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Book of Abstracts

ORAL PRESENTATIONS

INV-1

X-RAY STANDARDS: FROM X-RAY TUBES TO HIGHLY-CHARGED IONS.

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X-ray standards, i.e. X-ray line energies or wavelengths measured with the highest possible accuracy, have applications in many fields of physics. One can cite field as different as crystallography as well as medium energy particle physics. Current X-ray standards are based upon X-ray lines emitted by solid targets excited by electron bombardment or fluorescence. These lines are not very well suited for X-ray standards: they are broad and asymmetric because of the unavoidable presence of many vacancies (shake-off,...) and of auto-ionization. Their energy can only be obtained by direct measurement, and depends on the exact composition of the target surface (chemical shift) and on the instrumental resolution (because of the asymmetry). Their width is much larger than the resolution of the best spectrometers. Many known lines have been measured only once very long ago, in an uncontrolled environment. A complete survey of the current status of X-ray line energies and associated problems can be found in [1]. Several attempts have been made to remedy some or all of these problems and find better candidates. Recently low energy gamma rays have been advocated for such applications [2]. They are narrow transitions of nuclear origin, but are indeed difficult to manipulate (strong radioactive sources are needed), there are very few suitable lines, and the energy cannot be predicted. More recently X-rays from exotic atoms and highly charged ions have been used. Exotic atoms are atoms in which most or all electrons have been replaced by one unstable particle. Although their production is difficult, progress in accelerator, spectrometer and production techniques have enabled a reasonable use [3]. Highly charged ions are the most promising technique. Very narrow and intense transitions produced by an Electron-Cyclotron Resonance Ions source have been observed [4] and used [5] to characterize in detail an X-ray spectrometer and measure very accurately the energy and width of pionic hydrogen, a system of interest for the study of strong interaction. In this talk I will provide a review of the current problems and perspectives in this field. I will describe ongoing experiments in our laboratory intended to provide the first X-ray standard from highly charged ions.

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[2] γ -Ray Wavelength Standard for Atomic Scales, Y.V. Shvyd'ko, M. Lerche, J. Jäschke et al. *Physical Review Letters* 85, 495-498 (2000).

[3] Low-energy X-ray standards from hydrogenlike pionic atoms, D.F. Anagnostopoulos, D. Gotta, P. Indelicato et al. *Physical Review Letters* 91, 240801 (2003).

[4] High Resolution He-like Argon And Sulfur Spectra From The PSI ECRIT, M. Trassinelli, S. Biri, S. Boucard et al., *ELECTRON CYCLOTRON RESONANCE ION SOURCES: 16th International Workshop on ECR Ion Sources ECRIS'04*, Vol. 749, AIP (Berkeley, California (USA)) pp 81-84, (2005).

[5] On the characterisation of a Bragg spectrometer with X-rays from an ECR source, D.F. Anagnostopoulos, S. Biri, D. Gotta et al. *Nuclear Instruments & Methods in Physics Research, Section A (Accelerators, Spectrometers, Detectors and Associated Equipment)* 545, 217 (2005).

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DOUBLE K-SHELL PHOTOIONIZATION OF MAGNESIUM AND ALUMINIUM

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We report on measurements of the K-hypersatellite fluorescence x-ray emission of solid Mg and Al. The experiments were performed at the European Synchrotron Radiation Facility by means of high-resolution x-ray spectroscopy, using a von Hamos curved crystal spectrometer [1].

The diagram and hypersatellite x-ray spectra of Mg were measured at 9 different photon beam energies between 2746 eV and 3947 eV. The onset energy for the production of the double 1s vacancy states was found to lie at about 2750 eV. Above the threshold energy, a fast rise of the hypersatellite intensity with the excitation energy is observed but then the hypersatellite yields tend toward a saturation value, as predicted by the model of Thomas [2].

At saturation, the relative hypersatellite yield was found to be about one order of magnitude bigger than theoretical predictions based on the sudden approximation model. For the energy shift of the hypersatellite with respect to the parent diagram line, a value of 114.28(3) eV was obtained, in good agreement with the result of 114(1) eV deduced from a previous heavy-ion experiment [3]. Furthermore, the Lorentzian width of the hypersatellite transition predicted by theory underestimates significantly the value obtained from our measurements.

To verify whether the discrepancies observed for Mg are specific to this element or also affect other low-Z atoms, the hypersatellite measurements were extended recently to Al. The hypersatellite transition was observed for 11 different photon beam energies ranging from 3186 eV (onset energy) up to 5451 eV (saturation). Because for Al the hypersatellite line is overlapping with the second order L-satellite of the $K\beta$ transition, the latter was measured at a beam energy of 3122 eV, i.e. below the hypersatellite onset energy, and its normalized intensity subtracted from the hypersatellite yield at each higher excitation energy. The data analysis is still in progress but preliminary fits show that the hypersatellite yields of Al are also strongly underestimated by the theory.

[1] J. Hoszowska et al., Nucl. Instrum. Meth. Phys. Res. A 376, 129 (1996).

[2] T.D. Thomas, Phys. Rev. Lett. 52, 417 (1984).

[3] M. Koval et al., Phys. Rev. A 70, 062720 (2004).

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**BROADENING OF DIFFRACTION PROFILE CAUSED BY SURFACE
STRESS GRADIENT AND ITS STUDY BY FOURIER ANALYSIS**

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It has been shown earlier that strong stress gradient arising on the surface of materials after some superficial treatment causes diffraction line broadening. The interest to study this broadening is connected with the possibility to obtain important information about parameters of stress gradient using X ray diffraction methods. Fourier analysis, widely used in different fields of modern physics, can be applied to study this kind of distortions of diffraction profile. In the present paper the convolution and the deconvolution concepts of Fourier analysis were applied to determine stress distribution function that is responsible for the broadening of diffraction line. The developed methodology was tested by computer simulation of diffraction experiment with linear and exponential stress distribution functions. It was obtained good agreement between original and calculated functions.

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THE ENERGIES AND RELATIVE INTENSITIES OF L AND M LINES IN THE LOW-ENERGY RANGE

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A lot of the publications about fundamental parameters are from the 70s. Within recent years some new atomic databases were published in the internet. These contain – besides other fundamental parameters – line energies and intensities of K, L and M X-ray lines. However, these databases as well as the publications show considerable differences, a lack of accuracy, e.g. line intensities which are varying by three orders of magnitude, and missing lines when compared to measured spectra, especially for the low energy range. This is also true for some widely used but old publications.

These discrepancies, especially in the relative line intensities, cannot be explained only by errors in the measurements or uncertainties of depending fundamental parameters. As a matter of fact, line energies and intensities were interpolated or even estimated as roughly constant for a wide range of elements in the periodic system. Additionally, some significant lines like the M-zeta line were neglected in the databases or publications.

Even for elements with M line energies greater than 2 keV atomic databases show significant differences. For example, for a common element such as gold some databases show only three lines which agree with experimental spectra in line energy and intensity, whereas at least five lines are significant and clearly visible in experimental spectra.

In cooperation with Prof. Wendt of the Institute for Physical High Technology Jena, L and M line spectra were investigated and extended. Results of this work will be presented and some examples will be compared with other databases and publications.

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DOUBLE 1S PHOTOIONIZATION OF Ca AND V BEYOND MAXIMUM

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The single-photon two-electron process serves as one of the most sensitive probes of electron-electron correlations. Following the absorption of the primary photon two dominant double ionization mechanisms produce "hollow atoms", namely the electron-electron scattering (knock-out KO) and the shake process [1]. Shake prevails at high photon energies, while knock-out dominates at low energies and falls rapidly with increasing excitation energy to become negligible in the asymptotic regime. Thus, exploring the energy dependence of the 1s double ionization probability permits to investigate the initial-state correlations important for shake and the final-state electron-electron correlations governing the dynamics of the electron impact ionization (KO).

We report the observation of double K-shell vacancy production for Ca and V by means of high-resolution x-ray emission spectroscopy. Measurements of the hypersatellite and diagram x-ray spectra were carried out using a high-resolution von Hamos Bragg curved crystal x-ray spectrometer [2] at the BM5 beamline at the ESRF, Grenoble. The synchrotron x-ray beam was monochromatized by means of a (Ru/B4C)70 double-multilayer monochromator with an energy bandpass of $\sim 2 \times 10^{-2}$.

Ratios of double to single K-shell photoionization probabilities were derived as a function of the incident beam energy varying from 7 to 25 keV. These photon energies correspond to values just above the double K-shell vacancy production threshold, the region of the broad maximum and beyond. The observed energy dependence of the double K-photoionization probability with a falloff to values close to the asymptotic limit highlight the relative importance of the electron-electron scattering and shake processes in double 1s photoionization of Ca and V. The extracted ratios of double to single 1s photoionization in both the maximum and the asymptotic region compare well with the ones reported in [3].

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A STUDY OF K X-RAY SATELLITES, HYPER-SATELLITES AND KMMRAE STRUCTURES OF THE ELEMENTS $19 \leq Z \leq 25$

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In the field of X-ray emission spectroscopy X-ray satellites, hyper-satellites and KMMRAE structures merit detailed investigation. Determination of energies of pure hyper-satellites K_{α}^h L° is significant, as the energy levels of the "hollow atoms" have also been proposed as away of achieving population inversion for lasing for hard X-ray lasers [1]. In the present study energies and relative intensities of $K_{\alpha} L^1$ X-ray satellites, K_{α} hyper-satellites and KMMRAE of the elements $19 \leq Z \leq 25$ induced by photon excitation are measured using a Phillips 2404 wave length dispersive spectrometer. These data are supplemented with the available data for other elements, all by photon excitation to develop Z systematics.

The semi-empirical formula of Torok et al [2], to predict K_{α} satellite energy shift from the diagram line is modified and is in better agreement with experimental values obtained by photon excitation.. A semi-empirical formula for the prediction of the energy shift of the K_{α} hyper-satellite from the diagram line is also formulated. Fitting experimental $K_{\beta} L^1$ energy shifts from the diagram line as a function of effective Z, an expression for computation of this shift is obtained. As it is in very good agreement with experimental values, it is suggested that it may be used as a semi-empirical formula. Interestingly a broadly valid simple relationship is found between K_{α} hyper-satellite and satellite energy shifts and also between K_{α} and K_{β} energy shifts.

Three of the lines in the KMMRAE structures in all the seven elements chosen for measurement are assigned $K-M_1 M_2, {}^3P$, $K-M_1 M_2, {}^1P$ and $K-M_1 M_1, {}^1S$ transitions as their experimental energy shifts from the K_{β} diagram line are in agreement with theoretical values calculated using standard Auger transition energies from the compilations of Larkins [3]. Z systematics of relative intensities of satellites and K_{α} hyper -satellites are also studied. A simple relation ship is established between K_{α} and K_{β} relative intensities .The experimental energy shifts and relative intensities are compared with the values calculated using various theoretical models wherever available.

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**STUDIES OF THE L-FLUORESCENCE LINES OF TRANSITION METALS
EMPLOYING A SOFT X-RAY WAVELENGTH-DISPERSIVE GRATING
SPECTROMETER**

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A wavelength-dispersive grating spectrometer (WDS) that can be calibrated absolutely was built for various applications at the plane grating monochromator beamline for undulator radiation of the PTB at BESSY II. The device will be used to determine atomic fundamental parameters absolutely such as Coster-Kronig coefficients, transition probabilities of fluorescence and satellite lines as well as cross sections of resonant Raman scattering. The chosen energy range from 0.27 keV to 1.85 keV covers the K-fluorescence radiation of light elements (C to Si), L-fluorescence radiation of transition metals and M-fluorescence radiation of rare earth metals.

The design of the WDS provides very good mechanical stability, a high energy resolution (1:500) and good detection efficiency. The WDS consists of an entrance slit, a spherical reflection grating and a CCD detector, all three of which are arranged on a Rowland circle. The mechanical stability and the CCD detector ensure the long time stability of the device, which is necessary for a reliable calibration.

The concept of the device, initial calibration tests for its characterization and first application results will be presented. Regarding the latter, emphasis was put on a systematic study of transition metals employing thin self-standing foils.

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INV-2

X-RAY DETECTORS: NEW TECHNOLOGIES, CAPABILITIES AND CHALLENGES

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Recent x-ray detector technologies have allowed dramatic improvements in collection efficiency, energy resolution, and count rate capabilities. When combined with high speed electronics, and advanced computer control and automation, these technologies enable new analytical capabilities including:

- high sensitivity combined with high speed analysis
- higher spatial resolution x-ray analysis
- near live-time chemical mapping,
- 3-dimensional nanoscale analysis,
- microanalysis that can be directly compared to bulk analysis,
- and advanced chemical state spectroscopy of complex materials.

While the "perfect" x-ray detection system is still in the future, technologies such as the silicon drift and microcalorimeter detection systems have significantly expanded our expectations. These technologies are continuing to improve in efficiency, resolution, speed, and broaden in real applications.

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CONCEPTUAL CHOICES FOR MICROXRF SPECTROMETERS

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The major requirements for a spectrometer are reproducibility, LLD, resolution and sensitivity. For microXRF spectrometers the spot size or measuring box size is another requirement and the reproducibility depends on a.o. the spot size, the microXRF optical path configuration, the alignment errors and the size of the measuring box. Especially in applications with small measuring boxes, a deliberate choice should be made with respect to the microXRF configuration in order to achieve an adequate system performance.

In this presentation several microXRF spectrometer concepts are discussed. The dependency of the reproducibility on the focal spot size, the optical path configuration, the alignment errors and the measuring box size will be evaluated theoretically. Finally a number of experimental results will be shown.

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CHARACTERISATION OF MICROSPOT EXCITATION FOR QUANTITATION IN X-RAY FLUORESCENCE ANALYSIS WITH X-RAY TUBES

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For standard-less quantitative XRF-analysis based on the fundamental parameter method an accurate knowledge of the excitation spectrum is necessary. For the conventional XRF it is possible to calculate this spectrum, based on the most important parameters of the x-ray-tube [1]. Since the spectral distribution is changed by using a polycapillary lens to focus the radiation such a calculation is not possible in case of micro-XRF-spectrometers. For that reason quantitative analysis with micro-XRF-setups is mostly based on a calibration of the instrument with certified reference materials.

For a reference-free quantification a determination of the transmission efficiency of the X-ray lens used is necessary. Since there are no efficient theoretical models to describe that function of a polycapillary optic, it must be measured.

To compare two different concepts to measure the lens-transmission a commercial micro-XRF-Spectrometer was investigated. The x-rays are produced in a 30W-Mo-tube and focused using a polycapillary lens with about 70 µm spotsize. The fluorescence radiation is detected by a SDD-Detector.

For the characterization of the X-ray optic direct measurements of the excitation spot were carried out. To reduce the count rate and to get information about the lateral distribution a pinhole was used. It is made of Platinum and has a diameter of 10 µm. Along a linescan and in a distance of 5 µm direct measurements of the excitation spectrum in the focal plane were collected. Additionally a measurement under the same conditions but without the X-ray lens was carried out. With that data an energy dispersive description of the FWHM and of the gain-factor of the optic is possible, which leads to the transmission function. [2]

On the other hand scatter-measurements under well defined conditions were carried out with and without the X-ray optic. Dividing the spectrum of the X-ray lens by the one of the X-ray tube also leads to the lens-transmission.

All measurements were carried out with three different tube-voltage-operations and both with SDD-Detector and with Si(Li)-Detector. Calculated tube spectra were convoluted with both transmission functions to achieve the correct excitation spectrum. It is intended to carry out measurement of certificated reference materials and doing a fundamental parameter based quantification of that data with both excitation spectra. The comparison of the results should be helpful to validate the concepts of measuring the transmission function.

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DEVELOPMENT OF CONFOCAL 3D MICRO XRF SPECTROMETER WITH Cr-Mo DUAL EXCITATION

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A new 3D-micro XRF instrument based on the confocal set-up using two independent polycapillary x-ray lenses and two x-ray sources (Cr and Mo targets) was developed. A full polycapillary x-ray lens was attached to each x-ray tube. Another half polycapillary lens was attached to a silicon drift x-ray detector (SDD). The evaluated diameters of each x-ray beam at the focal distance were 0.035 mm for Mo target, and 0.055 mm for Cr target respectively. The focal spots of three lenses were adjusted at exactly same position.

The effects of Cr-Mo dual x-ray beams excitation were investigated. It was confirmed that the XRF intensity of the right elements increased by applying the Cr target x-ray tubes in the confocal configuration. In the proposed confocal configuration, 3D-elemental mapping of major elements in plant samples was performed non-destructively at ambient air pressure. Each elements of in plant samples showed the different mapping image in the different layer, respectively.

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DETERMINATION OF LAYER THICKNESSES OF FUEL CELLS BY 3D MICRO X-RAY FLUORESCENCE SPECTROSCOPY

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Depth resolution is the most used properties of 3D Micro XRS up to now. The development of a model for the sensitivity of the confocal setup facilitates the evaluation of depth profiles to determine layer thicknesses and elemental distributions. As an example for the capacity of layer investigation with 3D Micro XRS measurements of fuel cells will be presented. Beside the experimental setup the modelling of the layer structure will be described. Results of this modelling to determine the layer thicknesses are discussed.

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INVESTIGATION OF XV CENTURY FRESCOS BY MEANS OF SEM AND MICROANALYSIS

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On the occasion of recent restoration works carried out in the Basilica of St. Petronio in Bologna, Italy, a deep scientific investigation of the frescoes in the St. Abbondio and Bolognini chapels has been performed; the considered frescoes were painted by Giovanni da Modena and his 'bottega', one of the most important artist in Northern and Central Italy in the first half of XV century, and they can be dated around 1420 according to stylistic studies. These frescoes represent one of the most important masterpieces of the Bolognese painting school.

From these wall paintings, generally considered as executed with the well-known technique of 'buon fresco' in the relevant historical and artistic literature, a number of microscopic samples have been extracted probing significant areas of the artistic work and submitted to proper scientific investigation. Analyses have been carried out mainly by means of scanning electron microscopy (SEM) and associated EDXRS microanalysis. Therefore, by means of the X-ray spectra, the elemental composition of the samples has been univocally identified.

A stratigraphic study has been also carried out with usual optical microscopy techniques. We were able to identify the pigments used by the artist and, above all, to reconstruct the execution technique which resulted to be painted 'a secco' (on dry plaster). This fact is confirmed by the observation of legands such as animal glue below the pigment layer in all the considered samples. The large presence of glue and the frequently observed detachment of painted layers are clear signatures of the dry execution on the walls of the church, contrary to the traditional well-established recipes for the realization of frescoes. On the other hand, the compositions of pigments used in the large frescoes clearly correspond to the well-established recipes described in the contemporary and subsequent literature on the subject.

Finally, a comparison is proposed with similar analyses reported in the scientific literature, in order to point out possible characterization of the works of different 'botteghe' active in North and Central Italy during the XV century, based on statistical cluster procedure in a suitable multidimensional space of the relevant parameters as determined by EDXRS analyses.

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MICRO-XRF EXCITATION IN AN ELECTRON MICROSCOPE.

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An option for electron microscopes will be presented offering the possibility to excite the sample by X-rays. X-rays are generated by a tube attached to the SEM and concentrated on the sample surface by polycapillary optics to a spot of approx. 50 µm diameter. The excited fluorescence radiation can be detected by the EDS-detector that is available on most SEM. In contrast to electron excitation X-ray excitation does not generate a bremsstrahlung background and therefore the peak-to-background ratio is improved significantly. Limits of detection are typically in the range of 20 – 50 ppm for a measuring time of 60 – 100 s i.e. by a factor of 20 - 50 better than for electron excitation.

Another advantage of this arrangement results for quantification. Because of different cross sections for excitation by electrons and X-rays the sensitivity for light and heavy elements differs for both methods. Light elements can be analyzed with higher sensitivity by electron excitation but heavy elements ($Z > 20$) are detected more sensitive by X-ray excitation. By using both types of excitation it becomes possible to combine their analytical capabilities and to improve the accuracy of quantification.

The paper presents both the instrumental arrangement and also the quantification procedure. A few applications are discussed including examples for the combination of the quantification of both methods.

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INV-3

NEW TRENDS ON X-RAY ANALYSIS OF PAINTING MATERIALS

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The material analysis of paintings aims to better understand the technique of the artists and brings to light unique information for their authenticity and conservation: identification of the pigments, of their elaboration processes and alteration.

In this presentation, we will show how the growing use of analytical techniques based on ion beams, synchrotron radiation and laboratory or portable X-ray tubes has allowed new opportunities to characterise pigments:

PIXE and X-ray fluorescence techniques are used to identify the materials and the trace elements, which enable sometimes to distinguish between natural ores and synthesised products and to determine geographic provenances of minerals.

PIGE technique is sometimes of primary importance to identify light elements.

X-ray diffraction is a relevant method to analyse crystallised compounds and identify phases.

The combination of analytical techniques allows us to describe improvements in the selection and the preparation of specific materials, as well as in the know-how to formulate complex mixtures of pigments. We will illustrate these approaches with the study of ancient Egyptian cosmetics and paintings, the characterisation of Hellenistic pigments and of the practices of painters at the beginning of the Renaissance, such as Matthias Grünewald and Leonardo da Vinci.

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THE USE OF A EUROPEAN COINAGE ALLOY TO COMPARE THE DETECTION LIMITS OF PORTABLE XRF SYSTEMS. A FEASIBILITY STUDY.

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The investigation of archaeological and historical materials makes use of techniques that, though borrowed from other fields of research and industrial production, frequently have to be "re-invented" due to peculiar characteristics of the objects. Artistic relevance, limited movability, compositional and structural heterogeneity radically change the experimental approach and often require ad hoc designed equipment. These considerations also apply to X-ray fluorescence, one of the most widely used techniques in this field, with special regard to portable systems. It is very common that "home made" or prototypal portable spectrometers be used; even for the commercial ones, the market offers a huge variety of different solutions, inevitably resulting in different analytical performances. Such a diversified context brings forward the need for common criteria to evaluate portable spectrometers performances as well as the advisability of a large scale survey on the existing equipment.

This paper intends to demonstrate the feasibility of such an idea, which relies on simple protocols, on cheap, easily available reference materials and, obviously, on meaningful outcomes; furthermore it reports the results of a demonstrative intercomparison carried out among users of portable XRF spectrometers (with different x-ray tubes and detectors) in the area of Rome, Italy and Valencia, Spain. The experimental protocol consists in measuring the detection limits with the single standard method (see Jenkins R., Gould R.W. and Gedke D., *Quantitative X-ray Spectrometry* - 2nd edition, Marcel Dekker, Inc., New York 1995, 402) for 3 different measurement times. The adopted standard is the 50 eurocent coin, whose alloy, called nordic gold, is made of 89% Cu, 5% Al, 5% Zn, 1% Sn; besides the strong symbolic valence, the large spread of European currency guarantees maximum availability at minimum cost. The experimental data show that the use of different X-ray tubes and detectors results in detection limits that may differ from each other by a factor of 4 for Zn and of 50 to 90 for Sn. If one considers that: a) detection limits are among the most crucial features of any analytical system; b) elements in the neighbourhoods of $Z=30$ and $Z=50$ are extremely frequent in archaeological and historical materials; c) every portable XRF spectrometer is a compromise in which portability and good detection limits are one against the other and d) elements in the neighbourhoods of $Z=50$ are particularly suited to highlight the effects of such compromise on the analytical performance, then it comes out that the proposed protocol is suitable for a European survey concerned with the detection limits of the systems in use; furthermore, if data on commercial systems become available, it can provide a figure of merit on analytical performance, should one have to choose what system to purchase.

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**SY-XRF STUDY OF SILVERPOINT DRAWINGS OF HANS BALDUNG
GRIEN FROM THE KARLSRUHER SKIZZENBUCH AND THE
CORRESPONDING SILVER STYLUS (16TH C.)**

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Famous artists of the 14th to the 16th c. such as Jan van Eyck, Leonardo da Vinci and Albrecht Dürer used silverpoints among other instruments or materials like inks for drawings. Today, silverpoint drawings are very rare and belong to the most valuable treasuries of graphical art collections. New insights into the drawing technique and the genesis of these works of art can be obtained by characterising a fingerprint based on the chemical composition of the metal marks on the drawings. The study of drawings requires particular attention because the analysis has to be fully non-destructive and extremely sensitive. The metal alloy on the paper does not exceed some hundreds of $\mu\text{g}/\text{cm}^2$. Only external beam micro-PIXE and SY-XRF are known to be well-suited for the non-destructive analysis of silverpoint drawings [1]. About one hundred drawings were analysed in preceding works using external beam micro-PIXE at the C2RMF in Paris [2] and spatially resolved SY-XRF analysis at BESSY in Berlin [3].

The aim of this study was to compare some silverpoint drawings of Hans Baldung Grien in the so-called “Karlsruher Skizzenbuch” and one of the only rare silverpoints conserved today. One assumes that the stylus, which is fixed on the sketchbook, was used by himself [4]. Hans Baldung Grien is a well-known German Renaissance artist. He lived from about 1484 to 1545 and is a contemporary of Albrecht Dürer and Hans Holbein the Elder.

The measurements of the drawings and the silver stylus were realised at the FLUO beamline at ANKA Karlsruhe. The FLUO beamline has been proven to be well-suited for non-destructive analysis of silverpoint drawings. The results on the chemical composition of the metal marks of the drawings and on the original silverpoint show that the silver stylus could be used for the drawings of the sketch book. The stylus is made of a brass stylus covered with a thin copper-containing silver layer which does not contain any mercury on the contrary to the drawings. The strokes of the drawings bear copper and mercury as minor elements beside silver. Therefore, mercury originates from a characteristic alteration phenomenon of historical silverpoint drawings.

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IN SITE EDXRF ARCHAEOLOGICAL MEASUREMENTS OF THE GOLDEN GLOBE ON THE TOP OF SAN PETER DOME IN ROME

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Nowadays the field portable energy dispersive equipment achieved stability and portability that could not be foreseen only few years ago. A concrete example of this state of the art is the campaign of measurement performed in the July 2005 inside and outside the bronze golden globe placed on the top of the San Peter Dome. The golden globe was placed in site in 18 November 1593 by Giacomo della Porta, famous Italian architect that ended the Michelangelo work on the Dom. The globe is placed at a height of 131 meter having a 2.5 meter diameter and a weight of 1862 Kg. This large bronze artefact is composed of 36 plates solder together (we now know with autogenic soldering) in situ. Several signs of thunderbolt shots are evident. During the last restoration/maintenance work on the globe the Fabbrica di San Pietro gave us the possibility to perform some archaeometric investigations. In order to perform these measurement a big work of organization was needed and Dr. Gabrielli and Zander of the Fabbrica di San Pietro, together with the staff (Sanpietринi) of the fabricate gave us a big support.

The measurements carried out in such extreme conditions showed the high level of stability and reliability of the new generation of portable instruments equipped with miniaturized low power x ray tubes and SDD detectors. Inside the globe we performed 31 quantitative measures, 21 on the plates, 7 on the solders and 3 on the repairs. Several measures were also performed on the outside gilded surface to drive the restoration procedure. The globe was regilt several times since the first time therefore it was practically impossible to detect the original gold leaf.

With the EDXRF measurements it was possible to reach to the following conclusions:

a) the bronze alloy has 85.8 ± 0.5 % copper, 10.1 ± 0.3 % tin and 2.8 ± 0.1 % lead average composition, the uncertainties include the measures error and the variability of the alloys production.

b) some other minor elements were detected in the alloy: iron, zinc, silver and antimony.

c) the solders are autogenic, i.e. made with an alloy having a composition very similar to the plates soldered together (88.2 ± 0.4 % copper, 8.5 ± 0.3 % tin and 2.3 ± 0.1 % lead). Therefore, the plates were soldered in site.

d) The control of melting was excellent (the observed variability is small).

