube. The present spectrometer extended the range of detectable elements. Figure 1 shows (a) an XRF spectrum of 10 ng of As without X-ray total reflection and TXRF spectra of (b) 10 ng of Sc, Cr, Co, Zn, As, Sr, and Nb and (c) 10 ng of Pb that were measured by using the present spectrometer. The spectral backgrounds in the spectra in Figure 1 (b, c) were lower than that in the spectrum in Figure 1 (a). The Zn, As, and Sr Kα lines and Pb Lα line which the previous spectrometer could not detect were detected as well as the Sc, Cr, and Co Kα lines. It was difficult to detect 10 ng of Nb. Table 1 gives the detection limits for Sc, Cr, Co, Zn, As, Sr, and Pb. The detection limits were sub nanograms to several nanograms. The present spectrometer detected wide range of elements with trace amounts.

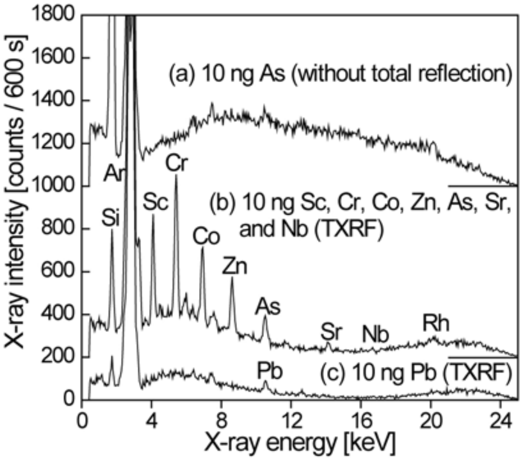

Figure 1. Representative XRF spectra measured by a portable TXRF spectrometer with a Rh X-ray tube. (a) An XRF spectrum of 10 ng of As without X-ray total reflection, and TXRF spectra of (b) 10 ng of Sc, Cr, Co, Zn, As, Sr, and Nb, and (c) 10 ng of Pb. The X-ray tube was operated at 25 kV and 50 μA.

Table 1. The detection limits for elements.

Element	Detection limit / ng
Sc	0.7
Cr	0.5
Co	0.8
Zn	1.0
As	1.6
Sr	6.3
Pb	3.3

[1] S. Kunimura and J. Kawai, *Anal. Chem.* **79**, 2593 (2007).

[2] S. Kunimura and J. Kawai, *Anal. Sci.* **23,** 1185 (2007).

PC-40

Tabletop spectrometer for Grazing Incidence XRF

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Secondary ion mass spectrometry (SIMS) is routinely used for determining profile shapes, junction depths, and doses of dopants in Si wafers. However, in case of ultra shallow junctions (USJ) SIMS is going towards its intrinsic limits. Whereas the depth resolution and quantification in the deeper regions are still sufficient with SIMS, the native oxide-induced matrix effects are limiting factors for the technique if dose and distribution in the first nanometres are required.

Therefore a more complete characterization of USJ, as demanded by microelectronics technological nodes will require the application of different complementary techniques such as Medium Energy Ion Scattering, Scanning Transmission Electron Microscopy, Spectroscopic Ellipsometry as well as Grazing Incidence X-ray Fluorescence Analysis (GIXRF). The development of the mentioned techniques and the understanding of their complementariness for USJ analysis will be the task of a research activity within the running EC project ANNA (European Integrated Activity of Excellence and Networking for Nano and Micro- Electronics Analysis). Within the frame of this activity the X-ray group of the Atomic Institute develops GIXRF as a laboratory source driven tool for USJ analysis. The technique relies on the measurement of fluorescence signals at various incidence angles of the exciting X-ray beam. As the penetration of the primary X-rays becomes larger as a function if increasing incidence angles, GIXRF provides information on the total implanted dose in the substrate material. Since GIXRF is very sensitive in the first few nanometres it delivers satisfactory results for sample depths where SIMS has its drawbacks.

To successfully accomplish GIXRF analyses a tabletop measuring chamber is currently under development.

In the present work the design as well as the current status of the prototype will be presented. Hardware and software requirements to meet the demands of depth profiling with GIXRF will be discussed. Moreover first results obtained on As doped Si wafers will be presented.