A cluster analysis was performed in order to put in evidence similarities among plates.

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**THE GILDED BRONZE PANELS OF THE "PORTA DEL PARADISO" BY
LORENZO Ghiberti: NON-DESTRUCTIVE ANALYSES USING
PORTABLE XRF**

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The east door of the Baptistery of Florence, which is universally known with the name Porta del Paradiso, was crafted by Lorenzo Ghiberti between 1426 and 1452. This celebrated masterpiece has undergone systematic investigations since 1966, the year of the flood. The studies were mainly aimed at assessing the state of conservation, understanding the corrosion mechanisms, and defining the criteria for its the future preservation. The increasing interest for the handicraft techniques of the Reanissance art foundry also stimulated some preliminary metallurgical studies. Recently, a dedicated technological investigation project was promoted by the Opificio delle Pietre Dure, the institution responsible for the restoration work. Within this project we carried out an overall recognition of the bronze alloys used to craft five of the ten main panels of the door using a homemade portable XRF instrument equipped with 60 kV, 1.6 mA, tube and a 5 mm² Si-Drift detector. About 230 measurements were performed mostly on the back side of the investigated panels focusing on the main casting, recasting, and plug areas. According with the few available literature data, our analyses confirmed the use of quaternary alloys. The preliminary calibration of the instrument allowed distinguishing among three different main alloy compositions while multivariate analysis of the trace elements provided information about possible different material stocks. These and other results that we discuss in the present work, represent the first objective support for a temporal collocation of the relieves and for understanding the casting and mounting sequence of Ghiberti's masterpiece.

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CHEMICAL AND PHASE CHARACTERISATION OF CERAMIC PIGMENTS

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Ceramic pigments are a highly heterogeneous group of substances in terms of chemical composition, crystalline structure, and resulting colours. This has given rise to various pigment classification schemes. The most widely used such scheme is the American DCMA (Dry Colors Manufacturers' Association) classification, which comprises 44 pigments, divided into 14 different classes, based on crystal structure. The pigments in each class differ in chemical composition, which is related to the different resulting colours.

In the ceramic industry, the most frequently used pigments from this classification belong to the following five classes: III (corundum-hematite), XI (rutile-cassiterite), XII (spinel), XIII (spinel) and XIV (zircon).

Pigment type, quality, uses, etc. are defined by variables such as specific surface area, chromatic coordinates, etc., and by pigment chemical and mineralogical composition. Mineralogical analysis by X-ray diffraction allows establishing the crystalline structure of the product and degree of pigment formation. Chemical characterisation by X-ray fluorescence spectrometry analyses pigment composition, determining the major pigment elements and other possible constituents such as diluents (SiO₂), mineralisers (F), fluxes (Pb), etc.

Though numerous studies are available on pigment synthesis and use, there is little information in the literature on pigment chemical and phase characterisation. The present study has been undertaken, therefore, to develop a methodology for pigment chemical and phase characterisation.

As each class of ceramic pigment indicated above displays specific characteristics in terms of crystalline structure and chemical composition, in this study a specific methodology has been established for each pigment group. The methodology details the elements to be analysed, their concentration range, sample preparation conditions and group of standards used for measurement calibration and validation, in addition to calculation of the correction coefficients of the L overlap and • matrix effect.

Finally, the methodology developed has been used to analyse a group of ceramic pigments, which represent the five DCMA classes of pigments most widely used in the ceramic industry

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OBSIDIAN PROVENANCE DETERMINATION BY USING THE BEAM STABILITY CONTROLLED BSC-XRF SPECTROMETER: THE CASE OF MILENA (SICILY)

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It is well known that the content of trace elements present in archaeological obsidians can give information on the provenance. Their quantitative determination can be obtained by using portable XRF spectrometers; however, x-ray tubes largely used as exciting source can be subjected to energy and intensity fluctuations and frequent calibrations of the systems are required in order to obtain quantitative data.

In the present work a portable BSC-XRF spectrometer (Beam Stability Controlled XRF) with a beam stability control, is used to determine the content of some trace elements (Rb, Sr, Y, Zr and Nb) characterizing obsidian samples. The control of the stability is not an electronic device operating on the applied high voltage and current but consists on a direct intervention on the beam emitted by the tube used as x-ray source.

The concentration of Rb, Sr, Y, Zr and Nb was determined in 57 obsidian artefacts coming from Milena, an important prehistoric site in the internal region of Sicily; quantitative determination was obtained by a method based on a multi-linear regression approach previously developed by the authors and based on a calibration procedure which used 26 petrologic standards. It should be emphasized that in the case of obsidians, a surface XRF analysis gives meaningful quantitative results since they are composed of an homogeneous matrix.

Milena artefacts were found on well defined archaeological layers dated back from the Neolithic to the final Copper age; this aspect is of relevant interest because only few data exists on stratigraphic obsidians in Sicily.

Analysed artefacts were randomly sampled in order to well represent the populations in the different periods. Results on compositional data of Rb, Sr, Y, Zr and Nb allowed to identify Lipari and Pantelleria islands as the main sources of the Milena obsidians and to evidence how the samples coming from these sources are distributed from Neolithic to the final Copper age.

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DETERMINATION OF OXIDATION STATE AND SPECIATION IN GEOLOGICALLY RELEVANT SYSTEMS USING XANES

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The oxidation state of heterovalent elements has a strong influence on the geochemical behaviour of these elements in geological systems and may influence the bulk properties of the system and, as a consequence, the evolution of the system through time. In this contribution examples of XANES studies on heterovalent elements in geological systems are shown that highlight the potential of this method in providing

a) spatially resolved valence information

b) information on speciation measured under geologically relevant conditions.

Fe is the major heterovalent cation found in terrestrial rocks and magmas and its oxidation state effects significantly thermodynamic equilibria as well as physical properties. As the Fe(II)-Mg distribution among mineral phases provides insight to the thermal history of rocks now exposed at the earth's surface evaluation of the Fe(III) content within the textural context of the phases is of particular interest. Such measurement can be performed by the application of micro-XANES at the Fe K-edge.

The Fe-oxidation state in silicate melts and magmas influences melt viscosities and melt densities. A better insight to the speciation, i.e. local structural environment, is of major interest to better relate melt compositions to their physical properties. XANES measurements under in-situ conditions (i.e. high temperature and pressure) help pointing out measurement artefacts that may be present in quenched samples and thus better constrain the properties under the relevant geological conditions.

Although Sulfur is only a trace element in magmatic systems it is still an important element for the whole system. First, it strongly controls the behaviour of several metals that are also of economic interest. Secondly, it plays an important role in explosive volcanic activity, which is capable of releasing large amounts of S into the atmosphere, significantly affecting global climate. The solubility of sulfur depends strongly on the oxidation state that may vary from S(II-) to S(VI+). XANES measurements provide unique information on the sulfur species present: either only sulfide and sulfate as often proposed or also sulfite that might be stable under intermediate redox conditions. The presence of a third species has important consequences on thermodynamic treatment of equilibria involving sulfur.

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IN SITU MONITORING OF MICROBIAL METABOLISM IN DIAMOND-ANVIL CELL BY X-RAY SPECTROSCOPY

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Many biotopes are situated in high-pressure environments, from deep subsurface rocks to deep-sea water and sediments. They are supposed to have been at the origin of life on the young Earth. However, due to the physical and chemical conditions, these biotopes are hardly accessible by standard techniques. In situ systems open perspectives to study these environments by avoiding the biases implied by successive cycles of decompression/sampling/compression.

Thus, we developed an experimental vessel based on a modified diamond anvil cell, with a single diamond anvil and a 400 μm -thick diamond window, designed by J-C. Chervin (IMPIC, Paris). The aim of the modification was to increase the image resolution and the quality of spectroscopic signals. The cell was conceived for its compatibility with Raman, IR and X-ray spectroscopies, and classical and confocal microscopies. We developed the use of quantitative Raman and X-ray spectroscopies to monitor microbial activities in the DAC.

Using this modified DAC, we monitored the in situ microbial metabolism of selenium by the bacterium *Agrobacterium tumefaciens* strain C58 under controlled conditions of pressure and temperature. These measurements were realised by X-ray fluorescence and XANES on beamline ID22 at the ESRF. A combination of μXANES and μXRF allowed us to monitor the speciation of selenium species in solution. In anaerobic conditions, the selenite is reduced by the bacterium to 1/3 elemental selenium and 2/3 selenide species. Some supplementary experiments were realised on beamline BM30B in the high pressure cell dedicated to the beamline. The reduction of selenium by strain C58 was monitored until 25 MPa.

This experimental setup allows us to monitor the in situ activity of living cells grown on the beamline by X-ray spectroscopy under controlled conditions of pressure and temperature. The development of in situ analytical systems could be useful for the study of deep subsurface ecosystems, where light and oxygen are absent, heavy metals present in great concentration, and pressure and temperature are elevated, i. e. the environment of the postulated “cradle of life”.

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**COMBINED MICRO-XRF/XRD STUDIES OF INCLUSIONS
IN DIAMONDS FROM JUINA AND KANKAN**

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The confocal X-ray micro fluorescence imaging technique was combined with scanning microdiffraction in order to study the element distribution of inclusions in diamonds from Juina and Kankan. Minerals trapped within such natural diamonds give uniquely detailed information on the chemistry and conditions during the diamond host formation at great Earth depths.

The applied confocal arrangement is based on coupling the detector with a polycapillary half-lens that restricts the collection of XRF-signal from a finite (10-20 μm) section along the full beam path within the sample. By restricting the accepted beam path, confocal XRF allows to directly collect local elemental information from deep-within the sample, limited by the penetration/escape depth of the analyte signal.

This work describes the evaluation and the interpretation of XRF/XRD data derived from experiments performed at the ESRF ID18F end-station (Grenoble, France). In the confocal arrangement, thin glass standard measurements (NIST SRM 1832/1833; 300 s) using Al CRLs show 10 fg to sub-fg absolute detection limits in the detectable atomic number range $Z=20$ to 48; for trace elements in glass (NIST SRM 613; 300 s) the relative detection limits vary from 10 ppm down to the 1 ppm level for the same atomic range. Additional experiments were performed with Raman micro spectroscopy, and with high energy micro XRF at HASYLAB beamline L (DESY, Hamburg, Germany) for rare-earth element determinations. Although the evaluation and the interpretation of the XRF/XRD data is still in progress, the results presented here point to the existence of a CO₂-rich reservoir at great Earth depth (>580 km) and to global fluid cycling to depths exceeding 300 km.

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HIGH PRESSURE-HIGH TEMPERATURE IN-SITU X-RAY DIFFRACTION INVESTIGATION OF EQUATION OF STATE AND RHEOLOGY OF SERPENTINES, A MATERIAL OF GEOPHYSICAL IMPORTANCE.

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We present measurements of serpentines thermodynamic and rheological properties at High Pressure–High Temperature (HP-HT) using in-situ synchrotron X-Ray Diffraction (XRD). Knowledge of these properties is crucial for the geoscientists to better understand processes occurring in subduction zones. Indeed, serpentines, which are hydrous silicates forming by hydration of the oceanic floor, play a major role in subduction zones dynamics. During subduction of oceanic crust they carry important water quantities into the mantle, where their dehydration at high pressure hydrates the mantle wedge, thereby significantly modifying its physical properties. This dehydration is probably related to intermediate-depth seismicity in cold subduction zones such as North-East Japan (e.g. [1]). Serpentines also have a supposed low viscosity and low density comparing to the mantle, which measurements would allow more accurate numerical simulations and comparisons with geophysical data.

Since it gives a rather poor signal in conventional XRD, a synchrotron beam is preferred to investigate this mineral with X-rays.

The room-T equation of state of antigorite, the high pressure form of serpentines, was determined in-situ with powder XRD at the ID30 beamline of ESRF, Grenoble (France). The bulk modulus obtained allows recalculation of antigorite stability field [2], which is now in perfect agreement with the latest results from experimental petrology.

In a second part we present results from antigorite HP-HT deformation experiments at GSECARS, APS (Argonne National Laboratory, USA) with a D-DIA apparatus allowing very low strain rates at high confining pressure. Strain was monitored in situ with synchrotron X-ray imaging, and differential stress was extracted from powder XRD 2D patterns (lattice strain measurement). Strain and stress were measured in relevant physical conditions for a subducting slab. The results show that these techniques developed on metals and very simple minerals (e.g. [3]) can be successfully applied to much more complex minerals to obtain rheological laws, as long as sufficient information is available on thermodynamic and elastic properties of the material. They also give valuable information on texture evolution during deformation.

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MICROCHARACTERIZATION AND IDENTIFICATION OF TIRE DEBRIS OF AIRPLANES

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Tire (rubber) debris is produced at touch-down of aircrafts and natural wear of tires. The carcinogenic effect of such particles has been described in many publications, but their identification either in lung tissue or among ambient atmospheric aerosol is still a challenge. In this work, the combination of scanning electron microscopy (SEM), low-Z electron probe X-ray microanalysis (EPMA) and micro-Raman spectrometry was applied for this purpose, aiming morphological, elemental, molecular and structural characterization of individual rubber microparticles.

Tire debris was collected from touch-down area of the runways of different airports. In order to identify tire debris in ambient air, size-segregated aerosol particles were collected in the vicinity of a runway of the international airport of Budapest, by means of a May cascade impactor.

A JEOL 733 electron probe microanalyzer equipped with an Oxford Pentafet X-ray detector was applied for SEM visualization and low-Z EPMA measurements, using 10 and 20 kV accelerating voltages. Results of the tire debris samples showed that the majority of the particles were carbonaceous with irregular shape, containing around 5 wt.% of Zn. Some particles contained also silicates. Raman shift on individual particles of the same samples has been measured with micro-Raman spectrometer (Renishaw InVia) at 514 and 785 nm wavelengths. Two broad bands of elemental carbon were identified in all samples. Si was found to be strongly bound to the carbonaceous matrix.

Using low-Z EPMA, the identification of tire debris in the 2-8 μm aerosol fraction was successful, and could be verified with micro-Raman spectrometry. The abundance of tire debris originating particles was found to be 1-5 % in different aerosol samples.

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**CHARACTERIZATION OF ELEMENTAL CONTENTS IN PM2.5
PARTICLES ORIGINATING FROM A MODERN WASTE INCINERATION
PLANT BY EDXRF ANALYSIS**

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Two major challenges in sustainable urban development are those of 1) finding substitutes for fossil fuels for the generation of electricity and heat and 2) developing a safe way to dispose of the waste originating from human consumption. Both these challenges can be met if the energy contents in domestic and industrial waste can be utilised in efficient heat and power plants. However, since the need for environmentally safe waste handling is greatest in densely populated areas in which many other sources of air pollution exist, it is necessary to keep emissions of air pollutants from waste incineration at an absolute minimum.

In the city of Borås, which is a medium sized city in the south-western part of Sweden, a new modern plant for electricity and heat generation has recently been installed and optimised with respect to internal parameters of efficiency and economy. The direct emissions of gaseous pollutants which are subject to restrictions are well below the allowed limits as stated by Swedish and European standards.

The aim of the present work is to study the particle pollutants with emphasis on PM2.5 in the ambient air and to identify the specific contribution from the new incineration plant. Many different sources contribute to PM2.5 in urban air. Thus, the general problem is to characterise and identify the particle pollution, which can be attributed to gases and/or particles emitted by the waste incineration plant. EDXRS was used for determination of concentrations of twenty elements in the aerosol. Combined with information on some gaseous species (SO₂ and NO₂) together with aerosol mass- and black carbon concentrations, all data were subjected to factor analysis in order to determine the characteristics of the different sources. Vehicle emissions, oil- and bio-mass fired stoves, industrial emissions and long range transported aerosols are believed to contribute to the observed data. Oil combustion was identified as one of the major sources to Ni and V in the urban air.

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**SPECIATION OF HEAVY METALS BY COMBINED MICRO-XRF, -XANES
AND -XRD IN POLLUTED SOIL FROM THE INDUSTRIAL SITE
OF VAL BASENTO, BASILICATA, ITALY**

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It is well known that the bioavailability and toxicity of heavy metals in soil are strongly connected to their solubility and therefore to their geochemical forms. The correct identification of the chemical forms in which heavy metals are present in soil is of extreme relevance for a proper risk assessment and to formulate effective remediation strategies.

In this investigation, soil samples from the industrial site of “Val Basento” (Basilicata, Italy), have been studied using a combination of synchrotron X-ray microanalytical techniques. This polluted site showed concentrations of toxic elements such as Hg, Pb, Cr, Zn, Cu, and V strongly exceeding the Italian legislation limits.

After an initial microscopic characterization of soil thin sections (20-60 micrometer thick) by EPXMA (Electron Probe X-ray Microanalysis), the same areas have been studied by a combined use of micro-XRF (micro X-ray Fluorescence), micro-XRD (micro X-ray diffraction) and micro-XANES (micro X-ray Absorption Near Edge Spectroscopy) employing a focussed beam of synchrotron radiation (SR) X-rays with a diameter of typically 15-20 micrometer.

More specifically, micro-XRF has been used to localize and quantify trace elements in the soil matrix and to find correlations among different elements present in the sample. At the same time, simultaneous micro-XRD patterns acquisition and micro-XANES point analyses supplied information about the nature of the soil minerals with which the heavy metals were associated.

From the first experimental results using such a combination of microscopic techniques at HASYLAB BL L, it appears that Cr, Zn, Cu, and V are usually associated with the iron minerals goethite, hematite and maghemite while Hg is mainly present in the form of HgS (cinnabar) and Pb as a lead sulphate mineral (anglesite and/or lanarkite) often linked to BaSO₄ (barite).

In addition, micro-XANES measurements on trace constituents such as Cr allowed to determine the oxidation state for this important pollutant. While in a number of locations, Cr was present under the relatively harmless Cr(III) form, at other locations, clear indications for the presence of the much more toxic Cr(VI) were present in the XANES data.

The results obtained up to now show that, despite a very high heavy metal total concentration in the investigated soils, these heavy metals appear to be present as scarcely mobilisable geochemical forms, indicating that the environmental danger connected to their presence in these soils is much lower than expected. At the end of this survey, the determined heavy metal speciation will be compared with the geochemical characteristics of the site under investigation so that it will be even possible to find out the sources of anthropogenic impact on the soils under investigation.

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CURRENTLY RESEARCH ACTIVITIES IN ENVIRONMENTAL AND SURFACE SCIENCE USING MICRO-XRF AND GRAZING-EXIT XRF SPECTROSCOPY AT THE XRF BEAMLINE OF THE LNLS

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Micro X-ray fluorescence analysis using synchrotron radiation has proved to be a very powerful analytical technique for trace elements detection in microscopically small areas. The intrinsic characteristics of the synchrotron radiation (high intensity, polarization and natural collimation) make possible to improve the sensitivities in comparison with the use of conventional sources [1]. Micro-pixels mapping of X-ray fluorescence intensities or concentrations in many variety of samples can be fast completed without intricate experimental set-up.

Some selected research activities carried out at the x-ray microprobe station of the XRF beamline of the LNLS [2], as well as a recently developed instrumentation that combine x-ray microbeam excitation and x-ray fluorescence detection at small take-off angles (grazing-exit geometry), will be shown in this work.

One research activity will be focused on the evaluation of environmental pollution sources by the micro-XRF analysis of different individual particles collected from coarse air suspended particle material.

Another subject of this work will pretend to show some results from the study of the 2D spatial distribution of arsenic in different rat's tissues after exposure to inorganic arsenic. This subject is as part of a more general research being performed to develop reliable animal's models of hydroarsenicism, which is related to several internal cancers in human being that had exposed to arsenic by naturally contaminated drinking water.

Finally, preliminary results obtained from the measurements of specially prepared stepped multilayer samples, using the combination of x-ray microbeam excitation and grazing-exit x-ray fluorescence detection will be given. This must be considered as the first steps toward using this set-up to develop experiments in which the reconstruction of 3D elemental distributions in thin samples is required.

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**DEVELOPMENTS IN DATA TREATMENT OF COMBINED
MICRO-XRF/XRD EXPERIMENTS**

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Several synchrotron microprobe beamlines, such as Beamline L of Hasylab (Hamburg, D) and Beamline ID18F of ESRF (Grenoble, F), provide the possibility to perform combined μ -XRD/ μ -XRF experiments. Although analysis of series XRF spectra, whether originating from one or two-dimensional scans, from conventional XY-type of tomographic (Y \square -type) scans, is already thoroughly discussed and implemented, there is a lack in software able to reduce large (one or two-dimensional) series of X-ray diffraction images, as collected by means of CCD cameras.

To aid the explorative data analysis of correlated series of μ -XRF spectra and μ -XRD diffractograms and to permit on-line feedback during lengthy μ -XRF/XRD scanning experiments, user-friendly data reduction software, called XRDU, is being developed. This paper will describe the current state of this program and the final aimed-for functionalities of the software. Also the associated methodological problems and challenges will be discussed.

The current status of the software will be briefly illustrated with applications deriving from the environmental sciences, mineralogy and geochemistry.

The first example concerns the speciation of heavy metals in soil from the industrial site of "Val Basento" (Basilicata, Italy). It is well known that the bioavailability and toxicity of heavy metals in soil are strongly connected to their solubility and therefore to their geochemical forms. The correct identification of the chemical forms in which heavy metals are present in soil is of extreme relevance for a proper risk assessment and to formulate effective remediation strategies. It will be demonstrated that correlated μ -XRF and μ -XRD is very suitable to identify, e.g., Hg-pollution to be present as HgS and Pb as lead sulphate minerals.

Secondly, the structural investigation of inclusions in sub-lithospheric diamonds from Juina and Kankan in order to increase the insight into the bulk chemistry, phase equilibrium and element cycling occurring in the deep Earth, is discussed. For example, inside some of the examined inclusions, new F- and REE-bearing phases were discovered by combined indications revealed via confocal μ -XRF and 2D μ -XRD mapping.

In addition to these experiments, results of the first μ -XRD/XRF tomography experiments at Hasylab Beamline L will be shown to illustrate the possible use of XRD for phase identification and 3D-phase mapping inside strongly heterogeneous samples. Results from artificially prepared phantom samples, consisting of nano- and micro-crystalline powders of e.g., Ni, NiO inside glass capillary containers will be discussed.

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**NON-DESTRUCTIVE CHARACTERIZATION OF ELECTROCHEMICALLY
DEPOSITED COBALT AND COPPER
TERTRASULPHOPHTHALOCYANINE ON GOLD ELECTRODES BY
MEANS OF SYNCHROTRON X-RAY MICROFLUORESCENCE AND X-RAY
ABSORPTION SPECTROSCOPY**

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Chlorophenols, PCB's and dioxins are momentarily three of most important pollutants in the world. The need for an adequate detection keeps on expanding given their increasing presence in waste waters, food and gasses. Conventional detection methods, however, are time consuming and expensive, implying the need for alternative methods. The goal of this paper is the development of an electrochemical sensor which makes the detection of these pollutants simple, cheap and fast. Its operation is based on the modification of gold electrodes with a catalyst, including cobalt and copper tetrasulphophthalocyanines (CoTSPc and CuTSPc).

Micro X-ray fluorescence (micro-XRF) analysis of the modified electrodes were performed to compare the amount of adsorbed CoTSPc/CuTSPc onto the gold electrodes and to determine the level of uniformity of the deposited layer in different cases. Experimental difficulty of the XRF CoTSPc/CuTSPc thin-film uniformity studies included the determination of low amounts of cobalt and copper (ca. 0.1-0.5 pg, assuming a 20 μm incident beam) in the presence of intense gold fluorescent/scatter signals, which made the use of tunable monochromatic synchrotron radiation (Beamline L, HASYLAB, Hamburg, Germany) necessary [1].

Complementary X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) studies were performed on the modified gold electrodes to obtain information on the oxidation state of Co/Cu and the local chemical environment around the Co/Cu species in the deposited thin-films. These measurements were performed at Dubble at the ESRF (Grenoble, France).

These X-ray studies contributed to the better understanding of thin-layer deposition processes on gold electrodes and provided information with respect to the deposited amount and local coordination environment of Co/Cu as a function of different electrochemical deposition conditions. This information is crucial for the development of a new generation of simple, fast and relatively cheap electrochemical sensors for the detection of various contaminants, such as benzene, chlorophenols, PCB's and dioxins

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**MICRO X-RAY FLUORESCENCE SPECTROSCOPY AT THE ENDSTATION
OF THE NEW μ SPOT BEAMLINE AT BESSY**

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μ Spot is a new microfocus beamline dedicated to X-ray spectroscopy and to scanning small and wide angle scattering at BESSY. As a special feature for micro X-ray spectroscopy a confocal setup is part of the experimental environment... ..

The contribution will describe the characteristics of the beamline, the instrumentation and the experimental environment. Emphasis will be laid upon the confocal setup and its potentials. Results of first application experiments will be presented....

Applications in life science, geology, art and archeology, materials science and other application fields of X-ray spectroscopy are encouraged and welcome. User operation will start in the second half of this year.

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SYNCHROTRON MICROXRF ANALYSIS OF INORGANIC DISTRIBUTIONS IN HAIR

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Hair grows at a rate of approximately 1 cm per month and incorporates major and trace components from the nurturing blood supply. Longitudinal analysis for organic and inorganic components has therefore been proposed to provide a historical representation of blood concentrations with potential application in biomonitoring and forensic drug and toxicological analysis. While metabolites of drugs can only occur within the hair after metabolism and incorporation from the blood supply, analysis of inorganic components is severely hindered due to the effects of contamination. High resolution (~130nm) images of thin hair sections were produced from hair samples above and below the skin level utilising synchrotron X-Ray Fluorescence (XRF). Most elements were found to primarily exhibit the influence of environmental effects not only on the outside of the hair, but internally as well, to the detriment of hair analysis. Cu and Zn however, demonstrated promise with minimal environmental effects and may be linked to other health disorders. Arsenic was also investigated in a suspected poisoning case. Micro-X-Ray Absorption Near Edge Structure (XANES) was applied to the analysis of the arsenic within hairs to deduce the origins of the arsenic as being of endogenous incorporation or exogenous application.

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INV-6

THEORY AND APPLICATIONS OF X-RAY ABSORPTION SPECTRA*

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There has been dramatic progress in recent years both in ab initio calculations and in the interpretation of x-ray absorption spectra, including both the x-ray absorption fine structure (XAFS) and the x-ray absorption near edge structure (XANES) [1]. These developments have led to computer codes such as FEFF8, which are in semi-quantitative agreement with experiment and permit an interpretation in terms of geometrical and electronic properties of a material. Such theoretical developments have revolutionized experimental investigations of complex materials with XAS. We first summarize these advances, focusing on the excited state theory underlying the real-space Green's function approach used in FEFF8. This "quasiparticle" theory differs significantly from ground state electronic structure or quantum chemistry calculations based on density functional theory and includes many body such as the screened core-hole interaction, inelastic losses, and Debye-Waller factors. Extensions that include corrections to the independent particle approximation are also discussed [2]. These developments are illustrated with a number of applications ranging from catalysts and minerals to bio-structures,

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**XAS ANALYSIS ON MESOPOROUS VANADIUM OXIDE THIN FILMS
BY SOL-GEL**

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Low-dimensional vanadium oxides (VOx) thin films, with their layered structure, are especially of interest because vanadium displays different oxidation states forming single and mixed-valence compounds with different properties and structural versatility. These bi-dimensional (2D) structures have considerable scientific and technology importance owing to their enhanced properties in catalysis and in electrochemistry as pseudocapacitor, nanoscale electrodes for lithium-ion batteries and in electrochromic devices.

In the present work the Extended X-ray Absorption Fine Structure (EXAFS) analysis on sol-gel derived VOx thin films templated using polyethylene glycol (PEG, Molar Weight 600) as the structure directing agent is reported. EXAFS spectroscopy was made on the vanadium K absorption edge (5465 eV) and performed at the Italian beamline GILDA at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.

The structure of the VOx networks has been described using Ifeffit with the V2O5 orthorhombic phase lattice as reference. The results indicate two different crystalline rearrangements for our samples.

The first is related to a planar disordered 2D network with two shells of doubly degenerate oxygen atoms located in the equatorial plane of the orthorhombic V₂O₅ unit cell as nearest scatterers around the central vanadium atom (the lengths of the V-O bonds are 1.66 Å and 1.84 Å ± 0.02 Å, respectively). The best fit for the second neighbour scatterer has been obtained for this crystalline phase assuming a single vanadium atom (V-V length of 3.41 Å ± 0.02 Å) of the adjacent unit cell.

The latter phase is characterized by a nearly 3D network, with both planar and axial order. The bond lengths are slightly displaced from the crystallographic data of orthorhombic V₂O₅. This feature could be explained considering this phase as an intermediate step between an hydrated V₂O₅ nH₂O phase (2D) and the orthorhombic phase (3D).

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INVESTIGATION OF COPPER PIGMENTS USING X-RAY ABSORPTION SPECTROSCOPY

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The scientific investigation of historical pigments gives a unique insight into painting techniques and their evolution through time and geographic location. In addition, the analyses of alteration mechanisms provide essential information for restoration and conservation treatments. This study deals with the non-destructive identification of different artificial and natural green copper pigments by means of X-ray absorption spectroscopy.

Copper compounds were widely used as green and blue pigments from ancient times until the 19th century. Natural minerals were used as well as artificially produced compounds. A lot of treatises and recipes for the preparation still exist. Furthermore, copper pigments can undergo chemical reactions with binding media, with other pigments, or with the substrate, these processes may cause damages. The knowledge of the chemical composition of the pigments as well as the reaction products is essential to elucidate the damaging process.

Pigments were usually identified by means of XRD, XRF, Infrared, and Raman spectroscopy. Due to the fact that interesting copper pigments as well as their corrosion products consist mainly of Cu and light elements (such as C, H, O), it is not possible to distinguish them by means of XRF. Some pigments and their corrosion products are not crystalline and therefore not detectable by XRD. The concentration of the copper compounds is often very low in comparison to the concentration of the binding media, and so the application of IR and Raman spectroscopy may be difficult.

Due to the fact that the shape of various XANES-NEXAFS structures reflect the influence of the chemical environment of the element copper, we started X-ray absorption measurements at the Cu K-edge in order to distinguish different copper pigments. Artificial samples were prepared following historical recipes. The experiments were carried out at the bending magnet beamline KMC-2 at Bessy II. A double Si/Ge gradient crystal (111) monochromator was used for monochromatization of the primary beam providing an energy resolution of $E/DE = 4200$. XANES spectra at the Cu-K-edge were collected in fluorescence as well as in absorption mode using an energy step width around the absorption edge of 0.5 eV.

The first results demonstrate that it is possible to distinguish different pigments as well as different alteration products with respect to the fine structure of the XANES region. In order to apply these findings to original samples we investigated the green colour on a reverse painting on glass. There exists a variety of these artworks containing this very impressive 'green'. All paintings belonging to this group were obviously prepared in the late 18th century in South Tyrol. Initial XRF measurements showed that this green is a mixture of lead white and a copper green pigment (without sulphur or chlorine), and following XAFS studies allowed to identify the green copper pigment as a mixture of malachite and azurite.

The present study demonstrates the possibilities of X-ray absorption measurements in the characterisation of copper pigments and their alteration products. It may be seen as a first step to establish X-ray absorption spectroscopy in this field of pigment investigation.

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**XANES STUDY OF CONTAMINATION AND DECONTAMINATION OF
COPPER IN DIFFERENT SOILS BY SORPTION AND DE-SORPTION**

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The present study aims to analyze the process of adsorption of copper in silty and clayey soil, and the mechanism of de-sorption with surfactant in the remediation process. Two types of soil from three different locations in dry state have been taken out for the experimental work. Sorption experiments were carried out by varying concentration of copper with different time intervals in the soil samples. The pH and ionic strength were controlled during adsorption experiments. It was observed that the concentration of copper remaining in the solution with different time interval was non linear. Concentration of copper was found to decrease rapidly up to 2 hours, then slowly up to 4 hours. The rate of adsorption increased with decrease in particle size of the soil. The K X-ray absorption edges of copper in soils were recorded on Technos EXAC 820 EXAFS Spectrometer equipped with rotating Mo anode as X-ray source. The radius of the Rowland circle was 300mm with Johansson type Ge(400) crystal ($d_{400} = 2.82 \text{ \AA}$) as a monochromator. The detector for I₀ was Proportional Counter and Solid State Detector (pure Ge) was used for I which was cooled by liquid nitrogen. The voltage was 20 kV and current was 150 mA. The absorber thickness was so adjusted to give $I / I_0 = 1/3$ on the high absorption side of the edge. The data were recorded on NEC PC using graphics Igor Pro. Soils contaminated with copper (4 mg/l and 8mg/l) were selected for de-sorption study. Concentration 0.4% v/v of liquid soap was used for decontamination studies. The variation in the X-ray absorption edges in the contaminated soil and de-contaminated soil was observed. It was observed that maximum decontamination of copper occurred within 1 hour in the silty soil, whereas 2 hours in clayey soil. The decontamination efficiency range of surfactant was found to vary from 45% to 55%, depending upon particle size of the soil and the strength of the copper.

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**CARACTERISATION OF Cl-CONTAINING PHASES FORMED ON
ARCHAEOLOGICAL ARTEFACTS USING MICRO XAS**

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Preservation of iron artefacts is one of the main problems encountered by scientists dealing with the restoration and conservation of the metallic cultural heritage. Indeed, the current desalinisation treatments allow slowing down the corrosion processes. However, they are not optimised in many cases. The limits of these treatments are mainly due to the poor knowledge of the Cl-containing corrosion products developed on the archaeological objects. The investigation of the iron corrosion mechanisms in soil and in presence of chlorine was based on a great analytical part. It deals with the local and structural characterisation of the Cl-containing corrosion products. The samples available are cross section from iron objects coming from particular archaeological excavation sites dating from 12th to 16th century AD. Previously, various classical techniques are employed to reveal morphological, compositional information of corrosion products; some others techniques are based on structural investigation, such as micro x-rays diffraction and μ Raman spectroscopy. In addition, micro structural characterisation using x-rays absorption spectrometry under synchrotron radiation was performed. The micro XANES and micro EXAFS experiments reported here concern analyses performed at Fe and Cl K edge, they were conducted on the ID21 (ESRF) and LUCIA (SLS/SOLEIL) beamlines. These studies allow obtaining fundamental results in the characterisation of the chlorinated phases. Two different Cl-containing crystalline phases were identified. The oxihydroxide beta-FeOOH akaganeite is a compound usually present in the corrosion products of objects exposed to a chlorinated environment. In addition, the study revealed the presence of a phase with a more strongly chlorine content, the beta-Fe₂(OH)₃Cl hydroxychloride. This result is significant because this phase was rarely observed before, on the archaeological samples, whereas it is present in considerable proportion on the observed artefacts. These finding help to gain new insights concerning the influence of such phases in iron corrosion mechanism. This will have to be taken into account for the improvement of the desalinisation methods of conservation restoration. The coupling of the characterisation of the Cl-containing corrosion products at microscopic scale, on the archaeological samples associated with the study of synthesised phases (akaganeite one) allow to understand the complex systems of long-term iron corrosion in soil and in presence of chlorine.

S.Reguer & al, NIM B 240 p 500-504, 2005

S.Reguer & al, Applied Physics A, in press

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**MICRO-XRF IMAGING AND MICRO-XANES ANALYSIS OF ARSENIC
HYPERACCUMULATOR FERN (PTERIS VITTATA L.)
BY USING SYNCHROTRON RADIATION**

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Arsenic hyperaccumulator plant, Chinese brake fern (*Pteris vittata* L.), could contain extremely high level of arsenic in its body (ca. 20000 ppm dry weight) when the plant was grown on a contaminated soil [1], and is now put to practical and commercial use in phytoremediation technology, that uses plants to remove hazardous substances from the environment, in United States and Japan. In order to understand the accumulation mechanism of arsenic in the fern, the chemical forms of arsenic have been studied with great eagerness [2]. On the other hand, the arsenic distribution has been investigated only in each plant organ such as pinnae or stems, and that distribution is still unclear at cellular and sub-cellular levels. The conventional SEM-EDS mapping is not suitable for this purpose because of the low sensitivity of the electron beam analysis for heavy elements such as arsenic, though the newly advanced SEM with a cooling stage under rough vacuum condition is suitable for obtaining clear three dimensional image of the plant cell. By this reason, the analytical methodology for elemental distribution at cell level has been only limited and the arsenic accumulation mechanism has not been fully revealed.

Recently, we have applied synchrotron radiation (SR) microbeam to elucidate the elemental distribution in the pinna accumulating arsenic [3]. It was first report that arsenic was obviously accumulated in specific tissue in the pinna. In the present study, the arsenic distribution in the arsenic hyper-accumulating fern was investigated using a SR X-ray fluorescence microprobe. The focused microbeam (ca. $1 \times 1 \mu\text{m}^2$) produced by Kirkpatrick-Baez optics was applied to the fern in order to determine the elemental distribution in plant tissue and cell. Fronds of varied ages were subjected to the XRF imaging analysis, and it was found that the arsenic distribution in the pinnae of fronds changed according to their stage of growth. The results indicated that high levels of arsenic accumulate at the base of sporangium with lamina of pinnae. On the other hand, the fern was subjected to the X-ray near edge structure (XANES) analysis in fluorescence mode without any sample treatment to directly elucidate the arsenic oxidation state in fern. It was found that arsenic exists as the As(III) form in pinnae, and as a mixture of As(III) and As(V) in rachis, while As(V) is present in cultivated soil. These findings indicate that the fern uptakes arsenic as As(V) from soil and that the As(V) is then partially reduced to As(III) within the plant, and finally arsenic accumulates as As(III) in a specific area of the pinna.

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**X-RAY SPECTRA, ELECTRON STRUCTURE AND VALENCE STATE OF
THE NEW TERNARY INTERMETALLIC COMPOUNDS
THEORY AND EXPERIMENT**

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X-ray photoelectron, emission and absorption spectroscopes have been used to study the electron structure and valence state of new ternary intermetallic compounds, which crystallize in the ThCr₂Si₂ and HfFe₂Si₂ types. The calculations of electron energy bands E(k) and partial DOS for compounds were performed by the semi relativistic linear muffin-tin orbital method without considerations of spin-orbit interactions. The eigenvalues were calculated at 244 points within a 1/16 Brillouin zone. Effective filling numbers of electrons in different bands of components in R.E.M2X2 compounds have been calculated. On the basis of the obtained X-ray emission spectra and calculation of density of total and partial electron states in R.E.M2X2 compounds, the localization of electron of s- and p-states of Si(P) has been established within the energy ranges 14-7 eV and 7-2 eV, respectively. These states of Si(P) are hybridized with 4p-states of M atoms. The electron occupation of the d-states of the M atoms has a dominant influence on the degree of their hybridization. Between the experimental and calculated X-ray emission spectra of R.E.M2X2 good agreement has been obtained, what justified the reliability of the performed calculations.

LIII –absorption spectra Ce and Yb in ternary Ce(Yb)M2X2 compounds were obtained at 78 K and 300 K using a tube spectrometer equipped with an RKD-01 co-ordinate detector. The mixed valence state of Ce and Yb was obtained in the investigated compounds.

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XANES ANALYSIS OF Fe VALENCE IN IRON GALL INKS

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Iron gall ink is one of the most important inks in the history of western civilization, of a widespread use from the middle ages until the 20th century. Unfortunately, these inks induce degradation of paper, causing severe damage to numerous historical artifacts. As a result, 60-70% of Leonardo da Vinci's oeuvre shows signs of deterioration, Bachs' written music is virtually falling apart, while numerous manuscripts by Galileo Galilei are completely destroyed. The two main reasons for iron gall ink corrosion are acid hydrolysis and oxidation, catalysed by ferrous ions. Reduction of Fe^{3+} by many organic compounds and superoxide anions enables a cycle of reactions, resulting in extensive and growing oxyradical damage [1]. Determination of the concentration of Fe^{2+} in inks of historic documents is therefore relevant in assessing the extent of further oxidation of cellulose and in devising of effective stabilization treatment.

In this study, we investigated the feasibility and reliability of Fe K-edge XANES spectroscopy as a tool in determination of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in historic inks. In XANES, the valence state of metal cations can be deduced from the energy shift of the absorption edge or pre-edge absorption features [2-5]. For atoms with the same type of ligand a linear relation between the edge shift and the valence state was established [2]. However, significant deviations from this empirical law were observed for compounds with widely different environments of the investigated atom. Different local symmetries are reflected in different K-edge profiles, which hinder the comparison of edge shifts [3]. In recent analyses of average Fe valence in iron gall inks by Fe K-edge XANES spectra [6] large uncertainties in the obtained results are reported.

We measured Fe K-edge XANES and EXAFS spectra of several model iron gall inks with different $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio determined independently by Moessbauer spectroscopy, together with some reference compounds with known Fe valence state and ligand environment, at the E4 and X1 beamlines of HASYLAB at DESY. For 18th century manuscripts a micro focused beam and the fluorescence detection mode at beamlines 9.2 and 10 of SRS Daresbury was used.

We examined different approaches to reliably determine $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio from the Fe K-edge shifts and to identify reference compounds for the Fe XANES analysis of the iron-gall inks. In addition, the effects of radiation damage of the sample in the high-density micro-focused SR beam and the resulting Fe K-edge shifts are discussed.

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**THE MONTE CARLO - LIBRARY LEAST-SQUARES (MCLLS) APPROACH
FOR THE INVERSE XRF ANALYSIS PROBLEM**

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The Monte Carlo - Library Least-Squares (MCLLS) approach to the non-linear inverse XRF analysis problem is described and treated including: (1) the overall approach, (2) correction of the spectral distortion caused by high counting rates with the CEARIPPU Monte Carlo code when necessary, (3) the Monte Carlo computer code CEARXRF that is employed including the details of the physics employed, (4) sample results for stainless steel and aluminum alloy samples, (5) a comparison of results with existing fundamental parameter approaches, and (6) an investigation of possible errors such as the omission of tertiary and higher-order excitation, photoelectron and Auger excitation, and Bremsstrahlung losses.

Within the last year or two a significant modification to the CEARXRF code has been completed which now makes the use of the MCLLS approach practical. That modification is the addition of differential operators (DO's) which allows first- and second-order corrections to the elemental library spectra that are produced for use in the linear library least-squares (LLS) analysis of X-ray spectra for samples of interest. While the approach has always been capable of the optimum accuracy possible in the non-linear XRF inverse problem (all pertinent XRF physics has been employed), this modification now allows near real-time calculations to be utilized. A graphical user interface (GUI) computer code has been developed for the MCLLS approach with differential operators.

In addition, preliminary results of a systematic study of the errors (primarily errors of omission) in existing fundamental parameters computer programs and in omission in the MCLLS approach such as not accounting for photoelectron and Auger electron excitation and Bremsstrahlung losses will be presented.

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A MULTIPLATFORM X-RAY FLUORESCENCE ANALYSIS TOOLKIT

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The ESRF has developed a series of tools for x-ray fluorescence analysis. These tools can be embedded into different programs or can be used combined into a single application. The ESRF freely provides PyMCA as an example of application supporting cartographic and quantitative analysis of small and large data sets.

Most relevant features are:

- Full support of the K, L and M shells (particularly relevant for imaging at soft x-ray energies)

- Multi-element detector support

- Quantitative analysis with monochromatic and polychromatic excitation beam

- Automated HTML report generation

- User friendly graphical interface

- Active development strongly based on user feedback to e-available authors

- Multiplatform support (Windows, Linux, MacOS X, Solaris, ...)

- Free for non-commercial use

Description of the algorithms used and practical examples will be presented.

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X-RAY FIT – WINDOWS BASED PROGRAM FOR ENERGY DISPERSIVE X-RAY FLUORESCENT ANALYSIS

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X-Ray Fit is program for Energy Dispersive X-Ray Fluorescent (EDXRFA) data processing (spectra and concentration equations), developed for 32-bits Windows based platforms. This product gives the opportunity for analysis of very bright range of materials using EDXRFA.

The program has follow abilities:

- Reading, pre-processing, processing (step by step or automatic) and saving spectra in selected format;
- System calibrations (energy and resolution) ;
- Different models for background subtraction (blank spectra and step function);
- Linear and nonlinear methods for intensities calculations for selected elements and lines (K, L or M);
- Different spectra types – X_Ray tube, source Fe55, Pu238, Am(Dy)241.
- Creation and edition of concentration curves by two main methods – sensitive curves or concentration equations, calculated using multiple linear regression.
- Separation of the concentration range to sub ranges and automatically calculation of the concentrations.
- Analysis of unknown samples and saving results directly in EXCEL format.
- Batch processing

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EVALUATION OF MCNP5 AND EGS4 FOR THE SIMULATION OF IN-VIVO STRONTIUM XRF MEASUREMENTS

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In order to optimize X-Ray Fluorescence (XRF) experiments, Monte Carlo simulations provide a valuable tool, which allow different system set-ups and experimental conditions to be explored in a controlled way. EGS4 and MCNP5 are two widely used Monte Carlo programs, which simulate the photon and electron transport in great detail and allow for the simulation of an arbitrary experimental geometry. Tested in 2001 by Al-Ghorabie FHH et al.[1], these programs failed in reproducing the outcome of a platinum XRF in-vivo measurement. The authors found that the discrepancy between measured and simulated results could be attributed to the free electron approximation made by the programs in simulating the Compton scattering. More recent versions of EGS4 and MCNP have updated their treatment for photon transport at low energies and have included Doppler broadening in the Compton profile. In this study we test the capability of these new versions of EGS4 and MCNP in reproducing the outcome of an in-vivo strontium XRF measurement.

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**IN VIVO DETERMINATION OF Pb IN BONE USING
L-SHELL EXCITATION**

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Lead (Pb) is a widespread toxic element which is taken up into the body by ingestion, inhalation and the skin. Excretion by the gastrointestinal tract and renal is done to a high percentage. The remaining Pb accumulates in bone with a half life time up to 10 years and is released due to bone turnover. The toxic effects of Pb start at a cellular level and lead to several impairments of physiological functions. For adults cognitive deficiencies are observed. Particularly the developing brain is susceptible to lead toxicity as only slightly higher concentration levels of Pb can lead to a reduced IQ. The determination of Pb in bone by XRF is possible in vivo and mainly done using K-shell excitation by ^{109}Cd isotope sources. In our approach the L-shell excitation with secondary target in orthogonal geometrie is chosen. A compact portable spectrometer was designed and constructed using a low power aircooled (75 W) Rh anode, Mo secondary target and a electrically cooled 50 mm² Silicon Drift Detector to avoid large generators or dewars. A block made of Cu for in vivo measurements was designed and realized after optimization of the relevant parameters like distance and collimator diameter. Results from these measurements are presented. Lower limits of detection for measurements on a plaster of Paris were around 3 $\mu\text{g/g}$ with 3.5 mm tissue equivalent material, simulating skin and adipose.

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TRACE ELEMENTS ACCUMULATION IN MIDDLE AGE HUMAN BONES

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Human bones from Middle Age were analysed by X- Ray Fluorescence spectrometry to evaluate trace element uptake from the soil into the bone structure and the behaviour of different bone structures for the uptake. Bone is one of the hardest structures of the human body composed by two different kinds of tissue: one compact (cortical), and the other one spongy (trabecular).

Trace element content in bones, from different historical periods, can give us information about environment and dietary habits of those populations by studying the elemental concentration in human remains of those periods. Some elements of environmental origin are incorporated during life in the skeleton material (antemortem incorporation). Cortical bone have been indicated as dose monitor for man elemental exposure, due to its small remodelling rate and the hardness of its tissue, it is considered not much susceptible to post-mortem effects from elemental intake from the soil. Post-mortem influence is particularly important in trabecular bone. Endogenous environment and the diffusion pattern of some elements can give information both for archaeological purposes and diagenesis processes affecting the apatite ante-mortem elemental content.

In this work we compare the elemental content for compact bone regions of femur, skull, tibia and mandible are compared to trabecular bone regions of ribs, omoplate, dorsal vertebra and femur from an extensive population buried in the same place. Titanium, Fe, Mn are tremendously enriched in spongy bones due to diagenesis from the soil in which the people were buried. Pb is an element that follows the movement of Ca in the body. Pb presents very low concentration levels in compact bones and values five times higher in spongy bones. This behaviour suggests post-mortem uptake from the soil and can be explained considering that this burial place was a parking car for more than 20 years, taking into account that there is no evidence of significant lead mining in this region during medieval period.

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**INFLAMMATORY CELLS AND PIN LESIONS AS PRIMARY FACTORS
IN THE DEVELOPMENT OF PROSTATE CANCER**

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The prostate gland is the most common site of neoplastic disorders in men. The knowledge about the pathogenesis of inflammatory cells, PIN lesions and prostate cancer is still under investigation. Inflammatory cells derived free radicals are considered as major and universal contributors to cancerogenesis. PIN is regarded as a precursor lesion to prostate cancer or a marker signalling the vulnerability of the epithelium to neoplastic transformation. Men diagnosed with biopsy-proven high-grade PIN have a 23–35% risk of developing cancer, shown in subsequent biopsy samples. Differentiation markers that are frequently changed in early invasive carcinoma are also changed in PIN lesions.

In this study prostate tissue samples with various disease states (inflammation, PIN lesions and cancer) were examined. The human prostate tissues were obtained during surgical operation. The samples were measured by SRIXE (Synchrotron Radiation Induced X-ray Emission), XANES (X-ray Absorption Near Edge Structure) and FTIR (Fourier Transform Infrared Spectroscopy). Our experiments show significant differences between elemental concentrations, oxidation state of iron and relative band intensity ratio of $\nu(\text{as})\text{-CH}_2$ to $\nu(\text{as})\text{-CH}_3$ in various pathological states of prostate tissues.

Our study confirms that mentioned earlier method can be used to distinguish healthy and pathological states in prostate tissues. Information obtained in this way may provide better understanding in processes turning healthy tissues into ill ones. Thus opening the way to find new medicines/treatments to prevent or slow down some harmful intracellular processes.

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**DIFFRACTION ENHANCED IMAGING AND X-RAY FLUORESCENCE
MICROTOMOGRAPHY TO ANALYZE BIOLOGICAL SAMPLES**

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X-ray imaging systems with Diffraction Enhanced Imaging (DEI) and fluorescence techniques were developed using synchrotron radiation for biomedical researches. The DEI experiment was performed in D10A-XRD2 beamline of the Brazilian Synchrotron – LNLS. The pre-monochromator, upstream of the beamline, was adjusted to 10.4 keV. The samples were positioned between two channel-cut (Si-333) mounted in a double axes diffractometer made of one solid piece of melted iron. A direct conversion water-cooled CCD camera of 1242 x 1152 pixels² of 25 x 25 μm² each were used as a two-dimensional detector. The DEI system can show details in low attenuation tissues. It is based on the contrast imaging obtained by extinction and diffraction characteristics. The X-Ray Fluorescence Microtomography (XRFCT) experiment was performed at the D09B-XRF beamline. For the X-ray fluorescence microtomography setup a monochromatic beam of 9.8 keV were used for the excitation of the elements in the sample. The fluorescence photons were detected by a HPGe detector at ninety degrees of the direction of beam. The incident beam was monitored by an ionization chamber and a fast scintillator detector was used to detect the transmitted radiation after the sample. The XRFCT is based on the use of the X- ray fluorescence emitted from the elements contained in a sample to give additional information to characterize the object under study. XRFCT allows one to map of the most important elements in the sample. In this work several breast and intestine tissues were investigated in order to verify the concentration of some elements correlated with characteristics and pathology of each tissue observed by the DEI technique for determination of internal detected elements distribution. All XRFCT were reconstructed using a filtered-back projection algorithm. In those samples it was observed the elements Zn, Cu, Fe in higher concentration and K in low concentration.

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CHARACTERIZATION OF BREAST TISSUE USING ENERGY-DISPERSIVE X-RAY DIFFRACTION COMPUTED TOMOGRAPHY

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X-ray diffraction spectra of structures with a short-range order, such as biological tissue, have one or more broad peaks; the higher the degree of order of the tissue, the sharper the peak. In particular it has been shown [1,2] that the different arrangements in collagen fibrils, believed to be related to breast cancer invasivity and staging, cause significant differences in the diffraction pattern of the tissue. Due to the typical wavelengths involved, diffraction imaging effectively acts as a probe at the molecular and supra-molecular level, and diffraction computed tomography joins the short-range information provided by diffraction imaging with the three-dimensional information provided by CT.

Previous work by our group [3-5] has shown the high potential of both planar and CT X-ray diffraction imaging for the detection of breast tumours. As a further step of the work, we have used diffraction CT not simply for detecting tumours, but for characterizing them.

For this purpose, we have developed a system for energy-dispersive X-ray diffraction computed tomography (EDXRCT) for imaging small-size breast tissue samples. The aim of the study is a thorough characterization of different types of healthy and neoplastic breast tissue in terms of their diffraction properties for understanding the molecular changes related to cancer staging.

The experimental set-up consisted of a W-anode X-ray tube operated at 70 kVp, a HPGc detector, a primary beam pinhole collimator and a conic diffraction collimator collecting scattered photons across a narrow angular range centred at 6°.

Each CT profile was acquired by scanning the sample in front of the primary beam collimator. Fresh tissue samples 6 mm in diameter were imaged and a spectrum was extracted for each region of interest in the reconstructed tomogram, each spectral component corresponding to a different value of the momentum transfer.

The spectra show a significant difference not only between normal and neoplastic breast tissue, but also between different tumour types. This could provide key information about the molecular changes taking place in cancer growth.

The results will be presented and related to the histopathologic appearance of the different tissue types.

The next steps of the study will include a systematic characterization of a wide tissue bank in terms of the diffraction properties of samples, to be related in particular to tumour staging

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TRACE ELEMENTS ANALYSIS IN NORMAL AND PATHOLOGICAL HUMAN TISSUES USING SYNCHROTRON X-RAY FLUORESCENCEAline. S. S. Saddock¹, Regina C. Barroso², Marcelino J. Anjos^{1,2}, Ricardo T. Lopes¹¹*Nuclear Instrumentation Laboratory - COPPE/UFRJ
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The major and trace elements and their ratios in human cancer and normal tissues may change significantly. The knowledge of the spatial distribution and local concentration of trace elements in tissues are of great importance since trace elements are involved in many biological functions of living organisms [1]. Regardless of the advances in the analytical techniques for determining elemental concentrations in the human body, there still a major lack of information concerning the correlation of trace elements concentrations in the tissues. The correlation between elemental concentrations in different human tissues might be a powerful method in biological and clinical investigation [2]. Application of X-ray fluorescence analysis to biomedical samples had provided important information about the content of trace elements and its distribution in a variety of organs [3]. The measurements were carried out at X-ray Fluorescence beamline (XRF). The sample was positioned in the image plane within an accuracy of 0.5 μm with a 3 axis (x, y, z) remote-controlled stage. The fluorescence spectrum was recorded with a Si(Li) detector with resolution of 165 eV at 5.9 keV. The measurements were performed in standard 45 \circ geometry, exciting with a white beam and using orthogonal slits. Pixels of 500 μm x 500 μm were obtained keeping a high flux of photons on the sample. The counting live-time for each pixel was 150 s/step and the average step size was 1.5 mm/step in both directions. Three sets of pathological and normal human tissues were analysed. In the first set, specimens (intestine, uterus, breast and lung) were embedded in paraffin wax with a thickness of 1 mm. In the second one, surgical specimens (uterus, breast and kidney) were extirpated and fixed in 10% formaline. The average thickness was 1 mm. In the third one, surgical samples (uterus, breast and kidney) were lyophilized for 48 h. After that, the samples were embedded in acrylic resin and surfaces were polished in order to obtain a smooth and plane surface, of 1 mm thickness. For each specimen, the component tissues were identified visually by the pathologist who made the specimen available. Histological analysis of adjacent tissue was available for reference. It was possible to determine the concentration of S, Cl, K, Ca, Ti, Mn, Fe, Co, Cu, Zn, Se and Br. The results show that there is a difference between normal and pathological tissues.