PC-41

A new Grazing-Exit-XRF setup at HASYLAB beamline L

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Total reflection x-ray fluorescence analysis (TXRF) operates with the incident beam impinging below the critical angle of total reflection on the surface of a flat polished surface of reflector. The interference between incident and reflected beam causes in case of microcrystalline samples an intensity increase of the fluorescence signal by a factor (1+R) where R is the reflectivity numerically close to 1. The additional effect due to the penetration depth in the nm region is a low background. Both effects are leading to excellent detection limits in TXRF and are widely used in ultra trace element analysis. Grazing incidence XRF (GI-XRF) uses the angle dependent wavefield intensity in order to characterize the structure of layered materials and the composition gradient of materials that are inhomogeneous along the direction perpendicular to the surface. The inverse GI-XRF with the incident beam perpendicular to the reflector's surface and collecting the fluorescence under grazing angle can also be applied [1]. This mode of analysis was named grazing exit X-ray fluorescence (GE-XRF) and is theoretically based on the reciprocity theorem [2]. The interference in this case is not between primary and reflected beam but among the superposition interference of the fluorescent waves emitted from the sample and observed under the critical angle of total reflection φ_{crit}.

A GE-XRF experiment was performed at HASYLAB beamline L using the newly designed equipment from the Atominstitut Vienna X-ray group. The setup was designed with the axis of rotation of the detector exactly in the plane of the reflector. The experiments were performed with the aim to study XANES self-absorption effects, which were observed previously in GI-XRF geometry.

A series of dried residues with different total amounts of arsenic masses on quartz reflectors were investigated. Angle dependent measurements of the samples were carried out by rotating the detector around the sample in the center of the reflector. The experimental data and the theoretical curves showed good agreement. The GE setup allows spatially resolved measurements of the sample. In order to achieve measurements with higher lateral resolution a polycapillary half lens was used to produce a focal spot of 40µm in diameter. With this setup 2D-scans of the samples have been performed and compared with data from confocal microscopy. XANES measurements of the samples were performed and compared with data gained for the same samples under GI conditions.

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PC-42

Influence of the sample morphology on Total Reflection X-Ray Fluorescence Analysis

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Total Reflection X-ray Fluorescence Analysis (TXRF) is a method for qualitative and quantitative analysis of trace elements. In general TXRF is known to allow for linear calibration typically using an internal standard for quantification [1,2]. Absorption effects concerning exciting and detected radiation are usually disregarded. This is justified because mostly small sample amounts are used. The thin film approximation in particular assumes a very thin sample and therefore differential absorption for photons with different energies can be ignored. Furthermore the elements in the sample are assumed to be homogeneously distributed. Hence the loss of the fluorescence signal due to absorption of the primary beam equally affects all elements and quantification by using an internal standard is justified. However, for higher total amounts of samples deviations from the linear relation between fluorescence intensity and sample amount have been observed [3].

The topic of the presented work is an investigation of the parameters influencing the absorption phenomenon. A simulation model was developed to calculate the influence of the absorption effects. Samples with different total amounts of arsenic have been prepared to determine the upper limit of sample mass where the linear relation between fluorescence intensity and sample amount is no longer guaranteed. It was found that the relation between fluorescence intensity and sample amount is linear up to ~100 ng Arsenic. The parameters necessary for the simulation (sample dimensions and volume) were determined by analyses with a confocal white light microscope. Even though the results of the simulations are not satisfying yet it could be shown that the key parameters for the absorption effect are the density of the investigated atom in the dried residues and the shape of the residue. Difficulties for the simulation appeared due to the determination of the density of the arsenic atoms in the sample. To improve the simulation model further investigations are necessary.

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[3] D. Hellin, J. Rip, S. Arnauts, S. De Gendt, P.W. Mertens, C. Vinckier, Spectrochimica Acta Part B: Atomic Spectroscopy 59 (2004) 1149-1157.