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**RESEARCH OF TRACE ELEMENT CONTENT
IN HUMAN MYOCARDIUM BY SRXRF**

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There is no much information on how metabolic processes running in the organism of a man with a myocardium pathology are linked. There are no systematic data on correlation among trace elements (inside and between tissues) that could indicate tissue degradation processes at the cellular level. One only can find in literature data on chemical trace element content in the heart as a whole or results of single analyses and investigations.

The work we are fulfilling in cooperation with the Institute for pathology of blood circulation is of systematic character, which relates both to selection of material to investigate and to the physiological task statement. There are two aspects of concept-and-instrument approach to the myocardium tissue study that should be marked. One of them relates to creation of experimental methods to investigate the myocardium tissue. The other is linked with the investigation of trace element content in different compartments of myocardium in dependence on the functional load on compartments of heart and the pathological process type.

For the purpose of SRXRF analysis, we have developed methods for myocardium tissue sample preparation. The samples are fragments of 2 to 5 mg of raw mass and of 0.5 to 3 mg when dried. We have done analyses and calculated metrological characteristics for 10 International standard samples of biological tissues. Basing on results of these analyses, we have selected samples for comparison (international standard samples) for different tissues depending on individual element-to-element concentrations.

The element analysis station on SR beams (INP SB RAS) makes it possible to measure samples in the energy range from 2 to 35 keV, i.e. to define such elements as Ag, Sn, Sb, I, and Ba by K-lines.

Preliminary results allowed us to find inter-correlations of such elements as Zinc, Copper, Nickel, Potassium, etc. Inter-correlations of individual compartments of myocardium have been found. It was found that contents of elements in the myocardium tissue of healthy people differ by orders of value from those of sick people.

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CONTRIBUTIONS OF SYXRF TO THE CERTIFICATION OF REFERENCE MATERIAL

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The certification of reference materials (CRM) is among the main tasks of the Federal Institute of Materials Research and Testing (BAM).

Traditionally, the results of direct XRF on solid samples have not been included into that certification process due the lacking sensitivity and correctness.

Instead of investigating the original sample dissolved in lithium borate glass and compared to artificially reconstituted samples in an iterative way until the X-ray spectra of sample and comparator got equal within the limits of statistical uncertainty.

Thus, the objective was stated to improve the reliability using synchrotron radiation for excitation. Moreover, thick standards of pure elements were irradiated under the same experimental conditions. A Monte Carlo Method [1] is able to take into account higher order effects. Starting from the net peak pulse rates of the sample and of thick standards of pure elements the inter-element-effects are treated iteratively until the data set of the sample is reconstituted. This delivers the best approach of the element contents of the sample.

The method has been successfully applied to the determination of trace elements in metallic CRM's such as Te and Sb at sub ppm level in copper (European Reference Material ERM®-EB-381-384) or Sn, Zr, Ga, Ti and V in $AlSi_9Cu_3$ (BAM 315).

In the case of certifying a thin Mo layer implanted in a Si wafer SyXRF turned out to be a valuable contributor to a BAM in-house certification procedure (together with ID-ICPMS, NAA, RBS). In addition SyXRF is the ideal method for testing the homogeneity of CRM candidates, which is the first step of certification.

On the contrary, there are still problems with the very precise determination of major components (e.g. Cu in Euro metal at a content of ca. 75%). The obtained deviation of 0,3% (relative) to the consensus value was good, but not good enough. One may conclude that the method is reliable up to the lower %-level. Attempts will be made to shift this limit to higher percentages.

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ENERGY DISPERSIVE X-RAY DIFFRACTION AS A MEANS TO IDENTIFY ILLICIT MATERIALS: A PRELIMINARY OPTIMIZATION STUDY

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There are many situations in which the rapid identification of a material is required. Generally this requirement is coupled with circumstances where conventional laboratory facilities may not be available, therefore it is important to establish the minimum requirements for a given identification task. This is particularly true in the case of X-ray identification of illicit materials at ports of entry, postal services or transport systems. As an example, this work concentrates on the use of X-ray diffraction profiles to identify drugs and investigates the minimum feature set of an X-ray diffraction system that could be employed.

Many drugs present a pseudo-crystalline structure which produces sharp x-ray diffraction peaks, characteristic of the scattering substance. Energy dispersive x-ray diffraction (EDXRD) has been proposed as a suitable method for detecting and identifying concealed substances in packages and parcels. A study of diffraction data from 8 samples of illicit drugs and 5 samples of cutting agents has been made. Spectra were collected with a range of counting times using a high resolution HPGe detector system, a tungsten target X-ray source and a variable geometry diffraction system. For each drug the diffraction data has been used to simulate different scenarios, i.e. speed of inspection system, source characteristics, detector characteristics, cutting agent, etc. For each simulation the significant regions of the spectra have been identified and used to classify the spectrum using multivariate analysis software. Preliminary results have shown that drugs can be detected with a sensitivity of 88% and a specificity of 96% if the software has been suitably trained and calibrated.

This paper will present the full data set and analysis and will identify optimum X-ray scattering systems that could be employed in the rapid, on-site identification of illicit drugs.

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XRF FOR U, Pu, Np, AND Am MEASUREMENTS

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In verification measurements for the safeguarding of nuclear materials the XRF technique is currently employed in the Hybrid K-Edge Densitometer (HKED) for U-Pu analysis in dissolved irradiated fuels as well as in mixed-oxide product materials. The underlying measurements are based on the energy-dispersive analysis of K-series X rays from uranium and plutonium produced by X-ray tube excitation. The same technique can be advantageously used also for the assay of Minor Actinides occurring in some advanced fuel cycles, which involve the processes of nuclear partitioning and transmutation. Analysis software and measurement procedures for this advanced application of energy-dispersive XRF analysis have been developed and optimized. Simulation studies using the MCNP code were carried out for predicting the yields of XRF K-lines from U and Pu with various matrices. The validation of this modelling has been done experimentally using a set of calibrated solutions of U and Pu in different matrices.

In this paper we will present our application of the XRF techniques for the assay of U and Pu in samples from the conventional fuel cycle, and for the assay of the Minor Actinides in nuclear materials for advanced fuel cycles.

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DIRECT DETERMINATION OF PRECIOUS METALS IN AUTOMOTIVE CATALYSTS USING HIGH-ENERGY POLARIZED BEAM XRF

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For accurate and precise quantification of precious metals in spent automotive catalysts, ICP-related techniques are usually applied. These kinds of analyses are very time-consuming due to various sample preparation steps, such as fire-assay and acid digestion. The goal of this research was to obtain a fast and direct determination procedure using EDXRF. A sample preparation method working directly on the ground material was optimized. The material was pressed as a pellet using wax as a binder; no internal standard was added. The standards used for this application were real automotive catalysts, prepared in the same way as the unknown samples. The concentrations of the precious metals in these standards were verified with ICP-OES. For this purpose a more complicated sample preparation was required, including NiS fire-assay. Epsilon 5 (PANalytical, Almelo, The Netherlands) was applied for the XRF analyses. It has a 600W Gd tube with a maximum voltage of 100 kV, giving the possibility of high-energy excitation. Its three-axial Cartesian geometry using secondary targets provides a low background signal and the possibility to choose the most sensitive excitation-condition for each element. When applying CsI as a secondary target, it became possible to excite the Pd- and Rh-K-lines. For the determination of Pt, a Zr-target was chosen to excite the Pt-L-series. The reproducibility of the XRF-analysis appeared to be better than 0.5%, while the precision of the whole method was approximately 1%. The accuracy was investigated using ICP-OES as a reference and similar performances were obtained. When irradiating 500 s for the CsI-target as well as for the Zr-target, detection limits for Pt, Pd and Rh proved to be better than 5 ppm.

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TOTAL REFLECTION XAFS AND IN PLANE X-RAY DIFFRACTION ANALYSES OF MANGANESE OXIDE NANOSHEETS

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Nanosheets are a unique class of nanomaterials that exhibit often interesting physical and chemical properties associated with a nano-scale thickness (less than 1 nm) and characteristic shape as compared to bulk materials. They can be obtained from a delamination of bulk crystal with layered structure.

Structure analysis of the nanosheet is important in the material utilization and the control of their physicochemical properties peculiar to the nanoscopic state; however the structure analysis based on the conventional diffraction analysis is difficult because of their low dimensionality and deterioration of crystallinity via the exfoliation. Nanosheet structure can be described as two-dimensional lattice having a periodic arrangements of constituent atoms parallel to the sheets and additional non-periodic arrangements of constituent atoms in a direction normal to the sheets. We have for the first time applied synchrotron radiation (SR) X-ray in-plane diffraction and total-reflection fluorescence-XAFS (X-ray absorption fine structure) techniques to the analyses of the periodic and non-periodic structures of the nanosheets, respectively. We have revised a commercial in plane diffractometer suitable for utilization of SR. On the other hand, we have developed a theta-Z stage suitable for the total reflection XAFS measurement.

We have applied these new techniques to reveal the structure of manganese oxide nanosheets, whose precursor is a layered ternary oxides with chemical composition of $AMnO_2$, where A represents alkali metals. The nanosheets were obtained by soft-chemical exfoliation of the layered manganese oxides. They are attractive functional materials as a new family of versatile manganese oxides with a wide-ranging application such as magnetic materials with colossal magnetoresistance. A combination of SR excitation and the total reflection of incoming X-rays provides enough signals for both analyses even from a monolayer of the MnO_2 nanosheets. In addition, mean oxidation states of constituent manganese ions in the MnO_2 sheets were estimated on the basis of a comparison of XANES spectra between the precursor and exfoliated compounds and bond valence sum calculations using the bond length obtained from the present EXAFS analyses. The obtained structural data disclosed that the MnO_2 sheets exhibited a slight elongation of the two-dimensional lattice and Mn-O interatomic distance compared with the host material due to the delamination. These changes correspond to below 1% expansion of the sheet area and 1~2 % expansion of thickness, which can be understood by reduction of the mean oxidation number of constituent manganese ions in the sheet through the exfoliation process.

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ULTRASOFT X-RAY REFLECTION AND EMISSION SPECTROSCOPIC ANALYSIS OF $\text{Al}_2\text{O}_3/\text{Si}$ STRUCTURE SYNTHESIZED BY ALD METHOD

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Metal oxides of high dielectric constant are candidates to substitute SiO_2 as a gate dielectric in complementary metal-oxide-semiconductor (MOS) devices. Al_2O_3 is one of the attractive “high-k” dielectric materials due to its considerably higher value of permittivity, higher resistivity and higher thermal stability than silicon oxide.

Atomic layer deposition (ALD) is one of the most promising method of forming MOS structures for the development of modern micro and nanoelectronics devices. Because of the extremely small size of the nanostructures, their formation requires the control of the growth process at the monatomic layer. The electro physical properties of such structures are determined not only by the characteristics of thin film but also by the characteristics of the interface between an insulator film and semiconductor substrate. The investigation of $\text{Al}_2\text{O}_3(30 \text{ nm})/\text{Si}$ system grown by ALD method is presented in this work. This system was investigated in the soft x-ray range using X-ray reflection spectroscopy and X-ray emission spectroscopy as a nondestructive depth-resolved characterization tools. The angular spectral dependencies of the reflection coefficient in the vicinity of Al L_{2,3}- edge were obtained using an s-polarized synchrotron radiation. The dependence of the shape of the aluminum and silicon L_{2,3} x-ray emission on the primary electron energy was obtained on the RSL-1500 spectrometer.

The reflection spectra fine structure was investigated near Al L_{2,3}- edge for different glancing incidence angles in wide angular range. The absorption spectra were calculated from the reflection spectra by means of Kramers–Kronig relationship. All calculated Al L_{2,3}-absorption spectra demonstrate two main peaks. Analysis of the correlation of the intensities of these peaks, the energy position and the value of splitting between peaks allows to associate these peaks with transitions to Al 3d and 4s states in amorphous Al. Analysis of the shape evolution with increasing of the incidence angle (with increasing of the depth probing) of the Al L_{2,3}-reflection spectra and absorption spectra shows the heterogeneity in the depth profile that evidences a non-homogeneous character of the Al_2O_3 film.

The extent and phase chemical composition of the interface of the $\text{Al}_2\text{O}_3/\text{Si}$ system has been studied using depth resolved X-ray emission spectroscopy. It was established that the investigated film is a layer of mixed Al_2O_3 and SiO_2 oxides, in which silicon dioxide is present even on the sample surface and its concentration increases as one approaches the interface with the substrate. It is assumed that such a complex structure of the layer is the result of interdiffusion of oxygen into the layer and of the silicon from the substrate to the surface followed by silicon oxidation.

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STANDARD AND TWO-WAVELENGTH X-RAY REFLECTOMETRY FOR INVESTIGATION OF NANO-SIZE LAYERS

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The methods of X-ray reflectometry for the ultra-thin metal and silicide films on the silicon measurement (thickness, roughness) were developed. Many scientific groups pay rapt attention on such films (1 ~ 10 nm) and also multilayered structures on the silicon substrates because of the raising of the technological requirements (particularly the thickness of the layer, the verge sharpness and so on). The problem become more complicated because of the fact, that when creating the layers (or multilayered structures) with thickness ~ 10 nm, the precision of the results is reduced due to the presence of the surface and intermediate polluting layers (e.g. oxide) and the possibility of the reciprocal diffusion penetration of the layers.

Using the method of X-ray reflectometry we analyzed the set of samples with Ni, NiSi and NiSi₂ films, that were received with the help of the magnetron sputtering and then annealed. It was shown, that the method of X-ray reflectometry is used for the control of the technological parameters of the thin films (thickness, roughness, thickness of the interface) on the various technological stages.

There were taken the measurements of the nano-sized layers parameters using the methods of the standard and double-wave X-ray reflectometry [1]. The measurements were taken on the double-wave reflectometer “X-Ray MiniLab” (manufactured by Unisantis SA) and experimental plant in Lebedev Physical Institute. For the solution of the inverse task – the reconstruction of the distribution of the refractive index in depth distribution and the definition of the boundary structure – the optimization method based on genetic algorithm was used.

In addition to the reflectometry, there were made the extra investigations for the samples with the NiSi and NiSi₂ films, using the methods of the atomic-force microscopy (AFM) and electronic spectroscopy for the chemical analysis (ESCA). It was shown, that the method of the reflectometry can be successfully used for the identification of the polluting layers (oxide, etc.) and for the exact measuring of the ultra-thin films and multilayer structures technological parameters.

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INV-10

SYNCHROTRON RADIATION INDUCED TXRF

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Using Synchrotron radiation as excitation source in TXRF offers several advantages over X-ray tube excitation in TXRF (Total Reflection X-ray Fluorescence Analysis) like detection limits in the fg range and also efficient excitation for low Z as well as high Z elements due to the features of synchrotron radiation. These low detection limits are achieved only using a multilayer monochromator. A crystal monochromator with a smaller bandwidth reduces the intensity, but allows XANES measurements in fluorescence mode to perform speciation at trace levels.

SR-TXRF is performed at various synchrotron radiation facilities.

At HASYLAB, Beamline L a vacuum chamber for SR-TXRF analysis is now available which can easily be installed using the adjustment components for microanalysis. The detector is a VORTEX Silicon Drift Detector (SDD) with 50 mm² active. Measurements were carried out with the Ni/C multilayer monochromator set to 17 keV on a sample containing 100 pg of Ni. Extrapolated detection limits of 4 fg have been obtained using the 50 mm² SDD for 1000 s live time. Various applications will be presented, especially of samples with very small amount of sample: As SR-TXRF is more sensitive than tube excited TXRF the sampling time of aerosol samples can be diminished resulting in a more precise resolution of atmospheric events. Aerosol samples, directly sampled on Si reflectors in an impactor have been investigated. Results will be presented.

Using the Si111 crystal monochromator also available at beamline L, XANES measurements to determine the chemical state have been performed, but with lower sensitivity as the flux transmitted by the crystal monochromator is about a factor of 100 lower than that transmitted by the multilayer monochromator. Detection limits for Cr of 40 pg for 30 s acquisition time have been obtained. Speciation of Cr in urban dust and pollen have been demonstrated. Preliminary results of XANES measurements for As in xylem from cucumber plants fed with AsIII and AsV are presented.

One of the main applications of SR-TXRF is the surface quality control of Si wafer surfaces. Two SR-TXRF setups are dedicated for wafer analysis, one at SSRL, Stanford, California and one at the PTB metrology lab at BESSY2 in Berlin. The setups will be described and results presented. On other SR-TXRF setups for chemical analysis will be reported.

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TOTAL REFLECTION X-RAY ANALYSIS OF BROMATE

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Bromate ions are a disinfection byproduct of drinking water ozonation due to bromine oxidation (water ozonation is an alternative disinfection technique to water chlorination). These ions are one of the emerging water contaminants and they have been considered as probable human carcinogen, even at low concentration levels. New regulations with maximum contaminant level of 10 ppb have been established and monitoring methods have been suggested [1]. The official method for bromate analysis is Ion Chromatography but interferences arise from other high concentration ions (usually chloride ones). Total Reflection X-Ray Fluorescence (TXRF) can analyze bromine with good detection limits without chloride interferences but it can not discriminate between bromide and bromate ions. In the present work a new method of bromate analysis by TXRF is introduced. Bromate ions were selectively concentrated on a PVC + Aliquat-336 membranes that have been prepared on TXRF quartz reflector surfaces. Different complexation substances were introduced in the membrane for bromine collection and o-dianisidin was proved as the best among them. Membrane collection prior TXRF analysis has already been used [2] for mercury analysis; Aliquat-336 is a reagent that has suitable for preparation of anion exchangers [3]. The prepared membranes collect both bromide and bromate so bromide complexing materials (masking agents) were introduced in the analysed solutions to prevent bromide collection; a more than 95% suppression of bromide collection was managed without any alteration in bromate collection. The reflectors with membranes were immersed in water (with masking agents) solutions with 50 ppb bromate and bromide concentrations and they were left to equilibrate for 24 hours; after this the reflectors were taken out of the solution and they were analyzed by TXRF. The effects of various experimental parameters were examined Minimum bromate detection limit lower than 1 ppb and good linearity at the concentration range 1-50 ppb was achieved.

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**X-RAY RESONANT RAMAN SCATTERING BELOW
THE Si-K ABSORPTION EDGE**

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The results of the first high-resolution study of x-ray resonant Raman scattering (RRS) below the K-edge of silicon are reported in context of importance of the RRS as a limiting factor for detection of light elements in Si by using the total reflection x-ray fluorescence (TXRF) technique. In this experiment, which was performed at the ID21 beamline at the ESRF in Grenoble, the x-ray RRS spectra were measured in the energy range 1790-1844 eV using a von Hamos crystal spectrometer having energy resolution of about 1 eV. The measured x-ray RRS spectra are compared with theoretical calculations based on the second-order perturbation theory within the Kramers-Heisenberg approach. Using this approach the oscillator strength distribution for unoccupied states in Si can be derived from the measured RRS spectra, giving thus a complementary information to the XANES/EXAFS methods on the x-ray absorption structure close to the K-shell edge of silicon. We demonstrate that the measured x-ray RRS spectra for Si can be scaled using simple approximate formula based on the Kramers-Heisenberg approach, which is of practical importance for TXRF applications. The total cross sections for x-ray RRS, as well as for the observed 1s-3p photoexcitation, measured below the K-shell absorption edge are discussed in details. Finally, the importance of high-resolution studies of x-ray RRS at Si-K edge will be given in context of TXRF and x-ray absorption techniques.

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ANALYSIS OF WINE SAMPLES BY MEANS OF TOTAL REFLECTION X-RAY FLUORESCENCE (TXRF) ANALYSIS

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A low power benchtop TXRF spectrometer was applied to different tasks connected to wine analysis. In addition to the analysis of potassium, calcium, iron and copper, which are crucial elements for the quality of wines, the applicability of TXRF spectroscopy for the control of legal limits was evaluated.

An additional analytical task of increasing importance is the origin and falsification control of wines by means of their trace element distribution.

The possibilities and limitations of TXRF spectroscopy for these applications plus several additional analytical tasks connected to wine analysis are presented on the basis of recently finished measurements and outlooks on future works.

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**TOTAL REFLECTION X RAY FLUORESCENCE IN METALLOMICS:
PARTIAL CHARACTERIZATION OF METALLOCARBOXYPEPTIDASE
PRODUCED BY TRIPANOSOMA CRUZI**

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Metal ions are utilized by biological systems in fundamental processes and its presence or absence results in health or diseases. The essential transition metals are used by cells as cofactors of enzymes or proteins and they contribute to the stability and activity. (metalloproteins). Therefore, the chemistry of a cell needs to be characterized not only by its characteristic genome but also by the metal and metal distribution among the different species and cell compartments, metallome. The term “metallome” introduced by R.J.P. Williams is synonymous with the instantaneously determined concentration of all inorganic species within a cellular system and denotes the metal-assisted function biochemistry. The metallomic information will comprise the identities of individual metal species (qualitative information) and their concentrations (quantitative metallomics). In this sense, the challenge of analytical techniques in the metallomic field includes the detection first and the determination after of metallic species in biological systems considering the analysis must to be carried in microsample volumes (several microliters or micrograms).

This presentation shows the use of TXRF X-ray fluorescence with total reflection geometry (TXRF) to characterize metalloproteases produced by *Trypanosoma cruzi*, the flagellate protozoan which is the causative agent of the American trypanosomiasis, Chagas disease. Protein purification processes as well as sample preparation procedure for TXRF determination are discussed. These results add to the knowledge of the peptidases present in the parasite and may offer a new target for the development of a rational chemotherapy against Chagas disease.

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SPECIATION OF NITROGEN COMPOUNDS IN NANOSCOPIC FINE AEROSOL SAMPLES USING TXRF-NEXAFS

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It is crucial to have analytical methods that enable to measure nitrogen compounds in the aerosol from a short sampling period while retaining the information on the size distribution of the particles. A near edge X-ray absorption fine structure (NEXAFS) investigation in conjunction with total reflection X-ray fluorescence (TXRF) analysis of minute depositions on wafer surfaces is able to contribute to the speciation of the atmospherically important low-Z elements (C, N and O) in nanoscopic (10⁻⁹ g) amounts of solid material collected on silicon wafer surfaces.

Aerosol samples were collected at different locations, at the international airport of Budapest, at a Hungarian background station, close to seashore in Italy and at the Italian base near Ross Sea (Antarctica). Aerosol collection was performed using a seven-stage May cascade impactor, on silicon wafers at stages 5, 6 and 7, with aerodynamic cut-off diameters of 1, 0.5 and 0.25 µm, respectively. The TXRF-NEXAFS measurements were carried out at the PGM monochromator beamline of PTB at the electron storage ring BESSY II. Based on linear combinations of standard reference spectra of (NH₄)₂SO₄ and NaNO₃, having identical deposition dimensions and size distributions to the sampled aerosol particles, the ratio of ammonium and nitrate could be quantified.

Nitrogen was present almost entirely as ammonium at stage 7 in all sampling locations. The ammonium to nitrate ratio shows a decreasing trend with increasing particle size in the range of 0.25–2 µm. More than 90% of nitrogen was present as nitrate in the continental stage 5 samples. The Antarctica samples collected at the same stage however showed a much lower nitrate to ammonium ratio (55% to 45%). For all sampling locations, the variation of nitrate-to-ammonium ratios could be well explained with the air mass backward trajectories.

Using TXRF-NEXAFS, the ammonium-to-nitrate ratio could be determined in Antarctic fine aerosols collected from less than 2 m³ of air, i.e. considerably lower than the sampling volumes usually used for ion chromatography analyses (30 m³). This reduced sampling volume can enable the characterization of Antarctic aerosols to be done in higher temporal resolution. For continental aerosols, a few minutes of sampling (less than 0.2 m³) was sufficient for analysis, even in rural locations.

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RECENT PROGRESS IN LOW POWER TXRF-SPECTROMETER TECHNIQUE

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Today XRF-spectrometer with low power x-ray tubes and thermoelectrically cooled detectors provide the customers with an analytical performance, which until a few years ago was reserved for spectrometers with kW X-ray tubes and LN2 cooled Si(Li) detectors. Even for low power TXRF-spectrometers the detection limit could be improved by an order of one magnitude in the last 5 years. This progress was provided more by the improved quantum efficiency of all components than by high power excitation sources.

Today TXRF-spectrometers have a well-developed technological base. Nevertheless, the development has not been finished yet. The combination of a high brilliant X-ray source with a focusing multilayer optic and a new SDD detector generation has made a further improvement of the analytical sensitivity as well as of the analytical performance possible.

For a high analytical sensitivity covering a wide range of elements the application of different excitation energies is necessary. Based on a monochromized 33 keV excitation source and an improved SDD Detector, the K-line detection limits for Cd, Sn, Ag and Sb were significantly improved.

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X-RAY SPECTROMETRIC METHODS TOWARDS AN INTEGRATED, IN-SITU ANALYTICAL CHARACTERIZATION OF CULTURAL HERITAGE MATERIALS/ARTIFACTS. AN OVERVIEW.

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The X-Ray Fluorescence (XRF) technique is well established for more than thirty years as a basic analytical tool for the non-destructive analysis of cultural heritage materials. Since the pioneer applications of the method from the early 70's [1, 2], many conservation laboratories at museums are nowadays equipped with portable spectrometers that allow the analysis of artifacts of different sizes or shapes utilizing the significant upgrade in X-Ray instrumentation during the last decade, i.e. miniaturized solid state detectors operating at room temperatures and low power, air-cooled X-ray tubes with optimized excitation geometries coupled together with high performance focusing elements or crystal monochromators. By this way, the well known analytical features of the XRF methods are also attained to a great degree during the in-situ measurements. However, their successful implementation from the environment of a specialized X-ray laboratory to the end-user in the cultural heritage field (conservator/archaeometrical scientist) is a challenge. Certain issues still remain to be addressed, and further documented: The type of the analytical information that XRF can provide according the analytical characteristics of the spectrometer, the type and state of preservation of the cultural material analyzed. How and to which level of accuracy the elemental excitation efficiency of a portable XRF spectrometer can be described in terms of fundamental parameters? Is it possible and useful to obtain a universal basis of comparison between the XRF analytical data that have been recorded by different portable spectrometers? Apart the conventional XRF analysis in the millimeter scale, recent advances in the analytical methodology enable the non-destructive, in-depth elemental analysis with resolution down to few tenths of micrometers [3]. In addition, recently developed X-ray based portable spectrometers can provide in-situ either structural analysis [4, 5], or near-surface chemical analysis using for the excitation process alpha particles emitted by a radioactive substance [6]. Thus considering a portable X-ray based laboratory, critical pathways need to be established in order to maximize the synergy of the techniques through improved analytical methodologies [7]. The above topics are overviewed and selected examples of analytical applications on different kind of cultural materials (pigments, metals, ceramics, etc) are critically discussed with emphasis given to methodological topics.

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COMBINED μ -XRF/ μ -RAMAN VS. μ -XRD FOR PIGMENT IDENTIFICATION IN ILLUMINATED MANUSCRIPTS AND PAINT MULTILAYER SAMPLESKoen Janssens, Wout de Nolf, Bart Vekemans, Geert Van Der Snickt*University of Antwerp, Department of Chemistry, Universiteitsplein 1, B-2610 Antwerp, Belgium*

For the non-destructive identification of pigments and colorants in works of art, in archaeological and in forensic materials, a range of methods can be used depending on degree to which the material under investigation can be sampled, is accessible for analysis and the structural complexity of the paint/pigment layer(s) of interest. Since in many realistic situations, materials of considerable heterogeneity need to be investigated, methods allowing information to be obtained from selected areas of the surface are strongly preferred.

Among the methods offering elemental information, μ -XRF (X-ray fluorescence) spectrometry is one of the few techniques with which it is possible to obtain spatially resolved information in a non-destructive manner on major and minor constituents of a variety of materials. On the other hand, by means of μ -Raman spectrometry, in a similar manner, highly specific identification of molecular species is possible. Both techniques, however, also have their limitations. Since XRF only provides information on elemental constituents, it is often not specific enough to allow for a full pigment identification while the presence of a strong fluorescence background often limits the applicability of Raman micro-spectroscopy.

In order to allow for the simultaneous use of both complementary techniques, a combined μ -XRF/ μ -Raman spectrometer called PRAXIS, consisting of a remote measuring head, attached to a easily transportable base unit, has been designed and constructed.

A third method, very frequently employed for phase identification of pigmented materials is X-ray diffraction and its microscopic equivalent, μ -XRD, which can be considered to be the 'gold standard' for this type of investigations.

In this paper, the extent to which the PRAXIS spectrometer is able to identify inorganic pigmented materials of various nature and stratigraphic complexity is compared to that of synchrotron-based μ -XRD.

Examples from the analysis of two generic types of pigmented materials, i.e., (a) illuminated parchments, usually featuring only one or two paint layers (in the case of recto-verso decoration of the same page) and (b) (embedded) paint layer fragments sampled from large oil paintings, will be discussed, with special emphasis on the green pigments employed.

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PORTABLE XRF ANALYZER WITH IMPROVED BEAM COLLIMATION FOR INVESTIGATION OF SMALL ELECTRONIC COMPONENTS AND OBJECTS OF ART.

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Field Portable XRF Analyzers are now very well accepted by alloy industries for sorting and positive materials identification and by environmental professionals for soil screening. As the result of pending RoHS Directive also a global electronic industry is interested in screening analysis of a variety of small and very diversified parts and components using XRF method. Portable XRF analyzers offer more than adequate analytical performance of nondestructive testing combined with high throughput. Unfortunately, all portable XRF analyzers use a “broad beam” geometry which is a serious drawback when small, surface mount components are to be analyzed. To perform analysis of such small objects the primary beam of x-rays should be confined to a spot of at least 2 to 3 mm in diameter. The existing capillary optics systems are very expensive, relatively large and typically limited to about 25 keV energy range. An alternative solution is to collimate the primary x-ray beam to the desired size, although at the expense of overall tube output. In this paper we will describe portable XRF analyzer with primary beam collimated down to 3 mm in diameter, equipped with miniature camera for exact positioning of the instrument over the analyzed spot. Characteristics of the collimated beam will be compared with those of a non-collimated system. Finally, we will discuss practical applications of a collimated beam in analysis of small electronic components, as well as in investigations of objects of art.

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**THE EXPERIMENTAL MODEL OF THE TUNABLE SOURCE OF
MONOCHROMATIC X-RAYS AND POSSIBILITY OF ITS APPLICATION
FOR DIFFERENT TYPES OF X-RAY ANALYSIS**

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The experimental model of the tunable source of monochromatic X-rays (TSXR) was developed using parametric X-rays [1,2] produced by non-relativistic electrons passing through a single crystal target. Tests had made with this model confirmed theoretical predictions for X-ray output and characteristics [3]. Brilliance of the developed X-ray source exceeds that for the conventional and rotor X-ray tubes, and even approaches to that for some synchrotron sources, but being much more compact and accessible.

The distinctive feature of the developed source is the possibility to tune X-ray energy at fixed electron beam energy. As the main experimental challenge for different types of X-ray analysis (for example, XAFS) are getting an X-ray source that can be tuned in energy, the presented source provides doubtless benefits.

In the present report the observed experimental spectra demonstrating X-ray energy tuning in the range up to 10 keV at the fixed electron beam energy (50 keV, 75 keV, 100 keV) are included along with estimations of radiation yield and description of the TSXR operation. Prospects of TSXR applications XAFS and X-ray imaging are analyzed.

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**CALCULATION OF X-RAY SPECTRA EMITTED FROM
A MICROFOCUS X-RAY TUBE WITH X-RAY OPTICS**

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Micro-X-ray fluorescence (μ -XRF) is becoming a new analytical tool in combination with the scanning electron microscope (SEM) [1], [2]. Due to the much lower spectral background in comparison with electron probe microanalysis the detection limits come in the order of some 10^2 ppm in case that an energy dispersive spectrometer is used, and even lower in case of a wavelength dispersive spectrometer. Small, low power X-ray sources with focussing optics are available as attachments to a SEM. The diameter of the illuminated specimen area ranges between 50 and 100 μm .

The iMOXS source manufactured by IfG operates with a microfocus tube having a side window and 12° target inclination. In order to have a means to calculate the tube spectrum we measured X-ray spectra for the target materials of interest (Mo, Rh, W) in a SEM with an energy dispersive spectrometer of known spectrometer efficiency (counts per incident photons) and with a carefully determined solid angle. Measurements were carried out for perpendicular electron incidence, for a take-off angle (TOA) of 35° and for high voltages ranging from 5 to 30 kV.

From the measured spectra the intensity of characteristic lines was found after subtraction of a physical background and deconvolution of K-, L- and M-series. These net line intensities were divided by the spectrometer efficiency, the solid angle of detection and the accumulated charge to get them as emitted photons per steradian per nC. Applying absorption correction one gets the X-ray yield Y . We applied the XPP absorption correction method [3]. $\log(Y)$ versus $\log(U-1)$ plots (U denotes the overvoltage ratio) were extrapolated to find the yields above 30 kV. From the yields the intensity of characteristic lines emitted for the conditions of the X-ray tube (high voltage, current, target tilt, and solid angle of emission) can be calculated. The related bremsstrahlung spectrum was calculated as a Kramers background with a scaling factor determined before in the experiments. Finally, the tube spectrum was multiplied with the transmission of the X-ray optics to obtain the source spectrum.

The transmission has been measured in a special test chamber and also calculated from a ray tracing model.

Calculated source spectra were imported in commercial XRF quantification software. With these more realistic excitation spectra specimens of several CRM's were successfully analysed using the standardless fundamental parameter mode of the quantification software.

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**ENHANCING DEPTH SENSITIVITY IN CONFOCAL XRF ANALYSIS
AND APPLICATIONS IN MINERALOGY**

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Confocal X-ray fluorescence spectroscopy using focusing optics in the excitation as well as in the detection channel has become a well established technique for obtaining elemental composition as a function of probing depth, thus enabling three dimensional mapping[1]. Nevertheless in the standard arrangement when a polycapillary is used on the detection side the depth resolution is generally restricted by the manufacturing properties of the capillary.

Experiments with varying excitation geometry at the fluorescence microscope facility of the ANKA synchrotron source demonstrate that the depth sensitivity can be markedly enhanced by choosing an incidence angle in the range of 15 to 30 degrees. Using a polymer CRL on the excitation side yielding $2 \times 4 \mu\text{m}^2$ beamsizes and a XOS polycapillary with $14 \mu\text{m}$ focus diameter at 17 keV on the detection channel depth resolutions down to $6 \mu\text{m}$ (Mo $K\alpha$) and $10 \mu\text{m}$ (Cu $K\alpha$) could be achieved. In addition to the increased depth resolution the sensing depth limit of the measurement into the sample is pronouncedly enlarged, since radiation from deeper layers can be obtained.

The enhanced depth resolution was successfully applied for depth profile measurements in thin platelets of mica. In the course of a study regarding the delamination process of Muscovite induced by metal cations, platelets of Muscovite have been exposed to a Cu-solution for about 240 h. At the ANKA fluorescence station the Cu distribution was mapped from the saturated border into the muscovite plate and normal to the surface of a $40 \mu\text{m}$ thick platelet. In order to look for potential exchange processes spatial correlations between Cu and the constituents of muscovite have also been analyzed. Preliminary evaluations indicate substantial Cu concentrations inside the platelet as the confocal technique allows distinguishing between Cu ions located at the surface and incorporated into the mica. In addition the results indicate that the potassium concentration is not influenced by the presence of copper ions.

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ANALYSIS OF Zn-Fe ALLOY COATINGS BY USING MEASUREMENTS UNDER TWO TAKE-OFF ANGLES

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Galvanneal is a steel product with a Zn-Fe alloy coating on the sheet steel surface. It is mainly used in the automobile industries. The coating weight of the alloy layer and the Fe concentration are important factors for the characteristics of the coated sheet steel.

The analysis of the coating weight as well as the Fe concentration are difficult tasks in conventional x-ray fluorescence analysis even if fundamental parameter methods are used. When Zn-K α and Fe-K α lines are measured, the obtained results for coating weight and Fe concentration vary strongly with even small intensity changes of Zn and Fe so that the precision of the analysis is unsatisfactory. When an alternative Zn-La line is measured, the measuring depth is shallow and only the surface layer in the coating is accounted for. The Zn-Fe coating layer consists of several metallic phases with different Fe concentrations, and their compositions change against depth in the coating layer. Consequently, the analyzed result from Zn-La lines does not represent the entire Zn-Fe coating layer.

We have developed a multi-channel spectrometer with two channels, differing by a low and a high take-off angle for each, Zn-K and Fe-K lines. For the quantification of coating weight and Fe concentration a new thin film fundamental parameter method has been developed, that allows to use intensity ratios of the Zn-K to Fe-K lines, for the low as well as the high take-off angle. By this method the obtained accuracy has been greatly improved and is now satisfactory for the intended practical application.

The spectrometer and the developed fundamental parameter method have also other useful features, for example that the coating weight of pre-treatment layers (such as phosphate on the Zn-Fe alloy coating) can be simultaneously analyzed. The spectrometer can also be used as regular multi-channel spectrometer.

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INV-12

QUANTITATIVE XRF ANALYSIS OF TRACE LEVELS IN GEOLOGICAL MATERIALS

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Quantitative elemental analysis by means of XRF has progressed over the years, as technology advances. Major strides have been made e.g. in the determination of low atomic number elements (Be, B, C...) – using wavelength dispersive X-ray spectrometry – where the detection limits have been reduced by more than a factor of 10; while the sensitivity increased by a factor of over a 100.

The other area where marked advances have been made is in the determination of trace levels of mid- and high atomic number elements in e.g. specimens of geological origin. Some of the underlying technologies and their relevance to applications will be illustrated.

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**EFFECTS OF ANGLES VARIABILITY ON QUANTITATIVE
ED-XRF ANALYSIS**

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Quantitative analysis by ED-XRF can be obtained using the fundamental parameters method based on the comparison with pellet standards in the approximation of constant irradiation and detection angles all over the sample surface (ideal case).

In this contribution we review the problem of errors which are intrinsic of the method in the more extended vision of considering realistic experimental set-up where angles are not exactly constant and the examined samples can in general be of any non flat or irregular surface and/or have different inclination from the one of the reference pellet. The errors are accounted for in the form of corrective shape factors. In principle, these factors must be separately calculated for each value of excitation and characteristic X-ray energies. Recurring to an ideal experimental set-up with constant angles in each point of the examined sample area, we obtain the result that the corrections due to irregular surface or incorrect sample positioning tend to value 1, or more in general to a constant value independent of excitation and emission energies, in the limit case when the direction of the exciting radiation coincides with that of the detected fluorescence X-rays.

Assuming realistic tolerance values for in-going and out-going directions, as fixed in some instrumental set-ups, the shape factors are estimated for regular or irregular distributions of local surface postures and possible positioning of the piece under examination. So one obtains quantitative evaluations of the limits that can be attained for the precision of the fundamental parameters method applied to real objects out off the ideal condition of constant angles.

The use of Silicon Drift Detectors capable of very high counting rates should allow lowering in reasonably short measuring time the statistical error under the above limits imposed by geometry; in order to avoid errors deriving from intrinsic X-ray tube instability an investigation aimed at achieving a system stable enough is still needed.

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**ENHANCEMENT OF X-RAY FLUORESCENCE OF LIGHT ELEMENTS
BY PHOTOELECTRON SECONDARY EXCITATION**

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Current methods in the quantitation of x-ray fluorescence analysis are generally based on theoretical calculations that account only for photon-in photon-out processes. However, modern applications of x-ray spectrometry require drastically improved relative uncertainties of the analytical results, which demands that secondary processes (such as the excitation by photoelectrons created as a consequence of primary ionizations) also be taken into account. A straightforward approach for determining the impact of a secondary process on the fluorescence intensity requires sufficiently accurate knowledge of the flux of the incident monochromatic radiation, the solid angle of detection and the fluorescence count rate. Reliable measurements of the incident photon flux and the detected count rate are obtainable through the use of absolutely calibrated x-ray detectors. For several low *Z* elements ranging from carbon to silicon, the energy dependence of the K-shell fluorescence enhancement by photoelectrons was investigated by means of thin samples in the lower micrometer range. The experimental results are compared with the corresponding theoretical calculations for selected cases.

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EXTENSIONS TO THE SHERMAN EQUATION TO HANDLE FINITE VOLUME EFFECTS IN FUNDAMENTAL PARAMETER METHODS

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Fundamental Parameter methods are successfully used in XRF analysis. The strength of the method is that it can handle wide concentration ranges and it forms the basis for standardless analysis.

All Fundamental Parameter methods use predicted intensities coming from a sample in one or another way. The predicted intensities are computed with the Sherman equation.

In its most simple form, Sherman's equation describes the intensities coming from bulk samples with 'infinitely' large thickness and area/volume. Extensions to handle thin films and layered samples were published in the last decades and are applied successfully.

The effects of finite area/volume are less known nor described mathematically.

In this presentation the mathematics to handle situations where the area/volume of the sample cannot be taken as infinitely large will be given.

Volume effects are applicable to micro-spot analysis, but also play a significant role in samples with heavy elements in very light matrices like heavy metals in oil and plastics.

For this type of samples the so-called wedge effect is significant but often neglected. The effect is caused by the fact that the volume that is *excited* by the x-ray source and the volume from which characteristic radiation can be *observed* are not the same and vary depending upon the density, the quantity and the area of the sample. Taking the wedge effect into account will improve the result significantly. Results achieved on various types of oil will be presented.

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**DIRECTLY FROM THE EDX SPECTRUM TO CONCENTRATIONS
A NEW APPROACH FOR A UNIVERSAL CALIBRATION CONCEPT**

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All common evaluation methods for “Standardless Analysis” in XRF are based on the use of fundamental parameters, which reflect the physical properties of the sample and excitation conditions. The theoretical intensities and consequently the concentrations of the analytes in the sample are calculated in consideration of matrix effects.

The major limitation of ED-XRF for a universal calibration up to now is the strong line overlaps and the countrate dependent resolution of the systems. Therefore, additional mathematical peak deconvolution methods have to be implemented, so that in a first step, the net peak intensities can be calculated. One major drawback is the additional step which is an additional source of error. The second one is that all known models make use of many fitting parameters and that the collection of a high number of pure element spectra is needed. Because of the difference between the spectra of pure elements and of real samples regarding their scattering properties and matrix effects the result are often mathematically correct but analytically wrong. The applications for these fitting strategies are very limited and get worse for complex samples.

To improve the “Standardless Analysis” with our S2 RANGER, we developed a new “Direct Correlation” method, which allows the direct correlation between the concentrations and the measured spectra without the intermediate step of determination of net intensities. Initial concentrations as the only set of variables are varied until an optimal fit of the measured and the “theoretical” spectra is obtained. The two major advantages are that only one fitting parameter has to be handled and the “Direct Correlation”-method works without the instrument-specific collection of pure element spectra. The technical configuration of the S2 RANGER with its Si-Drift-Detector and its fast digital multichannel analyzer provides high quality spectra with a high resolution even at higher countrates. The combination of the S2 RANGER and the “Direct Correlation”-method assures a high quality of the analytical “standardless” result.

The strength of the unique Direct Correlation method will be demonstrated on typical daily-routine XRF applications.

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**REFERENCE-FREE XRF QUANTIFICATION EMPLOYING
L-LINES OF HEAVY ELEMENTS**

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Reference-free quantification in X-ray fluorescence analyses requires the accurate knowledge of all experimental values both in the excitation and detection channels as well as of the fundamental parameters involved. The experimental data are accessible through calibrated devices such as photodiodes, diaphragms and energy-dispersive detectors. The latter are calibrated with respect to their efficiency as well as to their response behaviour. The relative uncertainty of the experimental data in total is about 2-3.2 %. Besides the instruments' contributions, the relative uncertainties of the XRF analytical results are moreover affected by the tabulated fundamental parameters of the elements, some of which only have estimated uncertainties.

Using reference-free XRF and transmission measurements, we have compared different fundamental parameter databases and included the energy dependency of the absorption jump ratio in the algorithms. To further reduce the uncertainties of the standard-free XRF, a product of the transition probability, the absorption jump ratio of the shell, and the fluorescence yield can be determined by transmission measurements of self-supporting one-elemental foils. Here, absorption correction factors depending on both the exciting and the fluorescent energy are obtained. With this additional measurement a significant reduction of the relative uncertainties for standard-free absolute fundamental parameter quantification from XRF measurements can be achieved.

Furthermore, the iterative entanglement of XRF spectra deconvolution employing detector response functions and of quantification is providing improved results.

We describe the progress of completely reference-free quantification using these techniques taking for an example the L fluorescence lines of heavy elements such as platinum.

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EXPERIMENTAL MEASUREMENTS OF TARGET THICKNESS

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The determination of PIXE cross sections and the concentration of elements in a material needs the knowledge of the target sample thickness. For this aim we have performed the measurement of the thickness by three different methods: absorption of X rays given by an ⁵⁵Fe source, transmission of alpha particles given by an ²⁴¹Am source and Rutherford backscattered of alpha particles produced by Van de Graff Accelerator with the use of the RUMP simulation code. The results give a thickness with uncertainties lying between 1 to 8% according the used method.

The comparison between the methods gives an advantage for the absorption of X-rays for its simplicity and accuracy, when backscattering spectrometry is preferred as a complementary technique for PIXE analysis.

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**DENSITY PROFILE UNFOLDING FROM COMPTON SCATTERING
MEASUREMENTS IN REFLECTION GEOMETRY**Jorge E. Fernandez¹, Marco Badiali², Alessandro Guidetti², Viviana Scot¹*¹Laboratory of Montecuccolino-DIENCA, Alma Mater Studiorum University of Bologna, via dei Colli,
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In this article it is reported a mathematical procedure which allows the unfolding of the density profile from the measurement of an integrated scattering signal containing prevalently the Compton component. An experimental device (patent claimed) has been used for the measurements. It uses the white x-ray tube spectrum (unpolarised) as radiation source and reflection geometry to maximize the Compton signal. The algorithm has been tested on light-element inhomogeneous samples which were uniform and non uniform in density. Incomplete primary volume and multiple scattering corrections are also discussed. The resulting density profiles are in good agreement with direct measurements of the profile performed with other means.

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X-RAY SPECTROSCOPY WITH DOUBLE REFLECTIONS IN SINGLE CRYSTALS

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Forbidden X-ray reflections occur in crystal planes for which interference is destructive. For special sharp directions along the reflection cone and specific crystal symmetries, however, the forbidden reflection might be simulated by double reflections from two different planes in the crystal [1]. The sum of the indices of the two planes equals the indices of the forbidden reflection. Such reflections occur also with allowed reflections, but they would be heavily overshadowed by the allowed reflection.

The main feature of a double reflection is that the beam of a monochromatic point source will be reflected into a point on a film or 2D counter system held perpendicular to the beam [2]. If two point sources are emitting the monochromatic radiation two points will appear on the film. For an extended 2D X-ray source an exact monochromatic image of it will be seen on the other end. As a matter of fact a separate image for each wavelength will be observed. Thus size, shape and intensity distribution of the spot may be observed. If some part of the spot is shadowed by Tungsten layers coming from the cathode, this will be seen. These and other properties of Double Reflection X-ray spectroscopy, such as absolute wavelength determination, will be discussed.

No strictly monochromatic sources exist. So the image belonging to one wavelength may overshadow partially other images belonging in a continuous spread of wavelengths representing the width of the "line". This might be overcome by minimizing the distance of source, crystal, counter system - which is not possible in observations on controlled fusion experiments. However, using the Double Reflection method combined with a curved crystal, one would obtain sharp lines having spatial resolution of rotation velocity profiles, ion density and ion temperature for individual spectral transitions along lines emitted by Tokamaks.

The intensity of double reflections is small compared to that of other lines. This is a result of it being dependent on several crystallographic coefficients, such as the polarization. It is strongly wavelength dependent. For each application the relative intensity has to be computed.

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**MULTILAYER INTERFACIAL MIRRORS AS COMPONENTS
FOR SOFT-X-RAY WDS MONOCHROMATORS AND TUNABLE
RADIATION SOURCES**

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Multilayer interferential mirrors (MIM) consisting in a periodic stack of bilayers with light and heavy alternating materials are now widely used as reflective devices with low resolution in the soft-x-ray domain.

In this communication, we will show that these MIM can also be used in the soft-x-ray domain as primary components to make monochromators with medium resolution for WDS and tunable radiation sources.

It is now possible to fabricate multilayer monochromators with medium resolution by etching according to the profile of a lamellar grating, MIM with a large number of bilayers. It will be shown both theoretically and experimentally that these multilayer gratings with appropriate characteristics can be used as soft-x-ray monochromators whose spectral resolving power is considerably improved with respect to mere interferential mirrors.

Moreover tunable soft-x-ray sources based on the interaction of medium energy electron beams with periodic multilayer structures are presently developed in several countries. The physical processes involved in this kind of source belong to the class of quasi-Cerenkov emission. Among them, they are resonant transition radiation and parametric radiation. We will present the basic concepts, some theoretical predictions and the first experimental results concerning this new type of sources.

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NOVEL GRAZING INCIDENCE X-RAY OPTICS

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We will refer on novel approaches and technologies for advanced grazing incidence X-ray optics. They include (i) design and development of novel very wide field X-ray optical systems based on lobster eye optics, (ii) application of innovative materials for X-ray optics, with focus on precisely optically shaped Si wafers and thermally shaped glass foils, and (iii) design and development of grazing incidence X-ray optics with multilayers, with focus on replication of multilayers to allow X-ray micromirrors with extremely small apertures (of order of 1 mm) with deposited multilayers to be produced. The X-ray optics described here offers a wide range of laboratory and other applications which will be also discussed.

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**NANOMETER MULTILAYERS AS MONOCHROMATORS
FOR X-RAY SPECTROMETRY**

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The principle of wavelength-dispersive X-ray fluorescence (WDXRF) analysis or electron probe micro analysis (EPMA) is based on the excitation of characteristic radiation of the chemical elements contained in the specimen under investigation. In order to separate the emission lines of the different elements, monochromators like crystals or nanometer multilayers are used. In this presentation we will focus on the development and improvement of multilayer monochromators for the detection of light elements of the periodic table (Be – S).

The photon wavelengths of the characteristic radiation of light elements are in the range of 0.7-11.4 nm. Correspondingly, the period thickness of the multilayers has to be in the same order. However with smaller period thicknesses the requirements for the interfaces between adjacent layers within the multilayer significantly increase. It has to be ensured that both interface roughness and interface diffusion has to be minimized at the same time. Additionally the stability of the deposition process must be extremely high since the multilayers consist of up to 1200 single layers. In this presentation we will report about recent improvements of different multilayer coatings (e.g. W/Si, W/B₄C, Mo/B₄C) in the period thickness range from 1-3 nm. We will present the improvement that was obtained and characterized by Cu-K(alpha) reflectometry. Finally, we will show the performance of the multilayers at the working wavelengths using synchrotron radiation at BESSY II.

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**SHAPED CAPILLARY X-RAY LENSES FOR μ XRF
AND μ EXAFS MEASUREMENTS**

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Mono-capillaries with small diameters can be applied as a substitute for pinhole collimators in local fluorescence analysis for obtaining small excitation spots on the sample as well as for μ EXAFS and μ XANES measurements [1]. They can give an intensity gain on the order of several thousands, especially when used in combination with synchrotron radiation sources.

Obtaining micro-focused beams with mono-capillaries can meet certain difficulties. First of all, the number of reflections inside a capillary must be minimized. This can be achieved using collimated or pre-focused synchrotron beam on a capillary input aperture, as well as by utilizing a special shape of the capillary channel: elliptic or parabolic [2].

For a μ EXAFS application, a quasi-parallel synchrotron radiation beam has been successfully focused with an elliptic capillary to a focal spot size on the order of 1 μ m with reasonable total flux.

A further improvement in capillary optic resolution is possible using a parabolic shape of the reflection surface. The main advantage of parabolic capillaries for focusing radiation is the existence of a focus, which lies at some distance from the capillary exit so that reasonable capillary-sample working distances can be realized.

In this paper we report on optical tests and applications of this new generation of polychromatic focusing optics.

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**CHARACTERIZATION OF STRONGLY FOCUSING
POLYCAPILLARY HALF-LENS**

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A prototype of a strongly focussing polycapillary half-lens designed and manufactured by X-ray Optical Systems was characterized at HASYLAB beamline L. Although designed primarily as secondary focusing element (positioned in front of the detector) for confocal micro-XRF and confocal micro-XAS experiments, and therefore having a relatively short total length (2 cm), it showed outstanding performance as a primary focusing device for radiation produced by (high-emittance) synchrotron sources and x-ray tubes.

When used to focus the primary beam, edge scans using a chromium microfoil revealed beam sizes of 3-6 micrometers FWHM in the range 22-12 keV, the beam size gradually increased to 19 micrometers in the 12-6 keV range. The high divergence of the focussed beam leads to a depth of focus of about 30 micrometers; the working distance from the tip of the capillary to the focal plane is 2 mm. Using an appropriate detector collimator it was possible to reduce the spurious XRF radiation, emitted by the glass material of the capillary lens into the detector, to the level emitted by sub ppm constituents in thin tissue sections.

A drawback of the present design is the high abundance of the halo (i.e., radiation transmitted through the capillary without reflection) at energies above 12 keV. Wire scans at 17 keV revealed a peak to background ratio of only 2000:1. However, by altering the lens design, it should be possible to reduce the halo abundance considerably. The potential of the capillary for microscopic trace element imaging is illustrated by several applications in the geological and archaeometrical field.

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**FEATURES OF PASSAGE AND FOCUSING OF X-RAY BEAMS
IN POLYCAPILLARY NANOSTRUCTURES**

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The technology of polycapillary optics is quickly improved during last years. The channels and walls sizes achieve hundreds and tens of nanometers. Thus there is number of complex phenomena at passage of photons through such structures. These phenomena demand the new approach for their description.

At focusing on small focal spots (<10 micron) there are problems caused by channeling and strong scattering on the lens exit. Besides, when thickness of a channel wall becomes less than c / ω (where c – light speed, ω – plasma frequency of glass) X-ray photon is not reflected any more but scatters.

In channels with several tens nanometers size the photon's behavior becomes quantum (it occupies one or several discrete levels in the channel, depending on its diameter). So the photon has as abnormally big absorption, so abnormally big transmission, depending on its quantum level in the channel.