PC-43

Micro TXRF Analyses of multiple residues on a flat substrate

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In the conventional total reflection x-ray fluorescence (TXRF), a large area of the sample surface is analyzed because the primary x-rays irradiate a large area of the surface. In the applications of TXRF analysis, the residue of a sample droplet on the flat sample carrier is measured. In this case, the analyzed object is the small residue itself. The x-ray fluorescence emitted from areas other than that of the residue just produces background peaks. Therefore, it would be a good idea to analyze only the micro region of the small residue, leading to trace elemental TXRF analysis [1]. In this work, TXRF of a micro-sized region has been attempted by using a simple pinhole. Single pinhole with an inner diameter of 1 mm was attached to the top of an energy dispersive x-ray detector. Standard solutions containing Fe, Cu, and Zn were dropped on the specific positions on a flat substrate. Finally, multiple residues were prepared on the single substrate plate. It was difficult to selectively measure each residue by a conventional TXRF, because the primary X-rays irradiated the whole surface of the substrate. The sample substrate was put on an XYZ stage controlled by stepping motors and a computer; therefore, each residue could be sequentially measured by micro-TXRF. In the case that each residue is prepared on the different substrates one by one, we have to exchange and adjust the sample substrate for every TXRF analyses of all samples. Our micro-TXRF method enables the sequential rapid TXRF analyses of multiple residues on the substrate.

[1] K. Tsuji, M. Kawamata, Y. Nishida, K. Nakano, K. Sasaki, Micro Total Reflection X-ray Fluorescence (Micro-TXRF) Analysis, *X-ray Spectrom.*, **35**, (2006) 375-378.

PC-44

X-ray Fluorecenece analysis using X-ray transparent thin films for sample surpport

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We have studied XRF analysis by using X-ray transparent thin film for sample support. Here, we will present XRF results obtained by two approaches.

(1) XRF sampling of the particles by adhesive tape

In some cases, it is difficult to take the sample of small particles on the outer wall or the statues. We used a thin adhesive tape of 30 μm in thickness. The sampling efficiency was checked for the dried residue on the glass plate by ED-XRF and TXRF methods. We confirmed that sampling the particles on the glass substrate was possible by using the adhesive tape [1]. Finally, we took the particles on the outer wall in the campus of the Osaka City University by the adhesive tape. The particles on the tape were analyzed by ED-XRF and micro-XRF methods.

(2) Preconcentration in agar thin films

The natural polymer (agar) was used for sample preparation of trace XRF analysis [2]. A 10 mL volume of the aqueous sample and 0.07 g of the dried agar powder were mixed. The mixed solution was heated on a hot plate and was poured into a hollow Teflon cup. After the solution was dried, the thin agar films (50 μm in thickness) containing trace metals were measured by EDS and WDS. The linear calibration curves of several elements showed a good linearity. The lower limits of detection (LLD) were 1.4 mg/mL for K, 0.26 mg/mL for Ca, 0.029 mg/mL for Mn, 0.11 mg/mL for Fe, 0.016 mg/mL for Ni, 0.030 mg/mL for Cu, 0.20 mg/mL for Cd, and 0.066 mg/mL for Pb, respectively. The proposed preconcentration method was applied to the several environmental waters.

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PC-45

Study of alteration of elemental contents In human whole blood and Hemocomponents following irradiation injury by SR-TXRF

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The total-reflection X-ray fluorescence using synchrotron radiation (SR-TXRF) is a very well-suited analytical technique to study the trace element contents in biomedical samples [1]. The aim of this study was to investigate the suitability of measuring mineral and essential trace elements as a monitoring tool for the diagnosis of alterations caused by irradiation procedures. Fresh blood specimens were obtained from Dr. Eliel Figueiredo Laboratory, Rio de Janeiro. The samples (n=956) were irradiated with doses from 2 to 3000 cGy using gamma radiation. After irradiation process, all samples were lyophilized [2] to remove the water content and then, they were submitted to the standard chemical digestion by adding nitric acid. All the measurements were carried out at the X-Ray Fluorescence beamline at the Brazilian Synchrotron Light Laboratory (LNLS), in Campinas. In the whole blood samples, the data show a decrease in the concentration of K, Fe (α > 95%) and Zn (α > 90%) as the dose increases over the dose range. In blood formed elements samples, there was a slight decrease of K level compared to the non-irradiated samples (α > 95%) up to 20 cGy. In blood plasma samples, K levels increase up to 4 cGy (α > 95%). However Fe levels (α > 90%) decrease for all dose range. The statistical analysis showed that the variation found for the Ca levels is not significant for the whole blood and hemocomponents samples. In this way, Ca levels were not found sensitivite to the irradiation dose.

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PC-46

TXRF-NEXAFS study of carbon and nitrogen compounds in fine particulate matter deposited on silicon wafers

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The impact of carbon- and nitrogen containing fine aerosol particles on human health and atmospheric chemistry is an important issue for several environmental studies. Near edge X-ray absorption fine structure (NEXAFS) measurements in the total-reflection X-ray fluorescence (TXRF) geometry offer non-destructive speciation of the atmospherically important low-Z elements (C, N and O) in minute samples collected by cascade impactors directly on the reflector surface.

Atmospheric particulate matter was collected at different urban and rural, continental and marine locations using a 7-stage May impactor having aerodynamic cut-off diameters of 1, 0.5 and 0.25 μm for stages 5 to 7, respectively. The TXRF-NEXAFS experiments were performed at the plane grating monochromator beamline for undulator radiation in the laboratory of the Physikalisch-Technische Bundesanstalt at the electron storage ring BESSY II. $(NH_4)_2SO_4$, $NaNO_3$, NH_4NO_3, graphite and $CaCO_3$ standard particles in the 0.25 to 2 μm size range deposited on silicon wafers were measured in identical conditions. Using a linear combination of the TXRF-NEXAFS spectra recorded for the nitrogen standards, a semi-quantitative ammonium/nitrate ratio was obtained.

The twofold effect of the increased traffic intensity on the aerosol composition can be clearly seen on the carbon TXRF-NEXAFS spectra. In the smallest size fraction (0.25–0.5 μm), a higher concentration of primary carbonaceous particles was observed. Higher traffic also increases resuspension of larger particles of crustal erosion origin, with calcium carbonate as a major component in Hungary. The ammonium to nitrate ratio shows a decreasing trend with increasing particle size in the range of 0.25 μm to 2.0 μm. The variation of nitrate-to-ammonium ratios could be well explained with the air mass backward trajectories.

The above results were obtained from samples collected from much smaller air volumes than usually used for filter sampling, supporting the applicability of TXRF-NEXAFS in the characterization of particulate matter with high time resolution.

PC-47

Effect of ethanol intake during lactation on brain mineral status of pup and young rats using X-ray total reflection spectrometry

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Nowadays alcohol consumption is one of the main problems of public health in the world. The hippocampus is a brain structure very vulnerable to the oxidative stress and, consequently it is more sensitive to the negative effects to alcohol consumption. The present study cover the lactation period since this is the time, which the growing-up and brain development is more intense than in prenatal period. Therefore, this work determined the elemental concentrations in the hippocampus of pups that received alcohol through the maternal milk, comparing their levels with the control group and the recuperated one. Female Wistar rats (20 days old) were separated into two groups: control group C.G and ethanol group E.G (n = 20) and male Wistar rats (20 days and 90 days old) were separated in three groups: C.G (20 days old and 90 days old), E.G (20 days) and recuperated group R.G (90 days old n = 28). The R.G received ethanol like the EG and then received commercial diet such as the control group. The mineral contents were determined using X-Ray Total Reflection Spectrometry with Synchrotron Radiation at the XRF beam line at Brazilian Synchrotron Laboratory. This technique was very useful in this study, since it requires small sample amount, which became possible to analyze the hippocampus of rats (mass about 50 mg). The ethanol intoxication leads a decreased in K, Ca, Fe and Cu levels only in the lactation period (20 days old) of female and male rats. These findings suggested that the R.G has got to maintain the levels of these elements, i.e., they reversed the changes caused by the ethanol intake. The ethanol absorption in the lactation period of female pups (20 days old) lead an increase in P, S and Cl levels, which occurs differently to male pups. Therefore, the ethanol leads to several changes in the mineral concentration, which can affect the growing and development of the brain.

PC-48

Depth profiling of Al-implanted Si by means of synchrotron radiation based high resolution grazing emission x-ray fluorescence

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Progress in semiconductor microelectronic technology requires improved diagnostic tools for the depth profiling of doping elements in semiconductor materials. In this perspective, the high resolution grazing emission x-ray fluorescence (GEXRF) technique combined with synchrotron radiation was tested in order to develop an effective method for studying the depth profiles of Al-implanted in Si. This technique has already proven its high detection sensitivity when being used for the detection of low level concentrations of Al on Si surfaces [1] (see Fig. 1). The depth profiling is achieved by measuring the dependence of the Al x-ray fluorescence intensity on the grazing emission angle around the critical angle for Al-Kα radiation. This dependence is uniquely related to the studied concentration depth-profile.