There are some ideas given in the report about arising negative refraction for x-ray photons in polycapillaries with nanometers channels. In this case the focusing of X-ray beams has number of important features distinguishing it from ordinary focusing.

The received results are of an important value for the future development of polycapillary optics and its applications.

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GAS DETECTORS FOR X-RAY SPECTROMETRY

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Gaseous detectors are widely applied to x-ray spectrometry in important areas such as astrophysics, medical instrumentation and high-energy physics. They are room-temperature radiation detectors with large and very large detection volumes and/or areas capability. These features, plus an inherent ruggedness and radiation hardness are important advantages over solid-state detectors in many applications.

There are two main types of gaseous x-ray detectors, both relying on signal amplification based on the primary electrons produced in the gas by the x-ray interaction. While detectors relying on charge multiplication processes (PCs, MWPCs,...) may present intrinsically simple construction and operation, gas proportional scintillation counters (GPSCs), relying on signal amplification through a light amplification stage, present superior performance: much higher pulse amplitudes with reduced statistical fluctuations and space-charge effects. Typical energy resolutions of PCs and GPSCs are ~13 and 8%, 8% and 4.5%, 5.5 and 3.5%, for 6, 22 and 60 keV x-rays, respectively.

Space-charge build-up, from the slow drifting positive ions of the gas, presents a significant drawback in the counting rate capabilities of PCs and MWPCs. The introduction of micropatterned electron avalanche multipliers (MSPs, GEMs, MHSPs,...), with the cathodes and anodes separated only by some tens of microns, have overcome this limitations as well as the assembling constrains of placing thin, long wires closely spaced.

On the other hand, GPSCs require gas purity, leading to the necessity for vacuum baked detectors with ceramic-to-metal joints and special gettering devices. In addition, the detection areas are limited by the photosensor for the scintillation readout, commonly a PMT. These constraints are the main reasons for its almost exclusive use in very specific applications where detector cost, bulkiness and complexity are not limitative, e.g. astrophysics. Recent achievements presenting simple, inexpensive and compact alternatives to multi-electron focusing structures and efficient gas purification have been developed, allowing the construction of GPSCs for portable and laboratory purposes. In addition, PMTs may be substituted by CsI-based photosensors (with the CsI deposited over MSPs, GEMs or MHSPs) or solid-state photodiodes to overcome the limitations associated with PMTs: power consumption, complexity, fragility and bulkiness.

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**SILICON DRIFT DETECTORS REFINED ON ENERGY RESOLUTION,
COUNT RATE PERFORMANCE AND RADIATION ENTRANCE WINDOW**

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The Semiconductor Laboratory of the Max-Planck-Institute and PNSensor in Munich are fabricating Silicon Drift Detectors (SDDs) since many years. These devices are continuously optimized to meet the high quality spectroscopic requirements of XRS and TXRF by making use of an ultrapure silicon process in a modern semiconductor facility, an advanced design with a very small detector capacitance and the concept of an integrated first amplifying transistor. We will report on recent developments improving energy resolution, count rate performance and radiation entrance window quality. It is a main objective in SDD production to reach optimum energy resolution for device operation close to room temperature, easily to be achieved with Peltier cooling. Therefore a new fabrication technology has been developed improving leakage current control. The excellent performance of the as-produced detectors demonstrate energy resolution values between 126 eV and 133 eV at -20 deg C for 10 mm² detectors and values better than 135 eV at -30 deg C for 20 and 30 mm².

Due to its very small signal capacitance of about 100 fF the count rate capability of SDDs is high. It ranges up to 10⁶ cps or 10⁷ cps for multi-element structures. Important is that by operating the SDD system in pulsed reset mode by making use of the integrated reset diode and feedback capacitance the energy resolution of the detector is not degrading with count rate. Measured values of 128 eV @ MnK at a count rate of 100 kcps are presented. Moreover, operating the SDD in CSA mode with pulsed reset delivers an excellent stable system with a peak shift less than 0.05 %. Since the quality of the detector entrance window has a large impact on the peak-to-background ratio and the light element detection capability, a great effort is put into the optimization of the entrance window and its boundaries. By covering the outer margin of the detector with a proper collimator, values of the peak-to-background ratio of 10.000 are obtained. Measurements of a thin entrance window are shown with an energy resolution of 65 eV for the Carbon line. The current focus of the investigations is the optimum balance between light element detection capability and radiation hardness. Up to date SDDs show a radiation hardness up to 10¹³ photons referring to a 10 year period of operation.

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IMPROVEMENTS IN SILICON DRIFT DETECTORS

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In the last years the performance of Silicon Drift Detectors (SDDs) has been improved dramatically. The new generation of the KETEK VITUS-SDD shows energy resolutions below 130 eV at 5.9 keV Mn K α . While still thermo-electrical cooling is sufficient to reach the detector operating temperature, active areas from 7 to 100 mm² are available now. Furthermore, the thickness of the detector crystals has increased to 450 micrometer and even thicker drift detectors are under development. A large improvement has also been achieved for the peak to background ratio of the VITUS-SDD that now reaches values of 10000 and above. Present VITUS-SDDs do not only show excellent energy resolutions at higher x-ray energies, but also for low energetic carbon and boron lines. Besides these performance improvements, the handling of SDDs has become much more comfortable, too. All bias voltages of the VITUS-SDD are easy to adjust and very uncritical in their values. They may be varied considerably without loosing detector performance. So it can be stated today that VITUS-SDDs can be operated as simple as PIN-diodes, while obtaining the performance of Si(Li) detectors.

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FABRICATION OF ARRAY DETECTORS WITH ONE HUNDRED SUPERCONDUCTING-TUNNEL-JUNCTIONS AND TA X-RAY ABSORBERS

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We have developed superconducting tunnel junction (STJ) X-ray array detectors to obtain a large detection area, a high detection efficiency, and a high counting rate. The array STJ detectors consist of one hundred Nb/Al-AlO_x/Al/Nb STJs with a size of 200 x 200 micro meter. Each STJ has a 4 micro meter-thick Ta absorber connected to the top Nb layer through a thin insulating layer. The absorbers act as energy converter from high X-ray energies to phonon energies, which are compatible with superconducting energy gaps. The array detectors realize in total a detection area of 4 square millimeter and a detection efficiency of over 90% for X-rays up to 6keV. In addition, it is possible to improve a spatial uniformity of X-ray signal outputs of the Nb-based STJ [1,2] by using the Ta absorber due to a fast diffusion of quasiparticles in the Ta absorbers. In order to minimize crosstalk, we have adapted a coplanar transmission waveguide (CPW) structure having a 8 micro meter-wide signal Nb line, 7 micro meter-wide ground gaps, 12 micro meter-wide ground Nb lines, and an impedance of 50 ohm. The detector layer structure has been optimized by changing thicknesses of each layer and an oxidization condition of the insulating layer to convert the X-ray energies to the output signals efficiently. The fabrication processes and the detector response to X-rays are discussed.

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DETECTOR DRIVEN PERFORMANCE IN EDPXRF

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BRAGG polarization as well as secondary targets in a Cartesian geometry are well known as tools to improve sensitivities and detection limits in EDXRF. The opportunities of using polarized X-rays are often limited by using inadequate solid state detectors. Therefore, a new generation of Silicon drift detectors (SDD) was examined for XRF applications and the results will be presented. The high dynamic range, the stable and excellent resolution within that range, a precise dead time correction together with a model to describe the incomplete charge collection are the basis for new applications. The stability of the spectrometer and the flexibility of the Cartesian excitation system open new opportunities to correct difficult line overlaps, e.g. between K- and L- lines.

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METALLIC MAGNETIC CALORIMETERS FOR HIGH RESOLUTION SPECTROSCOPY

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An increasing number of experiments and applications employ low temperature particle detectors which are based on a calorimetric detection scheme and operated at temperatures below 100 mK. In many cases this is due to the high energy resolution achievable with these detectors. Equally important benefits are often the increased flexibility in the choice absorber material and the fact that the detection efficiency can be arranged to be similarly high for radiation of different ionizing character.

Metallic magnetic calorimeters (MMC) make use of a metallic paramagnetic temperature sensor, which is in tight thermal contact with a metallic x-ray absorber. The paramagnetic sensor is placed in a small magnetic field. Its magnetization is used to monitor the temperature, which in turn is related to the internal energy of the calorimeter. High energy resolution can be obtained by using a low-noise, high-bandwidth DC SQUID to measure the small change in magnetization upon the absorption of energy. With recent x-ray detector prototypes an energy resolution of a few eV for x-ray energies up to 6 keV has been achieved. We discuss the thermodynamic properties, the energy resolution and general design considerations of MMCs as well as their application in high resolution x-ray spectroscopy, beta spectroscopy and absolute activity measurements of mixed photon and electron emitters.

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INV-15

TEN YEARS OF X-RAY HOLOGRAPHY

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With the appearance of nano-science the role of local methods is more and more important. Hard x-ray holography based on the inside reference point concept is a local probe of the atomic order in solids [1]. It gives the 3D real space image of atoms without the phase ambiguity inherent to diffraction methods. In this presentation a concise description of the basics of hard x-ray holography will be given. We will also introduce related methods. Experimental and theoretical developments will be overviewed and illustrated by examples. We will discuss new directions and future possibilities.

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**FLUORESCENCE TOMOGRAPHY AT THE ESRF BEAMLINE ID22:
RECENT ADVANCES AND FUTURE DEVELOPMENTS**

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X-ray fluorescence computed tomography (XFCT) is a recent imaging technique that can give quantitative information about the distribution of chemical elements inside a sample. It is based on the measurement of fluorescence radiation emitted from a sample when illuminated with a synchrotron monochromatic X-ray focused beam, following a 1st generation scanner sampling.

At the beamline ID22 of the European Synchrotron Radiation Facility, XFCT is now routinely proposed to users and 3D reconstructions can be obtained at the micron resolution for those elements having an atomic number higher or equal to $Z=14$ (Si). In this work we present the latest XFCT instrumental developments carried out at ID22.

After a brief presentation of the beamline, we will start by describing the micro-mechanics developments. In particular, a new in-house rotation stage has been designed that combines compactness together with high accuracy and low wobble/eccentricity. A xyz piezoelectric stage ensures high resolution and fast continuous scanning in helical mode for 3D analysis.

To measure low Z elements and reduce air scattering, dedicated helium chambers have been designed. Both sample stage and helium chambers are compatible with our recently commissioned 13 element detector as well as with single element Si(Li) or SDD fluorescence detectors.

Once acquired, data are fitted to produce one sinogram per chemical elements. 3D reconstructions are then computed based on the ITT (Integrated Tomographic Techniques) algorithm. This work will be illustrated with recent results obtained at ID22 in various scientific applications, among which biology and earth science.

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INVESTIGATION ON LECCE STONE POROSITY BY MEANS OF MICRO AND NANO X-RAY TOMOGRAPHY

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Continuous chemical and physical changes occur on the Cultural Heritage, depending on the establishment of a dynamic equilibrium with the environment, in which it is placed [1]. Its conservation has become, in the modern time, a more and more complex issue, mostly because of the increasing of the atmospheric pollution. In particular, regarding the stone materials, different phenomena can take place:

- Formation of black crusts caused by the reactions of SO_x with stone [2]
- Corrosion of the material due to the atmospheric pollutants, such as NO_x [3]
- Internal cracks of the natural inner structure due to frost-thaw cycles [4]

Water plays a very important role in all of these decay processes.

Lecce stone has a very high porosity (~ 35% measured by mercury porosimeter), and high capability to uptake water from the environment by capillary absorption (~ 12g of water absorbed for 100g of stone). In order to reduce the capillary absorption of the water, and then to prevent the deterioration, different kinds of hydrophobic organic products are applied on the surface of the restored buildings. Because the efficacy of the treatments depends mostly on the good penetration and distribution of the products in the pores, we have investigated the porosity and the internal structure of the stone materials with X-ray Tomography.

We have characterized, with X-ray Micro tomography (instrument SkyScan 1172, camera pixel size = 2.6 μm), different samples of Lecce stone with dimension of 3x3x3 mm³. Afterwards, the samples have been treated with three selected products, widely used for stone conservation: Paraloid B72 (Poly(ethylmethacrylate-co-methylacrylate), F-rubber (Poly(hexafluoropropene-co-vinylidene fluoride)) and a solution of Alkylalkoxysilanes oligomers.

The same samples were rescanned and porosity and other parameters of the material were calculated and compared, before and after treatments, in order to emphasize the changes due to the products application, in particular a decreasing of the porosity was observed.

At the same time small pieces of the (un)treated samples (ca 0.5x0.5x0.5 mm³) have been analyzed with X-ray Nano tomography (instrument SkyScan 2011). In these last scans a higher resolution (camera pixel size = 580 nm) has been achieved and it has been possible to see the distribution of the products inside the pores: most of them were partially filled by the products, while only a small part was completely full.

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PHASE-CONTRAST ENHANCED X-RAY TOMOGRAPHY OF MALARIA TRANSMITTING MOSQUITOES

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X-ray phase contrast tomography technique [1] was applied to support the development of the sterile insect technique (SIT). The SIT, in combination with other methods, is used for reducing the population of malaria transmitting mosquitoes [2]. The technology is based on the idea of releasing an irradiated, and therefore sterile, population of male mosquitoes to the environment of a given territory. The female mosquito mates only once per life cycle. Therefore if mating occurs with irradiated (sterile) male, the eggs will not hatch breaking the reproduction chain. The successful implementation of SIT requires that the irradiated population of male mosquitoes is otherwise healthy in order to compete with the non-treated males during the mating process. This demand implies that the treated insects do not undergo morphological changes due to irradiation.

The morphology of treated and untreated malaria transmitting mosquitoes (*Anopheles arabiensis* Patton, Diptera: Culicidae) was investigated with the use of X-ray phase contrast tomography technique. Two groups of mosquitoes were selected for measurements: irradiated mosquitoes, with a dose of 120 Gy from ⁶⁰Co gamma source, and not irradiated control population. Pupae and adult populations were studied. The mosquitoes were chemically fixed before measurements, their abdomens were sectioned out from the insect body, mounted on graphite rods and scanned in phase contrast X-ray tomographic setup. The measurements were performed at the Fluo-Topo beamline in the ANKA Synchrotron Facility, Karlsruhe, Germany. Monochromatic X-ray beam (12 keV) from a multilayer monochromator was used to obtain phase-contrast enhanced projections of the analyzed samples. The projections were collected with a CCD camera focused on a thin layer scintillator plate (cerium doped yttrium aluminium garnet – YAG:Ce). Tomographic scans consisted of 180 projections, each projection consisting of 1392 x 1024 pixels 16-bit grey level image. The 3D morphology of the analyzed samples was reconstructed by applying the filtered backprojection algorithm and by segmenting the resulting data with specialized software. The obtained reconstructions as well as the details on the mosquito fixing procedure, data acquisition setup, and the tomographic reconstruction algorithm will be presented.

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μ XANES SPECTROSCOPY APPLIED TO THE STUDY OF ORIGINAL IRON GALL INK CORRODED MANUSCRIPTS

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An important part of our hand-written European cultural heritage is drawn up with iron-gall ink. This type of ink consists in a mixture of vitriol, tannins and gum arabic. The so called “vitriol” mentioned in the ancient recipes is close to iron (II) sulphate. The tannins are generally extracted from gallnuts and contain large quantities of polyphenolic acids that are decomposed by hydrolysis into smaller molecules. Gallic acid is one of the major constituent of these extracts. The association of vitriol and tannins leads to the formation of iron-based solids, resulting in a dark colour which is characteristic of the ink.

When used on paper, iron-gall inks may induce high damages, especially when the papers are stored in a humid and warm atmosphere. For instance, most of Leonardo da Vinci’s oeuvre shows signs of degradations, Bachs’ written music is virtually falling apart, while numerous manuscripts by Galileo Galilei are completely destroyed. These corrosion phenomena are considered to be the result of two major degradation processes: first, the presence of tannins, iron (II) and iron(III) in the ink leads to very acidic pH values (between 2 and 4) and the cellulose is very sensitive to acid hydrolysis. Secondly, iron (II) catalyses cellulose oxidation mechanisms initiated by Fenton like reactions, thus contributing to its de-polymerisation.

Iron is also expected to be one of the major actors of the cellulose degradation mechanisms. Yet little knowledge is available on its chemistry within original iron gall inks, because of the experimental difficulties related to the analysis of original samples, and also because of the particularly rich chemistry of iron that allows a wide range of reactions: chelation with polyphenols, or with cellulose, redox reaction with gallic acid, and with polysaccharides, oxidation induced by oxygen, formation of oxo-hydroxy compounds, etc.

For a better understanding of the chemistry of iron in inked papers, we undertook microXANES measurements on original manuscripts, more or less seriously damaged. On most of them, iron was mainly iron(III). But some of the most damaged samples contain large proportions of iron(II), with a very heterogeneous distribution. microXANES measurements were also performed on laboratory samples. These consist in paper sheets impregnated with different solutions combining several proportions of iron(II) or iron(III) sulphate and gallic acid. Strong evolutions of the iron(II)/iron(III) ratios were measured within one year, showing that iron is not in a stable state and that the natural ageing of the samples can not be neglected. All iron(II) sulphate containing samples evolve spontaneously toward oxidation. On the contrary, iron(III) sulphate containing samples evolve in different manners, depending on the iron(III) sulphate concentration and on the gallic acid/iron ratio. Competing redox reactions are taking place, such as oxidation of iron(II), probably induced by the air oxygen, and reduction of iron(III) induced by gallic acid. This work shows that other reactions may also happen, and some new insight on the chemistry of iron gall ink corrosion will be discussed.

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3D MICRO XRS - VALIDATION OF A THREE-DIMENSIONAL MODEL OF THE SENSITIVITY FOR QUANTIFICATION

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3D Micro X-Ray Fluorescence Spectroscopy (3D Micro-XRS) as a new analytical technique has proven to be a useful tool for elemental distribution and chemical speciation measurements [1,2]. In contrast quantitation for 3D Micro-XRS is still a research issue. We developed a model of the spatial distribution of the sensitivity of the probing volume defined by the overlapping foci of the confocal setup [3]. The model serves as a basis for further quantitation procedures.

The sensitivity function replaces the calibration constant in conventional Micro-XRF. Due to the energy dependence of the total reflection angle of the optics the sensitivity as well as the characteristic width of the flux density are functions of the energy of the fluorescence. Both the sensitivity function and the widths of the flux density define the experimental setup and can be used to calibrate the system.

In this presentation, the validity of the model is shown. Measurements of thick reference materials have been carried out at the BAM line at the Berlin synchrotron BESSY. The sensitivity function shows the expected energy dependence. Additionally, the FWHM of the optics could be calculated. The dependence of the measurement on the angle of impact on the sample surface is in good agreement with the model used. Thus, it is shown that the measurement of a few thick reference samples is sufficient to have a full calibration procedure for the confocal setup.

As an application example the determination of layer thickness of a fuel cell will be shown.

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GRAZING-EXIT AND MICRO WAVELENGTH-DISPERSIVE X-RAY SPECTROMETRY (GE-WDXRS AND MICRO-WDXRS)

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Grazing-exit x-ray spectrometry (GE-XRS) is a related method to total reflection X-ray fluorescence (TXRF). In the TXRF, the primary x-rays irradiate the sample surface at grazing angles of incidence. On the other hand, in the GE-XRS, the characteristic x-rays are measured at grazing-exit angles, usually less than 1 degree. According to microscopic reversibility and reciprocity, GE-XRS can be applied to surface and thin-film analyses with low background, similarly to grazing-incidence XRS (GI-XRS) and the TXRF.

Compared to the GI-XRS, the GE-XRS has unique advantages. Since the x-ray emission from the sample is measured, we can use various exciting probes, not only x-rays but also electrons and charged particles in the GE-XRS. In addition, these exciting probes can be irradiated the sample at a right angle. This experimental geometry enables a localized analysis depending on the exciting probe diameter.

GE technique can be applied for wavelength dispersive (WD) XRS besides energy dispersive (ED) XRS. After brief explanation of GE-XRS and methodological characteristics using commercially available instruments, instrumentations of GE-XRS applied for WDS and EDS, and recent applications to XRF, EPMA and PIXE will be presented.

Another topic is micro-WD-XRF using a polycapillary X-ray lens, which is placed between the sample and the WDX detector. Even if primary x-rays irradiated the sample in a large area, it is possible to observe small region by using the polycapillary x-ray lens. Usually, for this purpose, a polycapillary half lens is applied. Fundamentals of micro-WDXRF and experimental results will be shown.

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HIGH-RESOLUTION WAVELENGTH-DISPERSIVE SPECTROMETERWolfgang Caliebe¹, Pavel Machek², Ulf Brueggmann¹, Edmund Welter¹¹*HASYLAB at DESY, Notkestrasse 85, 22603 Hamburg, Germany*²*Inst. of Inorganic and Analytical Chemistry, Justus-Liebig-University Gießen, 35392 Gießen, Germany*

We designed and built a high-resolution wavelength-dispersive spectrometer for high-resolution measurements of fluorescence lines, and for inelastic x-ray scattering. The spectrometer is located at beamline W1 of HASYLAB/DESY. The sample is excited with a highly monochromatic x-ray beam from a wiggler as a radiation source. The beam is focused into a spot with dimensions 2 mm x 4 mm (v x h). The monochromaticity of the incident beam is of the order of 1/2500, and the incident flux is about 10^{11} photon/s. The spectrometer is mounted inside a large vacuum tank to reduce absorption by air at lower energies. The spectrometer operates close to backscattering geometry for best energy resolution. The analyzer crystals are cylindrically or spherically bent Si single crystals, with bending radius of about 1m, and diameter of about 100 mm. The scattered x-rays are detected by a high-resolution CCD-camera. Detector and analyzer are mounted on Rowland circle, but the sample is usually mounted inside the Rowland circle. This dispersive set-up together with the rather large focal spot allows us to measure the complete fluorescence spectrum without scanning analyzer and detector. Typical energy ranges are 10 eV at the Cr K-beta fluorescence line or 40 eV at the Cu K-alpha fluorescence lines.

We have measured the Cr K-beta fluorescence line in different Cr compounds with different oxidation states and local symmetries, and the Cu K-alpha fluorescence lines at different energies close to the Cu K absorption edge. The Cr K-beta fluorescence line shows significant dependence on the oxidation state and on the symmetry, but the maximum of the fluorescence line does not show a linear dependence on the oxidation state, opposite to x-ray absorption spectroscopy, where the energy of the edge correlates well with the oxidation state.

The shape and energy of the Cu K-alpha fluorescence lines depend on the incident energy close to the edge, where resonant effects dominate. Below the edge, the energy of the maximum of the emission line shifts with the incident energy (Raman effect), but above the edge, the fluorescence line does not move. Close to the edge, the width of the fluorescence line is also significantly narrower than for energies above the edge. Furthermore, weak transition in absorption spectroscopy, which cannot be detected due to the life-time broadening of the core-hole, can be separated from the main transitions in the white line.

We plan to perform additional experiments this spring.

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**THE WDS ANALYSIS AT HIGH SPECTRAL RESOLUTION:
APPLICATION TO THE STUDY OF Mo/Si MULTILAYERS**

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The optical properties in the x-ray range of Mo/Si periodic multilayers depend on the quality of the interfaces within the stacks. If there is formation of interlayers due to diffusion processes at the Mo-on-Si and Si-on-Mo interfaces, the optical performances of the device will not be optimized. Then, it is important to characterize and quantify these interlayers, i.e. to know their composition and thickness.

We show in this communication that x-ray emission spectroscopy induced by electrons, analyzed at high spectral resolution by a WDS Johann-type spectrometer, is a convenient technique to characterize in a non-destructive way the interlayers of Mo/Si multilayers. The analysis is performed in the IRIS (Instrument de Recherche sur les Interfaces et Surfaces) apparatus equipped with an InSb (111) crystal curved under a radius of curvature of 500 mm. The detector is a gas-flow counter working in the Geiger mode. In this case the spectral resolution $E/\Delta E$ is about 5000 in the 1700-1900 eV photon energy range.

Because of the high resolution of the apparatus, the evolution of the shape of the Si $K\beta$ emission band (3p – 1s transition) as a function of the physico-chemical environment of the Si atoms is easily evidenced. In fact this emission band describes the density of occupied Si 3p states within the valence band. Because these states involve the less tightly bound electrons of the solids, the shape of the Si $K\beta$ emission band is sensitive to the environment of the emitting silicon atom and changes with from one silicon compound to another.

We study a series of Mo/Si multilayers, where the thickness of the Si layers is 2 nm and that of the Mo layers is 2, 3 or 4 nm. It is clearly seen that the emission band from the Si atoms within the multilayers is different from that of amorphous Si (a-Si), which should be observed if no diffusion process takes place at the interfaces. By comparing the observed emission band to that of a-Si and molybdenum silicides and using a simple diffusion model, we deduce the composition of the interlayers. Their thickness is also deduced and estimated to be 0.4 ± 0.1 nm or 0.9 ± 0.2 nm depending on the samples.

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RAILWAY INDUCED PARTICULATE EMISSIONS – A ONE YEAR SURVEY IN ZURICH, SWITZERLAND

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Public transportation systems are promoted especially in urban areas to reduce the use of individual vehicles. Compared to light duty vehicles, trains operated by electric engines have obviously no emissions of combustion aerosols per passenger and distance. Nevertheless, particulate emissions caused by railway traffic are detectable. Material abrasion from tracks, wheels, brakes and the overhead traction line enhance the concentration of typical railway specific elements in ambient air.

To get representative information about the contribution of railway traffic to the local concentrations of particulate matter with particle sizes below 10 micrometers (PM10), a field study was performed covering a time period of one year. The chemical composition of the aerosol samples was determined with wavelength-dispersive x-ray fluorescence spectrometry (WD-XRF). The measurement campaign involved daily sampling at three measuring sites influenced by railway traffic together with an urban background site without local railway exposition (Zeughaus). The sampling sites were situated at the entry to the main railway station of Zurich (Röntgenstrasse, Gamperstrasse) as well as at a very busy railway line with more than 700 trains per day (Juchhof). The aerosol particles were sampled on quartz filters in a distance of ~10 m from the railway tracks. To study the distance dependence of the railway induced concentrations of railway relevant elements such as iron, manganese and copper, additional samples were taken at Juchhof in a distance of 36 m and 120 m from the railway track. The substantial daily variations of the elemental concentration are due to meteorological influences based on atmospheric dilution and transportation processes.

The results of the measurement campaign showed:

- At a distance of 10 m from the railway tracks the PM10 concentration was 1.5 – 2.0 $\mu\text{g}/\text{m}^3$ higher than at the urban background site with an average PM10 concentration of 21.5 $\mu\text{g}/\text{m}^3$.
- The additional fine particles caused by railway traffic consist mainly of iron.
- Compared to the average iron concentration at the background site of ~0.6 $\mu\text{g}/\text{m}^3$ the iron content of the aerosol 10 m from the railway tracks increased to ~2 $\mu\text{g}/\text{m}^3$.
- The iron concentration decreased drastically with increasing distance from the railway track, so did the concentration of the other railway relevant elements copper and manganese.

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THE WAVELENGTH DISPERSIVE SYNCHROTRON MICROPROBE USED FOR MATERIAL ANALYSIS AT ISASLINE.

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Synchrotron radiation (SR) has been discovered to be an excellent excitation source for X-ray fluorescence spectrometry (XRF) and detailed studies have been conducted to establish the advantages of using synchrotron radiation for X-ray fluorescence spectrometry. Amongst others, the high brilliance of the source in contrast to a conventional X-ray tube, the strong polarization of the radiation and the low divergence of the beam applied to XRF have been the subjects of investigations [1,2]. However, nearly all published papers in this area of applications have dealt with SR induced energy dispersive X-ray fluorescence spectrometry (SR-EDXRF).

Previously, it has been demonstrated that the operation of a wavelength dispersive (WDX) spectrometer originally designed for an electron microprobe can be attached to a synchrotron radiation source [3]. The WD spectrometer regularly used for X-ray emission spectrometry is also suitable for micro-domain X-ray fluorescence analysis. Owing to the use of highly brilliant SR as the excitation radiation, small areas down to a few square micrometers can be analysed in a reasonable time. SR-WDXRF for material analysis offers the possibility of performing local analysis with a good spectral resolution and with optimal excitation conditions.

At the time a complete SR-WDXRF device was developed and mounted at ISASLine at DELTA synchrotron facility in Dortmund, Germany. The spectrometer will be presented in detail. Also the different capillary optics to achieve smaller excitation spots with higher photon fluxes will be discussed. First experiments under normal atmospheric conditions as well as under vacuum were performed. The analysis of low-Z elements (B, C, O, Na, etc.) will be presented and the performance of the spectrometer will be illustrated by line-scans and area maps.

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**HIGH RESOLUTION STUDY OF X-RAY RESONANT RAMAN
SCATTERING AROUND THE L3 EDGE OF Xe**

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In this work the inelastic scattering of linearly polarized photons on Xe around the L3 absorption edge has been studied. The experiment has been performed on XAFS beamline at synchrotron Elettra. A series of $L\alpha_{1,2}$ and $L\beta_{2,15}$ x-ray emission spectra of Xe were recorded along the polarization direction of the incoming photons using the high energy resolution crystal x-ray spectrometer in Johansson geometry while changing the energy of the incoming photon beam from 4780 – 5005 eV with the 1 eV step. The combination of high resolution x-ray spectrometer and well energy collimated photon beam resulted in overall experimental broadening of 1.1-1.4 eV which is well below the L3 atomic level width of Xe (2.82 eV [1]). This enabled us for the first time the characterization of the resonantly enhanced and narrowed emission lines originating from the decay of $[2p_{3/2}]nd,ns$ excited states [2]. The measured spectra were decomposed into the radiative contributions from excitations into the continuum and discrete states in order to obtain relative intensities and energies of the lowest discrete transitions converging into the L3 edge.

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APPLICATIONS AND USES OF X-RAY FLUORESCENCE FOR A CLEANER, SAFER AND HEALTHIER ENVIRONMENT

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XRF techniques provide powerful analytical tools to characterize all types of materials. Recent advances in WDXRF and EDXRF can be “exploited” usefully to analyze toxic elements and compounds in aerosol filters, contaminated waters or soils, plastics, used oils, recycling materials, food products and other consumable goods. Indeed, significant improvements in the overall sensitivity, limits of detection with element specificity and ease of use are helping to address environmental applications by XRF. In addition, regulations and controls are also driving both industries and public institutions to comply for a cleaner, safer and healthier environment. RoHS and WEEE regulations are one such example. EDXRF has proven itself to be one of the most effective techniques for such applications. High performance WDXRF is used for monitoring very low concentrations of toxic elements in soils and sediments, raw materials and plastics. This presentation aims to cover a variety of XRF applications in both industrial and public sectors related to the safety, quality and cleanliness of the materials

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POSTER PRESENTATIONS

STUDY OF ANGULAR, INTENSITY AND ENERGY DISTRIBUTION OF 279 keV GAMMA RAYS COMPTON SCATTERED FROM K- SHELL ELECTRONS

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Among the various processes of interaction of x-rays or gamma rays with matter Compton scattering is the one which predominates in the intermediate energy range. The study of Compton scattering has a varieties of application in the different areas like electron distribution in an atom, non-destructive testing of samples of industrial and medical interest etc. Generally, Compton scattering is considered to occur from an electron which is free and stationary and the cross-section for this process is determined accurately by well known Klein-Nishina formula. When the energy of the incident photon is comparable with the binding energy of the electron in the inner shell (especially K-shell) of high atomic element, the electron is no longer considered as free and stationary and the cross-section for free electron is then corrected for a factor which take into account the binding effect of the electron. Various relativistic and non-relativistic theories are developed to account for this correction which is based on form factor approximation, incoherent scattering function approach and S-matrix formulation. On the experimental side, there are some measurements at this energy but the results are scanty and inconclusive due a number of parameters involved in the determination of cross section. In view of this fact, we have performed the experiment to determine the angular, intensity and energy distribution of 279 keV gamma rays Compton scattered from K-shell electrons of molybdenum, silver and tin at various scattering angles ranging from 30° to 150°.

Principle of measurements is that when a gamma ray is scattered incoherently by an electron in the K-shell, the electron is ejected from the shell and as a result fluorescence K X-ray is emitted. The probability that this type of scattering will be accompanied by the emission of K X-ray is defined by the K-shell fluorescence yield of the atom. The measurements are made to select scattered gamma rays in coincidence with the fluorescence K X-rays that follow the ejection of K-shell electrons, with a slow fast coincidence set up having resolving time of 25 nsec. This method not only enables to distinguish between gamma rays scattered from K-shell electrons and gamma rays scattered from free and more loosely electrons, but also gamma rays scattered coherently from the K-shell electrons. Gamma rays of energy 279 keV are obtained from a radioactive source of ²⁰³Hg of strength 400 mCi. The scatterer is viewed by two NaI(Tl) scintillation detectors, one sensitive to scattered gamma ray of dimensions 51 mm x 51 mm and the other of dimensions 38.5 mm x 3 mm sensitive to fluorescence K X-rays of the element. The observed coincidence counts are corrected for chance and false events. Our experimental results for K-shell to free electron differential Compton cross-section ratio increases with the increase in scattering angle and are lower than the Klein-Nishina values at small scattering angles. Our experimental results are compared with the available theoretical and experimental data.

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CHEMICAL EFFECTS IN THE K X-RAY EMISSION SPECTRA OF SULFUR

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In this work the chemical effects in the x-ray emission spectra of several different S compounds have been studied by using high energy resolution x-ray spectroscopy employing crystal spectrometer. Our previous study about chemical effects in the Ka spectra of S compounds [1,2] has been extended also to the Kb emission spectra, which has been usually adopted as most suitable for the chemical speciation of sulfur [3,4]. The Kb emission spectra induced by irradiating the samples with the bremsstrahlung from the Cr x-ray tube have been measured with a high resolution crystal spectrometer in Von Hamos geometry. The energies and widths of the main components (Kb1, Kb', Kb'') in the Kb emission spectrum are given as a function of the sulfur oxidation (valence) state. In addition the sulfur K x-ray absorption near edge structure spectra (XANES) of the same targets were also recorded on the ID21 beamline at the ESRF synchrotron. The quantitative comparison of the chemical effects in the Ka and Kb emission spectra as well as the XANES spectra has been made for different sulfur compounds (sulfide, sulfite, sulfate) and the possibility for the chemical speciation of sulfur has been discussed.

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EXPERIMENTAL DETERMINATION OF X-RAY RESONANT RAMAN SCATTERING CROSS-SECTIONS FOR SEVERAL ELEMENTS AND COMPOUNDS

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The x-ray resonant Raman scattering (RRS) is an inelastic process that occurs when an atom interacts with an incident photon having an energy slightly lower than that of one of the absorption edge. For an interaction in the 1s states, the two-state model considers a virtual K-hole in the intermediate state and a final state with an L-hole (or M-hole), an electron in the Fermi levels (or in the continuum) and a x-ray photon.

X-ray resonant Raman scattering was observed for the first time many years ago, nevertheless there is a lack of knowledge about cross sections and their energy dependence. Some authors have reported deviations between the measured values of mass attenuation coefficient and the corresponding theoretical ones of the order of 10 %. For this reason a precise determination of RRS cross sections will contribute to improve the current values of photoelectric absorption coefficient. In addition, resonant Raman scattering can produce, under certain experimental conditions, unexpected peaks in x-ray fluorescence spectra.

This work presents experimental measurements of x-ray resonant Raman scattering for Fe, Cu, Zn and different copper oxides. In addition, measurements of RRS for the L-edge of Er are also presented. The measurements were carried out in the XRF station of the LNLS using monochromatic synchrotron radiation. Several energy scanings were performed to analyze the Raman peak (below the threshold), the energy of the absorption edge, and the fluorescent line (above the absorption edge) in order to determine the resonant Raman yield.

Data analysis includes several complex stages including non-linear fittings, theoretical cross-sections convolutions, instrument-function deconvolutions, etc. The results agree very well with previous measurements published by other authors for the case of Fe, Zn and pure Cu. The results for the L-edge RRS cross sections are the first one ever reported. Finally, the analysis of different oxides of Cu showed variations depending on the oxidation state.

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SHAPES OF THE K X-RAY SPECTRA OF HEAVY ATOMS PREDICTED ON THE BASIS OF THE MCDF CALCULATIONS

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The multiple ionization of inner shells in collision processes makes the origin of the measured K X-ray spectra of target atoms very complicated. In order to be able to obtain from the spectra the information about the L- or M-shell ionization probability it is vital to make use of the results of theoretical calculations of the positions and intensities of various K X-ray lines. Our aim has been to examine for a heavy atom the effect of the additional single and double L- and M-shell ionization on the shapes and structure of the K X-ray spectra, by performing theoretical calculations on various Pb KL^1M^0 , KL^2M^0 , KL^0M^1 and KL^0M^2 satellite lines [1], corresponding to X-ray transitions from the initial states having apart from a K-shell hole also an L-shell hole, two L-shell holes, an M-shell hole or two M-shell holes, respectively. We have calculated the positions and intensities of the studied lines with the extensive multiconfiguration Dirac-Fock method (MCDF) with the inclusion of the transverse (Breit) interaction and QED corrections [2]. We have chosen to investigate Pb, since being a heavy, but not extremely heavy, element ($Z=82$), it can be regarded as a representative one for heavy atoms. It is also an element studied by experimentalists, e.g., in nuclear reactions [3,4]. We have constructed example theoretical (the sum of the Lorentzian natural line shapes) spectra of Pb for the $K\alpha_{1,2}$ lines, the $K\beta_{1,3}$ lines, as well as the $K\beta_2$ and $KO_{2,3}$ lines. Each spectrum corresponds to a probable experimental situation and is a summary spectrum including contributions from all the above-mentioned satellite lines as well as from the K X-ray diagram lines. It has been found that most of the satellite contributions overlap with one another and also with the diagram contribution, so that only the KL^2M^0 lines (except for the $K\beta_3$ and $K\beta_2$ lines), as well as the KL^1M^0 lines (except for the $KO_{2,3}$ lines) are reasonably well visible in the summary spectrum. Other satellite contributions cause very small deformation of the summary spectrum (like e.g., the $K\beta_1L^0M^1$ and $K\beta_1L^0M^2$ lines), are involved in a very complicated structure (e.g., the $K\beta_2L^2M^0$ lines and all the $KO_{2,3}$ lines except for the KL^2M^0 ones) or cannot be recognized in the summary spectrum (like $K\alpha_1L^0M^1$ and $K\alpha_1L^0M^2$ lines). Thus our theoretical spectra should be crucial in both interpretation (the decomposition) of the spectra and designing new experiments (choosing the optimum conditions), involving the K X-ray spectra of multiply ionized heavy atoms induced by various light or heavy projectiles.

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**IONIZATION EQUILIBRIUM IN MULTICHARGED ION PLASMA
WITH FAST ELECTRONS**

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Bremsstrahlung x-ray emission from plasma with fast electrons depends on ion charge in plasma. Discharge and laser produced multicharged ion plasmas often have nonequilibrium electron distributions with fast (high energy) electrons that may have a profound effect on ionization balance.

In the report the influence of high energy electrons on ionization balance in the collision-radiation equilibrium model is considered.

Nonmaxwellian electron distribution by the energy, found out by adding of fast electrons with various concentration and energy, used for calculations of impact processes rates on the basis of Hartree-Fock-Slater (HFS) quantum-statistical model in the average ion approximation. The calculation approach for the rates of inelastic electron-ion interaction processes with arbitrary electron distribution function based on the method of distorted waves (DW) with the using of numerical and semiclassical wave functions for discrete and continuous spectra calculated in self-consistent HFS potential. Results of calculations of the ionization equilibrium in argon plasma in the temperature range of 5 – 1000 eV with fast electrons with energies from 1 to 10 keV and relative concentrations 0.1 – 10 % are analyzed. Basically, the calculations for the density of electrons $\sim 10^{18}/\text{cm}^3$ were made.

It is shown that fast electrons increase the impact ionization rates in multicharged ion plasma and consequently significantly change its ionization equilibrium state. The bremsstrahlung emission from plasma is recalculated with presence fast electrons.

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**A THEORETICAL STUDY OF THE X-RAY SPECTRA EMITTED
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The principle of Electron cyclotron resonance ion sources (ECRIS) has been proposed in the sixties, yet a detailed understanding of the way they work, in order to improve their capacity is not yet available. Atomic physics is a very important tool for studying the plasma. A brief historical review and a discussion of future prospects can be found in reference [1]. In an ECRIS the energy for plasma generation comes from resonant electron heating by microwaves. ECRIS are characterized by their capacity to produce substantial amounts of highly charged ions and by high electron temperatures. X-ray emission, including bremsstrahlung. Characteristic lines, caused by these high energy electrons due to electron-ion collisions can be used for ECRIS plasma diagnostics. The shape of the continuum spectrum may provide information about the electron temperature in the plasma. On the other hand, characteristic radiation has also been seen as an indicator of electron temperature, making use of the energy dependence of K-shell ionization by electron impact beyond threshold. Furthermore, the degree of ionization of the ions can also be obtained from the K X-ray lines energy shifts due to the removal of outer electrons [2].

In this work we study the contribution of the most important atomic processes, occurring in an ECRIS, which contribute to the creation of excited states from the ground configurations of Cl ions and lead to the emission of K X-ray lines. Theoretical values for inner-shell excitation, K and KL ionisation cross sections, energies, and radiative and radiationless transition probabilities for the de-excitation processes are calculated in the framework of the Multi-Configuration Dirac-Fock (MCDF) method [3]. With reasonable assumptions about the electron energy distribution, a theoretical K X-ray spectrum is obtained, which reproduces closely recent experimental results.

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COMPARISON OF BACK-FOIL SXRF AND EPMA FOR THE ELEMENTAL CHARACTERIZATION OF THIN COATINGS

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The focusing of high flux photon sources for X-Ray Microscope systems requires heavy and expensive equipment, with X-Ray focusing elements and mechanical systems, not easily available. An alternative to that equipment is the arrangement proposed by Cazaux [1]. An incident electron beam is focused on a thin target and the specimen in thin film form is set on the back of this target. The X-Ray beam of limited dimensions produced in the target is used to ionize the sample. The X-Ray beam is scanned by scanning the electron beam. This setup has been used in a SEM for Scanning X-Ray Microradiography and Microfluorescence [2]. Back-foil scanning X-ray microfluorescence, developed in a scanning electron microscope and applied for the analysis of very thin coatings (1-200 nm) is compared with electron probe X-ray microanalysis (EPMA). Both experimental results and Monte-Carlo calculations are used in this respect.

In this paper, experimental results of the signal to background ratio (S/B) in the case of back-foil XRF for different film thicknesses as a function of the detection angle θ , are examined. When the angle is increased, the S/B ratio is improved, due to further reduction of the background caused in turn by greater absorption of continuous radiation within the anode and an increase of the analyzed film area. Back-foil scanning X-ray microfluorescence (SXRF), used in optimized experimental conditions, is found to be more sensitive than EPMA, especially in the case of very thin overlayers. The reduced background in the case of back-foil XRF gives the possibility to increase the measuring time so that the sensitivity of the technique is considerably improved compared to that of EPMA.

Lateral distribution of the total X-ray signal from a film in back-foil XRF is also examined. The distribution is approximately Gaussian. The resolving power of the technique, defined as the minimum distance between two points for which the X-ray signals are resolved, is a few μm . This is much better than the resolving power in conventional XRF and of the same order of magnitude as in EPMA.

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**DEPTH SENSITIVE INVESTIGATION OF PERSIAN TILES WITH 3D
MICRO X-RAY FLUORESCENCE SPECTROSCOPY**

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3D micro X-ray spectroscopy (3D micro-XRS) is an advanced method by which it is possible to combine X-ray fluorescence analysis (XRF) and X-ray absorption near edge structure spectroscopy (XANES) for investigation in a certain depth of the sample. First measurements already showed that the method facilitates investigation on elemental distribution and chemical speciation at the same spot in a certain depth of a material (Kanngießner et al. 2003, Höhn et al. 2006).

New results on this methodological development are presented in order to evidence the potential of this method and the problems to solve in order to apply it for the investigation of complex materials. First analyses concern Cu-containing layered laboratory samples. Various XRF and XANES-spectra at the Cu K-edge were measured at different positions in depth on these well-known samples. The spectra revealed the complexity of fluorescence and absorption phenomena that have to be considered while performing depth-resolved micro-XRF and micro-XANES. Therefore, it is necessary to elaborate a mathematical treatment for absorption correction of the XANES data.

In the frame of a French-German interdisciplinary project on Persian tiles from the 19th century of the Qajar period (Voigt 2002), this new method already proved its versatility on original samples. With the help of the non-destructive 3D micro-XRS measurements, original Persian tiles, which are conserved in the Ethnological museum of Berlin, were analyzed non-destructively with respect to the material employed, the manufacturing process, and decoration techniques. First results are shown which help to clarify the questions concerning the coloring pigments, the thickness of the glaze, the application method of the pigment layer.

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P2-3

THICKNESS DETERMINATION OF NANO-LAYERS - CHALLENGES FOR COATING THICKNESS ANALYSES

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Decreasing structure sizes in micro-electronic devices lead to smaller and smaller analysis areas in the tens of microns range as well as metal layer thicknesses in the nm-range. Detection and quantification of a few atomic layers on small features requires optimized analytical strategies and methods. For quality control in micro-electronics analytical techniques need to be developed to improve sensitivity for the quantification of nano-layers. This poster contribution discusses possibilities for the analysis of thin layers and gives examples of results obtained on multi-layers and alloy layer structures. In addition to that application examples for micro-spot analyses in micro-electronics will be presented.

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μ -XRF AND μ -XANES AT CALCIFICATION FRONTS OF HUMAN ARTICULAR CARTILAGE

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One of the main threats to human health from heavy metals is associated with exposure to lead (Pb), which is associated with chronic diseases in the nervous, hematopoietic, skeletal, renal and endocrine system. Although much progress has been made to limit Pb exposure in industrialized countries, primarily through the elimination of leaded gasoline, workplace exposures and leaded pipes, most adults have already accumulated a substantial body burden of Pb. Most of the affiliated Pb is deposited in human bones, where it is stored up to 20 years and accounts for 90–95% of the total lead body burden. Pb is able to displace Ca^{2+} by cation exchange processes in the hydroxyapatite crystal –the main constituent of bone–and is liberated from it in cases of increased bone turnover such as osteoporosis, pregnancy, hyperthyroidism and hyperparathyroidism. Besides these phenomenological studies on the release of Pb from human calcified tissue analytical studies are essential to gain insight on storage sites and storage mechanisms on a microscopic scale.

Therefore detailed synchrotron radiation induced micro X-ray fluorescence analyses (SR μ -XRF) have been carried out to study the distribution of Pb in bones from human joints (femoral heads and patellas). As a very recent result we found a highly specific accumulation of Pb in the tidemark, which is a metabolically active mineralization front (thickness about 5–10 μm) between calcified and non-calcified articular cartilage and plays an important role in developing osteoarthritis. From the results obtained for single tidemark bones one would expect an accumulation of Pb in both tidemarks of bones showing tidemark duplication. However, Pb shows a strong accumulation at the older of the two tidemarks, while it is not present at the younger one. A comparison of the Pb distribution with the one of other “tidemark-seekers” (e.g. Zn) exhibits a time difference in the accumulation of different metals at the calcification fronts of human calcified tissue.

The finding of elevated Pb levels in cartilage compared to the subchondral region of the bone (about 10 times higher) motivated a study on the chemical speciation of Pb in both compartments of calcified human tissue. Comparing results from micro X-Ray Absorption Near Edge Structure (μ -XANES) measurements in the tidemark with the ones from adequate standard materials gives information on the chemical bond of Pb in human cartilage.

Results from a first μ -XANES experiment carried out at HASYLAB beamline L will be presented in this paper. μ -XANES scans at the tidemark of a femoral head and patella, and on a set of standard materials namely Pb-hydroxyapatite, PbO, PbS, PbCO_3 , and PbSO_4 have been compared and will be presented.

Although suffering from weak counting statistics one could estimate from the results, that most of the accumulated Pb in the tidemark is bound to hydroxyapatite

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LIME IN THE AIR: AEROSOL PARTICLES IN THE COLOMBO REGION, SOUTH BRAZIL

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There is broad agreement that airborne particles have important consequences for health, visibility, climate, and human health. For instance, a chronic exposure to particulates has been associated with increased rates of asthma and other respiratory sicknesses, with loss of lung function, and with increased risk of pneumoconiosis, also called mineral dust diseases. Two important parameters should be taken in account in this context: the respirable fraction of submicrometric aerosol particles which can deposit at the bifurcation of the conductive airways and penetrate into the alveoli, and its composition. Due to the high amount of limestone deposits in Brazil, the production of lime is one intense industrial activity in such areas. The lime production begins with the quarrying and crushing of limestone and the conversion into fine powder is obtained through heating in a kiln. Filter devices should be used to control small particles emission, although the use is restricted. In the South of Brazil, regional air pollution caused by the lime production has become a serious problem with potential effects to human health and the regional environment. Colombo is a city near Curitiba (capital of Paraná states) with 200,000 inhabitants. Between 2000 and 2004, approximately 2 million tonne of lime were produced in this city. In Colombo city, the association between the lime production and the number of persons who needed respiratory treatment in a local hospital is accentuated, indicating that such activity can cause deleterious health effects in the exposed workers and population. Microanalysis can be very useful to characterize the composition of individual particles by investigating the presence of particular elements, which allows us to discriminate between specific particles types. In the present research, an electron probe microanalysis method, called low-Z EPMA, was applied. By the application of the low-Z EPMA technique, the chemical composition of individual particles was quantitatively elucidated, including low-Z components like C, N and O, as well as higher-Z elements. Information concerning the bulk composition is provided by EDXRF. Samples were further analysed for chemical and morphological aspects, determining the particle size distribution and classifying them according to elemental composition. Five classes have been detected based on major elements concentrations: alumino-silicate, carbon-rich, organic and calcium carbonate and calcium oxide. In view of the chemical composition and size distribution of the aerosol particles, local deposition efficiencies in the human respiratory system were calculated for that particle classes. To the authors' knowledge, this is the first time that single-particle analysis using low-Z EPMA has been performed systematically on lime aerosols from Brazil.

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**BRONZE AGE ADOBE BRICKS FROM TURENG TEPE (EASTERN IRAN):
MINERALOGICAL AND GEO-CHEMICAL CHARACTERISATION.**

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A study has been carried out on adobe bricks from Tureng Tepe, an archaeological site in east Iran, north of the Gordan River.

Adobe bricks are made of clay and chaff, mixed, moulded and sun-dried.

A multianalytical approach was adopted; mineralogical, geochemical and physical features were determined by powder X-ray diffraction (XRD), X-ray fluorescence (XRF), Atomic Absorption Spectroscopy (GFAA), sieving and sedimentation. The chemical analysis involved the determination of trace elements.

The analyses were performed to identify the kind of raw materials used and to compare the results with the data relative to clays, clay-water mixtures and fired materials that were recovered on the archaeological site. The analytical data were statistically elaborated.

Some firing experiments were carried out on the clays to compare the fired and unfired samples.

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IN SITU ANALYSIS OF NEOLITHIC BLACK AND RED ROCK ART PIGMENTS FROM SALTADORA CAVES (SPAIN) BY PORTABLE EDXRF SPECTROMETRY

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Most prehistoric rock paints were produced using inorganic pigments, primarily iron and manganese minerals that yield red and black paints, respectively. In Europe, the use of mineral pigments has started in the Palaeolithic, and Neolithic rock art manifestations are particularly abundant in eastern Spain. The rock art pigments are often fragile and precious materials whose study requires both non-destructive and in situ analytical methods to identify their elemental composition as complement to stylistic analyses. However, the manifestations of the prehistoric rock art paintings are, in most of cases, in places of difficult access. This fact supposes a severe restriction to the analytic studies that can be carried out in situ.

Our aim in this research was to demonstrate the usefulness of portable EDXRF spectroscopy for in situ analysis to investigate the elemental composition of the prehistoric rock art paintings (~7000 b.C.) located at the “La Saltadora” caves in Valltorta Valley (Coves de Vinromà, Castellón, Spain). We have analyzed the collection of 20 figures placed in the hard access natural shelter IX.2. These paintings represent human and animal figures in red or black pigment.

A portable EDXRF spectrometer developed at the Material Science Institute of the Valencia University was used to obtain the elemental composition of the wall paintings. The spectrometer employed was an Eclipse-II X-ray tube (silver anode, $V_{max}=30$ kV, $I_{max}=1$ mA) and a Si-PIN Peltier cooled detector (FWHM=180 eV) mounted on a mechanical device with an XYZ stage. A 600W portable fuelled gasoline power generator was used during the measurements.

This preliminary study was undertaken using only portable EDXRF spectrometry in order to make the in situ characterization of not previously analysed rock art paintings that will facilitate future sampling decisions to use other analytical methods to obtain additional information about their chemical composition and structure, and the presence of extenders and binders to determine the pigment preparation methods.

EDXRF analyses of black pigments, unusual pigments in the Neolithic rock paintings from eastern Spain, show the presence of manganese minerals and were not considered for radiocarbon dating sampling. Iron oxides are present in all red figures with similar X-ray fluorescence spectra. A singular case is a red deer where the presence of arsenic was detected as trace element only in a part of their surface. This fact can be attributed to the use of two different iron based red pigments and therefore this figure is a good candidate for sampling.

In conclusion, the main chemical elements of the red and black paints were clearly identified in all the samples and this study confirms that portable EDXRF spectrometry can be used for the in situ identification of rock art pigments and can help us to take sampling decisions that minimize the aggressions to the work.

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SOME CONSIDERATIONS ON XRF USE IN MUSEUM MEASUREMENTS – THE CASE OF MEDIEVAL SILVER COINS

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We present two applications using in-situ XRF technique on medieval silver coins from the National Museum of Romania’s History in Bucharest. The ED-XRF measurements were performed with a spectrometer consisting of a 30 mCi ^{241}Am annular gamma source and a Si(Li) vertical detector (200 eV FWHM at 5.9 keV). When the medieval silver coins are surface-corroded, a major disadvantage of ED-XRF is its relatively low information depth. Applied to corroded objects non-destructively, it has to be considered that the results obtained from the surface do not represent the chemical composition of the core, the surface of the coin presenting an enrichment of the noble constituents. A very interesting case was the one of the *brakteaten pfennige* (one side thin foil coins), minted by the medieval German princes and bishops (Xth – XIIth centuries). The National Museum of Romania’s History has some hundreds of such coins in its collections, and a quick sorting of them was necessary. A way of solving this problem was to use in-situ ED-XRF measurements. Very few coins were high fineness silver coins, for which the following composition: Ag=96%, Au=0.75%, Pb=0.65%, Cu=2.05% was determined. However, most of the coins were silvered coins, with either copper or bronze or leaded bronze (Pb=65%, Cu=22%, Sn=12%, Sb=0.4%) core, being covered with a very thin silver layer. This thin silver layer contains a lot of mercury, which remained from the silvering (plating) procedure using Ag-Hg amalgam. A possible explanation for these numerous silvered coins can be the fact that the old German silver mines were probably exhausted during XIth century, only in the XIVth century being discovered new mines in Saxony (e.g. Freiberg and Schneeberg). However, during this period (Xth – XIIth centuries) the construction of the great cathedrals had started, and there was a high need for money; therefore, a strong debasement of these silver coins took place. A more extensive study was performed on the medieval silver coins named *groschen* that circulated during the late Middle Age on the Moldavian territory. The fundamental historical problem that raised this study was the fact that Moldavia is a region where there are no silver mines. One possible hypothesis was that the first monetary emissions of Moldavian Medieval princes were made using foreign coins, which were melted and reused. Many types of silver medieval coins were analyzed: Moldavian, Bohemian, Hungarian, Tatar, Walachian and Polish, all coined between the XIVth and XVth century and the results of different coins groups were compared. The conclusion is the precious metal was most likely obtained by melting foreign silver and copper coins (for some of coins, copper is the main element, reflecting a high debasement). One can find coins with composition similar to the foreign ones, depending on the military alliances and commercial exchanges typical for the respective period (high Ag content for the period when Moldavia was under Poland suzerainty and relatively lower Ag content for the periods of alliance with Hungary).