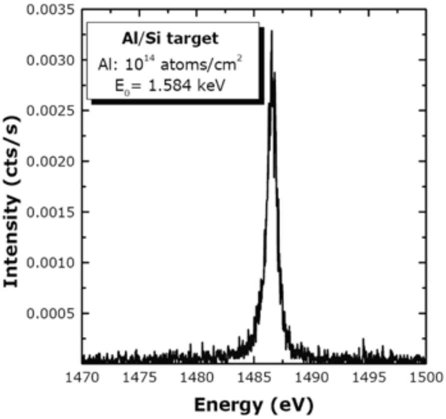

Fig.1: High-resolution grazing emission x-ray Kα fluorescence line from Al impurities in a Si wafer.

We report on depth profiles of Al-implanted Si at energies of 30, 50 respectively 100 keV implanted with a dose of 10^{16} ions/cm^2. Measurements were performed at the ESRF ID21 beam line by means of the Fribourg high-resolution von Hamos x-ray spectrometer [2]. Since the critical angle of Si is larger than that of Al, the bulk Si x-ray fluorescence was limited to a surface layer of only a few tens of nanometers which resulted in a relative increase of the Al x-ray fluorescence signal. The background due to bulk Si was further decreased by selecting the beam energy below the K-absorption edge. Thus, the sensitivity and the quality of the Al depth-profile measurement were enhanced. By means of the described high resolution GEXRF excited by synchrotron radiation the depth profiles can be determined accurately and the effect of thermal processing (annealing, diffusion) on the concentration profiles can be evinced.

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PC-49

Determination of trace metals in bottled commercial drinking water using TXRF in Nairobi, Kenya

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Heavy metals in drinking water can be a hazard to human health depending on their concentration. Health concerns within the Kenyan population have been increasing and a larger population is drinking commercial bottled water as opposed to tap water or direct from rivers.

Samples of bottled water were purchased from shops in Nairobi Central district, slums and city outskirts (rural). From each bottle 10 µl portions were pipetted and carefully dropped on TXRF sample carriers. The carriers were thoroughly pre-cleaned with HNO_3, HCL and distilled water. Three portion replicates from each bottle were left to dry overnight at 25 ^{0}C in a vacuumed oven. They were then analysed on the Vienna TXRF module under x-rays from a Phillip X-ray tube that was powered by a model 710H Siemens high voltage generator.

The obtained spectra were analysed and concentrations of the elements of interest quantified using QXAS software from IAEA. Analytical calibration was achieved by preparing standard solutions of Ti, Cu, Zn and Pb and obtaining spectra the same way and under the same spectrometer setup. Most of the harmful elements that were analysed were below detection limits (DL). Cu and Mn were seen in spectra of portions from slum and rural. Investigation of concentration values, 50 % of DL for below DL concentrations, of the analysed elements showed a high standard deviation of K and Ca in upmarket bottled water and low in those from the slums and rural. However Ti, Fe, Zn and Pb had similar deviations in all shops. The high variability in this preliminary work needs further investigation for it may be a precursor of high contamination if measured against the allowed maximum contaminant levels by USEPA.

[1] United States Environmental Protection Agency (USEPA). Water on tap, pp23; book pp23 on www.epa.gov/ visited on 20th February 2008.

Acknowledgement:

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PC-50

On-Line X-Ray Fluorescence analysis of Iron-ore mixtures on a conveyor belt

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In ferrous metallurgy it is very essential to determine the composition of iron-ore mixtures used in sinter production on-line above the conveyer belt. In this paper we propose for the first time to apply energy-dispersive X-ray fluorescence analysis (EDXRF) for on-line quantitative determination of Fe and CaO in iron-ore mixtures. We used an EDXRF spectrometer *Con-X 02* (Bruker Baltic) mounted by an original suspension bracket directly above the conveyer belt of the agglofactory at the Magnitogorsk iron and steel works, Russia. To minimize the influence of changes in the distance between material and spectrometer on the X-ray fluorescence spectra the analysis geometry is chosen when the X-ray tube primary radiation cone is situated inside the collection cone of the detector. For the element composition calculation we used software based on the fundamental parameters method. This program accounts for the distance to the measured material, the lump size, unknown and changing amounts of elements unseen by the spectrometer. We obtained a standard deviation of 1.0% for Fe and 0.6% for CaO. The accuracy of EDXRF was verified by more than 70 comparisons with chemical analysis measurements.

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The application of standardless material Identification for the analysis of precious metal alloys and RoHS samples

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The “Standardless Material Identification” is a useful tool in many applications when samples of unknown material or structure are investigated. The user will get automatically the type of material and in a further step the quantitative analysis with best calculation and calibration routine is performed. For this standardless method no large base of standard reference materials is needed. The base for the different classes of materials is calculated theoretically by defining the ranges of concentrations or coating thickness of the materials. This method is more flexible and easier to use compared to methods based on reference materials.

Two applications are presented in more detail:

1. Analysis of precious metals. Many different types of alloys are used in jewellery, dental and technical applications. It is often even not known, if the material is coated or not. The “Standardless Material Identification” will find the correct material to perform the analysis with the required high accuracy for the Au, Pt or Pd content.

2. Analysis according to the RoHS directive. RoHS causes the necessity to analyse trace elements in electrical and electronic equipment, which consists of a large amount of different materials. In particular many different types of coatings like Sn, Ag, Au are used. For good trace analysis the knowledge of the matrix is a precondition. With the “Standardless Material Identification” the different types of coatings, metals or polymers that are used in electrical and electronic equipment are identified.

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Quality improvement of FP quantification for thickness and composition of alloy layers by XRF methods

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Precision of FP quantifications is defined by the accuracy of instrumental parameters as well as by atomic data and modelling of the physical processes. In order to improve results for thickness and composition of metallic layers we tested a bulk and layer based recalibration routine using independently characterized samples.

Alloy layers such as Pd-Ni and Zn-Ni are often used in industrial surface coatings, and are therefore excellent examples for FP quantification testing. We selected alloy layer standards for thickness and composition in the range of Pd70-100 and Zn80-95. Three specific alloy samples were chosen as standards for Pd-Ni alloy composition, and were analyzed with independent methods. Thicknesses ranged from about 1 µm to 10 µm for Pd-Ni layers. Among the Zn-Ni layers two layer samples were checked independently and thicknesses of all Zn-Ni samples ranged from 2-35 µm.

Results of the original FP calculations of alloy layer systems were not always satisfying (see table 1). The amount of Ni in Zn-Ni alloys was too variable and thicknesses were systematically underestimated. In the case of the Pd-Ni alloy layers, deviations from the given values could be as high as 10%, but differ apparently among different instrument parameter sets.

After recalibration using independent standards these deviations for all the Pd-Ni layer standards were less than 1% relative for composition and thickness. In case of the Zn-Ni samples the calibrated results showed a somewhat higher variability, which seems to be related to the production process.

This approach, using independently characterized bulk and layer standards and calibrating thickness and composition separately, seems to be very helpful for analyses of alloy layers because in many cases compositions of these layers are less well known compared to their thickness.

Table 1: Comparison of FP and recalibrated results measured on two different x-ray systems

Pd-Ni alloy layers					
Standards	certified	Instrument 1		Instrument 2	
		FP calculated	recalibrated	FP calculated	recalibrated
1	1.16 µm	0.91µm	1.15 µm	1.15 µm	1.16 µm
2	4.95 µm	3.95 µm	4.96 µm	4.87 µm	4.93 µm
3	9.55 µm	7.64 µm	9.55 µm	9.43 µm	9.57 µm
4	70 % Pd	68.4 % Pd	70.48 % Pd	69.13 % Pd	70.00 % Pd
5	80 % Pd	78.5 % Pd	79.85 % Pd	79.96 % Pd	79.98 % Pd
6	90 % Pd	90.4 % Pd	90.41 % Pd	91.16 % Pd	90.01 % Pd

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Development and characterization of new polymeric reference materials with the aid of XRF, LA-ICP-MS and Sy-XRF

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Polymers are essential materials in our modern society. Due to their use in numerous fields of application, polymer materials are subjected to a series of restrictions and regulations regarding the presence and concentrations of a number of additives and fillers.

The use of solid sampling techniques such as X-ray fluorescence spectroscopy (XRF) and mass spectroscopy with inductively coupled plasma and laser ablation (LA-ICP-MS) for the elemental analysis in plastics becomes more and more popular. As both techniques are strongly matrix dependent, the use of matrix matched and highly characterized reference materials is the favorable method for calibration.

A set of 10 different materials based on acrylonitrile-butadiene-styrene terpolymer (ABS) was produced by a specially developed extrusion process at University of Applied Sciences Münster containing different amounts of Br, Cd, Cr, Hg and Pb. [1] The resulting granulates were formed to solid discs using injection molding. The exact elemental concentrations were determined by neutron activation analysis (NAA) at the Hahn-Meitner-Institute Berlin for Br, Cd, Cr and Hg. The concentration of Pb was determined by ICP-MS after acid digestion.

The determination of macroscopic homogeneity was carried out by measurements with the aid of XRF. Therefore 18 samples per batch were measured as granulates in standard liquid cups and the results were compared. All materials showed good macroscopic homogeneity.

Determination of micro homogeneity was preliminarily carried out with the aid of synchrotron micro XRF spectroscopy (Sy-XRF) for one batch at the BESSY. The results were compared with measurements carried out by LA-ICP-MS. The investigated material showed highly satisfying homogeneity for all elements.

The materials were successfully used for the calibration of XRF and LA-ICP-MS measurements. They are therefore considered as candidate materials for the certification by the Federal Institute for Materials Research and Testing (BAM).

[1] C. Mans, S. Hanning, C. Simons, A. Wegner, A. Janssen, M. Kreyenschmidt, Spectrochimica Acta 62B (2007) 116-122.

PC-54

Delay of ruthenium escape in the presence of some fission product elements

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The RUSET (RUthenium SEparate Effect Test) experimental program was launched in order to understand the main phenomena in connection with escape of Ru from spent fuel at severe accident processes with air ingress. In separate effect tests Ru oxidation rate and content of Ru in escaping air flow have been studied. The results showed that Ru evaporates in form of RuO_3 and RuO_4 and the amount of RuO_4 in the outlet air was in the range of 10^{-6} bar, far above the value that would be expected from equilibrium. It was also observed that other fission products and UO_2 influenced the concentration of RuO_4 in the ambient temperature escaping gas and caused a time delay in appearance of its maximum values.

The main objectives of the last test series were identification of those fission products which play role in this time delay. Above the high temperature solid state reactions in the reaction chamber presumably reactions in the decreasing temperature outlet area delayed the release of Ru in the escaping cooled down air.

To understand these latter chemical reactions and the thermo chromatographic effects, quartz rods with 2 mm diameter were placed into the decreasing temperature outlet tube. The outer surface of quartz rods was investigated by micro-beam X-ray fluorescence (µ-XRF) in order to determine the axial distribution of the inactive simulated fission elements deposited along the sampler rods with acceptable resolution.

The measurements were performed using a silver-anode fine-focus X-ray tube. The beam was focused to 80 µm (FWHM) by means of a polycapillary minilens (IfG, Germany). The samples were fixed to a computer-controlled sample stage vertically and were moved in front of the capillary in vertical direction. The scanning results showed that MoO_3 and TeO_2 deposited together in temperature range between 600 and 300°C, while the Cs deposition occurred between 800 and 300°C.

PC-55

Total Reflection X-ray Fluorescence (TXRF): A future routine analysis tool in structural biology?

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Metal ions are essential for the function of biological systems, about 30% of all proteins require metals. They are involved in many crucial biological processes such as respiration, metabolism, photosynthesis, cell division, muscle contraction, oxygen transport, neurotransmission, and gene regulation. Knowing the metal content of a protein therefore directly translates into new knowledge.

We have evaluated the applicability of total-reflection X-ray fluorescence (TXRF) and synchrotron-based TXRF (SR-TXRF) to quantify the concentration of trace elements in protein samples. TXRF is well suited to study protein samples since it allows the quick quantification of all relevant elements using a comparable small sample volume. Neither crystals nor high protein concentrations are required, allowing measurements at various stages of a research project.

For a correct quantification of protein-bound metals the concentration of trace elements in the pure buffer has to be determined also. To ensure a correct quantification matrix effects have to be taken into account; ideally both protein and buffer should form a thin film during drying. Therefore we studied the influence of different reflector types on the drying properties of buffer and protein samples with spatial resolved XRF[1]. In addition, we developed a standard to be used for elemental analysis in structural biology which allows quantifying and correcting any matrix effects present.

Possible applications of TXRF as presented on the poster include:

- Determination of metal occupancy
- Searching for contaminants
- Loading experiments

[1] G. Wellenreuther, U.E.A. Fittschen, M.E.S. Achard, A. Faust, X. Kreplin, W. Meyer-Klaucke, Spectrochimica Acta Part B: Atomic Spectroscopy (submitted) (2007).

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