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APPLICATION OF LOCAL X-RAY-FLUORESCENT ANALYSIS FOR PAINTS ELEMENT COMPOSITION DEFINITION IN PAINTINGS

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There are results received at studying separate products of arts from Art collection of State Tretyakov Gallery (ancient icons and pictures). While studying the masterpieces, the method of local fluorescent analysis with application of Kumakhov's X-Ray polycapillary lens has been used. Results under the analysis of an ancient icon of artist A. Rublyov "Troitsa" ("Trinity") and many artists of Russian avantgarde like Shagal, Udaltsov and others are submitted.

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**NON DESTRUCTIVE SEMIQUANTITATIVE ANALYSIS OF RENAISSANCE
PICTORIAL MULTILAYERS BASED ON EDXRF ANALYSIS AND
REFLECTANCE SPECTROSCOPY**

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The painting technique of Renaissance artists (XV-XVI cent.) is based on laying down different pigment thin superficial layers (so called *velature*). The information of artist's palette can be achieved by stratigraphic analysis, preferably with non destructive techniques. The traditional method of stratigraphic analysis is, in fact, based on optical observation of cross sections and it requires micro-destructive sampling. The possibility of exploiting IBA (Ion Beam Analyses), as PIXE and PIGE, has been recently considered, but *in situ* analyses are not possible.

We propose the association of Energy Dispersive XRF analysis (EDXRF) with visible and near infrared reflectance spectroscopy (vis-NIR RS) which are both achievable by portable instruments. By XRF analysis one detects chemical elements of the pigment layer sequence down to the ground level, while reflectance spectra are characteristic of the most external layer. Inclusion of near infrared component allows in fact extending the analysis down to tens microns of thickness. The identification of pigments in the most external layer by reflectance spectra makes possible that composition of the underlying layers be inferred. The zones to be investigated by our method are selected with infrared reflectography (from 0.8 to 1.1 micron), which in most case allows to extract restored areas from the original ones. At the same time infrared reflectography gives some additional information on painting materials.

Our method was tested on a set of more than 150 paint layers of different composition. We used monolayers of pure pigment or mixed with lead white, monolayers of mixed pigments, multiple layers of pure pigments or mixed with lead white, multiple layers of mixed pigments. The choice of pigments was according to tradition from consulting treatises and essays on painting from 13th century to the beginning of 20th century and looking at the stratigraphic data published by various research institutes in the last 30 years.

The method allows the determination of layer sequence and the average thickness of each layer can be estimated as well.

As example of *in situ* application we cite the examination of "Madonna col bambino e un coro di cherubini" and "Pala di San Zeno" by Andrea Mantegna (1431-1506).

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**SULFUR ANALYSIS ON STONE MONUMENTS
BY A FIELD PORTABLE EDXRF SYSTEM**

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An important part of the world's cultural heritage is represented by stone monuments and a very dangerous weathering process on stone monuments is induced by human activity, by air pollution. One of the worst pollutants for stone monuments is connected to sulfur compounds and in the last word to gypsum. Gypsum is a slightly soluble compound and it can be washed away by rain, leaving the surface of the stone clean but eroded and ready to start the process of corrosion again.

With field portable EDXRF instruments it is possible to conduct in situ investigation, mapping, registration and evaluation of stone degradation phenomena connected to sulfate formation on stone and stone like material by the quantification of sulfur concentration directly connected to the gypsum presence.

The EDXRF instrument used in this work is a commercial system composed by a miniaturized low power air cooled tungsten x ray tube and a SDD Peltier cooled detector.

The EDXRF instrument was calibrated with a series of standard expressly produced for this work ranging from 0.25 % to 15 % of sulfur content. Correlating the counts of the sulfur peak with sulfur concentration it is observed a straight line ($R^2=0,9979$). Several maximum excitation energies have been tried to find the best working point. The silicon escape peaks of the calcium had to be kept in mind for their superimposition with the sulfur peak.

In this memory we are going to discuss the working method established and the results fulfilled on several stone monuments as "La fanciulla di Anzio" an ancient roman statue kept in the Roman National Museum, the tomb of pope Bonifacio VIII by Arnolfo di Cambio kept in the Vatican Basilica, stone decorations from Locus Feronie and a gypsum copy of the "Discobolus" kept in the Gypsum Museum in Rome.

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**THE EQUESTRIAN STATUE OF BARTOLOMEO COLLEONI:
DIAGNOSTIC ANALYSIS BY MEANS OF A PORTABLE EDXRF SYSTEM**

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The equestrian statue of Bartolomeo Colleoni (by Andrea del Verrocchio around 1480), currently under restoration, was systematically analyzed, for diagnostic purposes, with a portable EDXRF (Energy Dispersive X Ray Fluorescence) system in situ.

The statue was analyzed with 63 measurements; three series of measurements for each of the 21 chosen areas, with the aim of characterizing the patina, the superficial enrichments and the alloy.

The areas of measurement have been chosen to include every sub-part of the statue (composed by several sections soldered together), therefore every section has at least one measurement.

Two of the three series of measurements were accomplished on the patinated surface at high and low excitation energy in order to characterize the patina, while the third series of measurements were achieved after a mechanical removal of a small portion of the patina to characterize the bronze alloy with a high excitation energy.

The results regarding the quantitative analysis of the different alloys are presented. A cluster analysis has been performed and the results sort out the different parts of the statue in different homogeneous groups, such as the two legs of the anterior part of the horse, the front part of the body of the horse, the head of the horse, the left posterior leg of the horse, the calf of the rider and a soldering section that all belong to the same group. An example of a second group is the tail, which is very rich in tin and stands on its own. Regarding the measurements at low energy on the patina surface the elements sulfur, chlorine and potassium were analyzed. Water samples of the venetian "canali" were collected to relate the elements found on the patina with the marine aerosol.

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**NON-DESTRUCTIVE INVESTIGATION OF OLD GRAPHICS PAPER
WITH THE USE OF X-ART M ANALYZER**

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Old graphics pieces from the Russian Museum and National Library collections were analyzed with the use of X-Art M spectrometer – modified version of X-Art instrument described in [1]. The main efforts were made to clear up the authorship and the time of creation for these pieces taking into account that standard approaches used previously gave no results.

The typical number of elements analyzed in the paper samples was about 15 varying from P and S up to Pb. Relative element contents determination allows to attribute graphics pieces, and the final goal of this work should be a supplement to the existing data base on the old papers.

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AUTHENTICATION OF POSTAL PIECES BY X RAY FLUORESCENCE ANALYSIS WITH SPATIAL RESOLUTION

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The authentication of philatelic pieces is a complicated task that usually requires several processes, including the inspection and evaluation of experts, the observation with optical microscopes, UV assessments and IR examinations. Everyday, the utilization of more complicated technologies is more and more frequent in order to obtain more accurate results. Raman spectroscopy, electron probe microanalysis and diffraction techniques have been reported. There are very few references of the application of XRF techniques to philately and, certainly, applications of this technique to philately in Argentina are not known.

The utilization of XRF in philately can be very diverse but its basic application consists of qualitative (quantitative if possible) elemental determination of the components of the different inks used, either on stamps, postmarks or postage stamps. One of the most immediate analysis consists of studying the inks of the postmarks. The presence or absence of certain elements that are characteristic of inks (modern inks or inks of some predetermined period) can decide the authenticity or fake of a piece.

In this work we present measurements by X ray fluorescence with spatial resolution of postmark inks of several postal pieces, some of them recognized by experts as authentic ones and others as fake ones. By means of qualitative analysis, different comparisons were performed in order to evaluate the possibilities of this technique for the detection of falsifications.

The measurements were carried out using a conventional spectrometer with sample-positioning stages; microbeams were attained by micro-collimators and also a mono-capillary. The results obtained in this work indicate that XRF with spatial resolution is a suitable technique for the authentication of postal pieces through the identification of the elements that constitute the used inks. XRF represents an excellent complement of other techniques and a significant help to the evaluation performed by experts.

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XRF INVESTIGATION OF PIGMENTS IN WALL PAINTINGS BY PARMIGIANINO

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During the restoration works in the Churches of San Giovanni Evangelista and Santa Maria della Steccata in Parma (Italy), various submillimeter sized cross-section samples from frescoes by Parmigianino (Francesco Mazzola, 1503-1540) have been collected. These samples are a selection of the main chromatic elements of Parmigianino's paintings; the study of cross-sections provides information about the composition of each layer of paint. The characterization of these layers is important both for the knowledge of the work of art and for the development of proper restoration strategies.

X-ray fluorescence spectra recorded from uncoated samples without elaborate preparation provide a reliable non destructive method for the identification of pigments, complementing other techniques such as Raman Spectroscopy.

The XRF experiments were carried out on D15 beamline at LURE, Orsay (France). The setup of the beamline allowed the acquisition of data with spatial resolution of 10 microns, in both X and Y directions. The beamline was well adapted to obtain the elemental maps of the samples. To visualize the elemental density, each element is then plotted separately on a distribution map, using a MATLAB Mapping Function Program, developed by the authors. The technique proved useful to identify the pigments that Parmigianino used in different combinations, mixed together or applied in subsequent layers. Also, the evidence of extensive restoration has been indicated by the presence of more recent pigments.

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X-RAYS TECHNIQUES FOR THE STUDY OF LASER CLEANING OF BRONZE AND COPPER COINS

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The corrosion process of ancient bronze artefacts represents a very serious problem because of their high historical and cultural significances. Owing to the interaction of metal with the environment, thin layers of corrosion products, called patina, grow spontaneously on the object surfaces and they can even create long-term problems for its stability [1-2]. The chemical composition and physical properties of patina are influenced by a wide range of factors, such as environmental (burial, marine, outdoor, indoor, etc), atmospheric (urban, rural, industrial, etc) and meteorological (relative humidity, precipitation, pH value, etc) conditions. Nowadays, lasers [3] are applied for cleaning processes of bronze patinas. A fundamental step of the conservation treatment is the identification of corrosion products. For this aim, the characteristic X-ray fluorescence technique, associated to pulsed laser ablation, constitutes one of the best choices since they allow non-destructive, multi-elemental and fast analyses without any specific sample preparation. In the present work, we estimated the chemical composition of bronze and copper coins, and of the surface patina, laser removed, by Energy Dispersive X-Ray Fluorescence (EDXRF) and X-Ray Diffraction (XRD). In particular, we measured the chlorine and sulphur concentrations [4-5] before and after the laser treatments (UV excimer and IR Nd:Yag lasers). We used a versatile portable EDXRF apparatus, with a W-anode working at 30 kV voltage and 5 μ A current. X-Ray diffraction analysis was performed by a Philips X'PERT automatic diffractometer Bragg-Brentano configuration. Preliminary results confirmed that the laser ablation processes can be used on bronze coins in order to remove corrosion products [5] and to diminish chlorine and sulphur concentrations without damaging the coins matrix

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3D-MICRO-XRF/XANES, MOBILE XRF AND MICRO-PIXE OF PERSIAN TILES OF THE QAJAR PERIOD (2ND HALF OF THE 19TH C.)

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In the frame of a Franco-German interdisciplinary project, Persian tiles from the 19th century of the Qajar period are investigated with the help of different non-destructive analytical methods. The Persian tiles, which are conserved in museums in Berlin, Edinburgh, London, and Paris, are analyzed with respect to the material employed, the manufacturing process, and decoration techniques.

One of the most known Qajar potters and tile makers is Ali Muhammad Isfahani. Being native from Isfahan he was working in Tehran between 1884-5 and 1893-4 AD. His workshop was frequented by Europeans that visited Tehran during the last quarter of the 19th century and brought different tiles to European collections.

A very important source on Ali Muhammads working procedures is a treatise on the process of tile making which was published by Robert Murdoch Smith in Edinburgh in 1888. In addition, Ali Muhammad sent samples of pigments, body materials and glazes used in his workshop. These samples are still preserved and today kept in the Victoria & Albert (V&A) Museum in London.

Due to the ability of Ali Muhammad and other Persian craftsmen to imitate every style requested by a customer, the art historic approach of stylistic analysis is limited. Therefore, scientific investigations have been started including different non-destructive XRF, XANES and PIXE analyses [1,2,3] of the glazes, pigments and bodies of the tiles.

These analyses are aimed as a case study of the working procedures of the potter Ali Muhammad Isfahani because of his importance in this genre and the material available, ranging from written recipes over original workshop materials to the final objects in the collections of the museums.

Results obtained on a series of representative tiles chosen in different European collections are presented. Synchrotron-induced 3D-micro-XRF/XANES is performed on two tiles from the Ethnological Museum, Berlin. Mobile XRF is used at the V&A Museum in London for the investigation of Ali Muhammads body material, glaze and pigment samples as well as of two tiles signed by him. External micro-PIXE is employed on some small tile fragments from Isfahan and Tehran and tiles which are evidently made by other Persian potters of this time selected in French collections.

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**QUANTITATIVE ELEMENTAL ANALYSIS OF DELLA ROBBIA'S GLAZES
WITH A PORTABLE XRF SPECTROMETER
AND ITS COMPARISON TO PIXE METHODS.**

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A portable XRF spectrometer is under development at the Centre de Recherche et de Restauration des Musées de France (C2RMF), in Paris. The instrumentation at its current stage has been successfully used in many occasions to analyse various important works of art. Recently it has been utilised for the analysis of two glaze sculptures located in the cathedral of Sevilla (Spain) and attributed to the Della Robbia's workshop.

Some of the XRF measurements have been carried out in air, other ones in He atmosphere.

The aim of this study is to perform a quantitative analysis only with a new portable XRF spectrometer in order to determine the elemental composition of the glazes. The results will be compared with the ones previously obtained with the PIXE and μ -PIXE technique at the C2RMF on other Della Robbia's works of art located at the Louvre Museum[1].

The data provide a subdivision of sculpture, which is compatible with what is shown from historical documents and artistic considerations.

In the present work we will discuss also on the sensitivity and the accuracy of portable XRF measurements.

The present work is supported by the European project EU-ARTECH (Access, Research and Technology for the conservation of the European Cultural Heritage), contract number RII3-CT-2004-506171.

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**MEASUREMENT OF GOLD LEAF THICKNESS BY ATTENUATION
OR SELF-ATTENUATION OF X-RAYS**Roberto Cesareo¹, Stefano Ridolfi², Marina Donativi³, Stefano Quarta³¹*Dept. of Mathematics & Physics, University of Sassari, Sarrari, Italy*²*Ars Mensurae, Rome, Italy*³*Dept. of Material Science, University of Lecce, Lecce, Italy*

The non-destructive determination of gold leaf thickness and composition in paintings and frescos is important for a better understanding of the provenance of the gold and of the technology of the epoch. Gold leaves are typically present in paintings and frescos of the Italian Renaissance of the 13th and 14th Centuries, as background, haloes or decorations in paintings and frescos. Gold leaves were obtained by hammering coins (for example venetian "zecchini" or florentine "ducati"). Energy dispersive X-Ray Fluorescence (EDXRF) is well suited for analysis of works of art, it has been widely employed for analysis of pigments, and was recently employed also in the determination of gold composition and thickness in the haloes of Giotto's Chapel of the Scrovegni in Padua. It was deduced that the gold of the haloes was of high fineness, and having a thickness of 1.1-2.1 micrometers. This conclusion was obtained by using the altered L-lines of lead, which was employed by Giotto as preparation, in the form of lead white.

Not always in the Renaissance paintings there is below gold a preparation containing a heavy element which L-lines are absorbed by gold in an anomalous manner. In these cases, however, the self attenuation of gold L-lines can be employed in a quite similar manner. This possibility was usefully tested by using standard gold samples.

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**ANALYSIS OF ILLYRIAN TERRACOTTA FIGURINES OF APHRODITE
AND OTHER CERAMIC OBJECTS USING EDXRF SPECTROMETRY**

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The modern scientific techniques and methodologies, developed especially for the study of archaeological objects (archaeometry) can extract important cultural information. For example, the ancient ceramic technology reflects a lot of parameters of a cultural society, such as technological know-how, economy, trade, competition, hierarchy, religious influences and so on.

In this paper we will present the results obtained during the study of some terra-cotta figurines of Aphrodite and related ceramics. The objects were found under water close to the bank of Seferan Lake which is situated about 2 km from the ancient Illyrian settlement of Belsh (central Albania). The discovered objects included about 30 figurines of Aphrodite with different sizes and shapes and 10 ceramic objects, mainly wares. Most of the figurines were covered with a black layer of not uniform thickness. According to the archaeological evaluations the objects belong to IIIrd century BC. No ancient ruins or buildings were found near the lake. It is thought that the site could have been acting as an open sanctuary devoted to Aphrodite where people offered to the deity by throwing figurine votive to the lake.

X-ray fluorescence was used for the determination of the type of raw materials used for the manufacture of the terra-cotta figurines and for the investigation of the objects' provenance. This later objective was based on the comparison of the composition of Seferan objects with the composition of the same period ceramics from the city of Belsh and other areas, such as Durres and Apollonia, which have been the nearest big and developed cities that have had close relations with the ancient center of Belsh. Raw clay samples collected around the lake and also in the areas of Belsh, Durres and Apollonia were included in the comparison. The composition of the black layer that covers some of the figurines was also investigated.

The analytical results obtained from all the samples allow us to conclude that, from the viewpoint of composition, the objects found in Seferan Lake are not similar with the objects from neighboring sites of Durres and Apollonia, which means that they should not be imported. On the other side, the similarities observed with some of the objects from Belsh and two of the raw clays indicate that with much probability these objects should be local products.

The analyses performed on the black cover material showed that this layer was not of organic nature, as was initially suggested, but is made of an iron rich material. It is not clear if the black layer was intentionally prepared during the manufacture of the figurines or was created due to the weathering of the objects under water.

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X-RAY FLUORESCENCE ANALYSIS OF PIGMENTS USED FOR THE PAINTING "SAN FELICE IN TRONO" BY LORENZO LOTTO

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The painting "San Felice in trono" (canvas, 139x57 cm.) was found by Bernard Berenson at the end of 18th century, who attributed it to Lorenzo Lotto [1].

The picture, probably completed in 1542 and unique section of a polyptych, survived a fire of the Cathedral of Giovinazzo (Apulia, Italy) in XVI century. Therefore, it was transferred to Saint Domenico church in Giovinazzo, whereas it was found by Berenson and where it is still located.

Energy Dispersive X-Ray Fluorescence analysis (EDXRF) was carried out in order to study the pigments used by Lotto for this picture. In particular, it was possible to identify the elements that compose the principal pigments (red, green, blue, white and yellow). The analysis was performed with a portable apparatus [2].

Experimental results demonstrate the presence of lead all over the surface of the picture. This may be due to a thin layer of white lead, under the painting, probably used by the artist as preparation.

The red pigments are interesting; there are three types: one basically composed of Hg and S (cinnabar), the second of Pb (minium) and the third of Fe and Hg with trace of S (a mixture of cinnabar and red ochre). The green pigments are composed of Cu (malachite) or Fe (green earth). The blue pigments are mainly constituted of Cu (azurite). The white pigments are only composed of Pb (white lead) and the yellow is composed of Fe (yellow ochre).

Moreover, we proved that it is possible to study the stratigraphy of pigments in presence of cinnabar and white lead. The cinnabar thickness may be approximately evaluated by determining the ratio of the Pb-L α to Pb-L β lines, that are differently absorbed by cinnabar.

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**EXTRACTING INFORMATION OF AN WORK OF ART:
“THE HORSE OF GRENADIER”**

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If an object is considered work of art and a study is required to verify certain properties beyond the range of normal sight, the application of some methods is a tool of utmost importance to evaluate, determine conservation conditions, verify possible restorations and elaborate a general diagnosis of the object.

In this work, total reflection X ray fluorescence (TXRF) and infrared reflectography (IRR) several analytical tools namely, were combined in order to get information of a painting. TXRF is a microanalytical technique very suitable for the analysis of pigments doing the microsample needed to perform the analysis.

IRR is one of the non-destructive testing methods traditionally adopted in the analysis and diagnosis of paintings and is a very effective tool to discover invisible or hidden details in the pictorial layer.

This paper describes the investigation made on an oil painting on canvas “Horse of Grenadier” (Argentina, 1950) from Darwin Temprano. The study revealed an artist’s regret under the pictorial layer confirmed by XRI as well as a possible repainting or restoration procedures detected by TXRF.

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**SUITABILITY OF THE NITON-XLP ANALYZER FOR IN-SITU PXRF
ANALYSIS OF PANEL PAINTINGS**

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Since the 1970's, XRF has been used extensively for the characterization of inorganic components in works of art.

The success of XRF for conservation purposes is due to its wide application field (glass, metals, ceramics, etc) and the fact that it is a non-destructive technique. Several technological advances during the last decade have made it possible to develop user-friendly portable XRF units which can be used for in-situ analysis of work of art. Within the framework of a collaboration between the University of Antwerp, the Royal Museum of fine Arts in Antwerp, and Fondis Electronics, it was possible to evaluate the suitability of this type of equipment for the identification of pigments in polychrome paint layers in panel and easel paintings from the 15th-20th C.

Results from the analysis of paintings of well-known Flemish artists such as J. Van Eyck, P.-P. Rubens, J. Jordaens, J. Ensor and J. Smits will be presented, allowing to objectively document the gradual broadening of the pigment palette of these artists.

Of special interest are the 'new' pigments that 19th C. artists such as Ensor and Smits had at their disposal compared to their predecessors. Next to that, benefits and drawbacks of the PXRF instrument, equipped with a low power X-ray tube and a drift chamber X-ray detector will be discussed through comparison with other methods and literature data.

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XRF APPLIED TO ARCHEOLOGICAL SAMPLES

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The use of XRF and XRD techniques in the study of cultural heritage artefacts has become very popular in the last years due to the ' non destructive ' and ' non invasive ' properties of these analysis and to the possibility of making in situ XRF measurements by portable instrumentation.

In the National Laboratories of Frascati we are studying a considerable group of terra-cotta samples, IV BC., coming from the excavation in Pratica di Mare (ancient Lavinium close to Rome) by the application of XRF and XRD techniques. The aim is to identify the sample's elemental composition (XRF semi-quantitative analysis) as well as the mineral composition (XRD). Combining these two kinds of analysis it is possible to reconstruct the history of the artefact by determining both its provenience and its technical construction.

The instruments used are:

- a Seifert two axis powder diffractometer with copper tube and a scintillator detector and ; a X;ray micro analyser prototype, produced by the Unisantis company, whose main characteristic is the presence of patented Kumakhov's poly capillary optics, with a traditional Si(Pin) detector and X;ray source. The capability of a such optic to focus the X;ray beam on a spot less than 50 microns allows analysis of sample's small areas in a very short time.

The submitted paper will discuss the results up to know obtained.

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XRF APPLICATIONS IN ARCHAEOOMETRY: ANALYSIS OF MARAJOARA PUBIC COVERS AND PIGMENTS FROM SARCOPHAGUS CARTONAGE OF AN EGYPTIAN MUMMY

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This work presents two applications of X-Ray Fluorescence in archaeometry. In the first case was evaluated the composition of decorated pottery pubic covers (tangas) from the Marajoara culture. Ceramics from Marajó Island (located at the mouth of Amazon River, Brazil) represent one of the most beautiful and sophisticated styles of the pre-Columbian art and its decorative techniques show intricate designs of geometrical forms, representing a mythology based on the local fauna. The period of major growth and expansion of Marajoara Culture occurred between the 5th and 14th centuries and its disappearance occurred during the first decades of the European domination as a result of wars and missionization. However, due to the use of ceramics in funerary rituals, their art has survived until the present days. Decorated pottery tangas were used by Marajoara girls, probably as part of puberty rites, and were anatomically adjustable to the body, containing holes on its corners for string attachment. The analyzed samples were two tangas and four fragments from the National Museum collection. One fragment (sample 22245) presented a different design pattern that seemed to indicate a different provenance. EDXRF was performed at the Nuclear Instrumentation Laboratory (COPPE/UFRJ), using a Si(Li) detector from ORTEC with resolution of 180 eV at 5.9 keV and a mini x-ray tube with Mo anode. The angle of the incident x-ray beam was 16° and the detector was placed at 90° to the sample surface. The elements identified in the samples were: K, Ca, Ti, Mn, Fe, Cu, Zn, Ga, Rb, Sr, Y, Zr and Pb. Principal Component Analysis (PCA) was used to evaluate the provenance of the samples, revealing that the samples were separated in three distinct groups.

The second application involved the evaluation of pigments used in decorative paintings from sarcophagus cartonage fragments of an Egyptian mummy, using X-Ray Microfluorescence with Synchrotron Radiation technique. This female mummy (n.158) is considered one of the most important pieces of the National Museum (Rio de Janeiro, Brazil) because of its unconventional embalming with legs and arms swathed separately. This embalming procedure probably was used by a Theban family from the Roman period (1st century BC), whose tomb was recently discovered. The results obtained for the cartonage samples were compared to those obtained for a linen wrapping fragment of which provenance was known. The objective of this work was to characterize the elemental composition of the cartonage pigments and to verify if they were according to those used by Egyptian craftsmen in the Roman period. The measurements were performed at the XRF beamline of the Brazilian Synchrotron Light Laboratory (LNLS), using white beam and a Si(Li) detector with resolution of 165 eV. The elements found in the samples were: Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr, Hg and Pb. The possible pigments were: Egyptian blue, Egyptian green frit, green earth, verdigris, malachite, ochre, realgar, chalk, gypsum, bone white, ivory black and magnetite. Hierarchical Cluster (HCA) and Principal Component Analysis (PCA) were applied to the results.

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SYNTHESIS AND CHARACTERIZATION OF ORGANIC-INORGANIC COMPOSITES : FROM "MAYA BLUE" TO MODERN HYBRIDS

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The main characteristic of organo-mineral hybrids is to exhibit original properties resulting from the combination of those of the mineral host and of its organic guest. Historically, in their search for stable dyes resisting heat and moisture, ancient civilisations elaborated artificial hybrids : pigment lacquers (1st millenium BC), Maya Blue pigment (ca. 800 AD.), ... by respectively fixing or encapsulating the dye molecule on a mineral or in a clay matrix. Nowadays, the same approach is followed in the research on new organo-mineral composites based on microporous materials and with potentials in optics and optotronics. The structure of the ancient composite materials and the nature of the interactions between the molecule host and its matrix are controversial. The complexity of ill-ordered clays or silicates, as observed in many archaeological samples, is a limiting factor for obtaining accurate results. An essential stage is the preparation of synthetic materials in sufficient quantity. We attempt to describe these materials thanks to the elaboration of modern analogous materials, obtained by incorporation of indigo dye in ordered aluminosilicate structure like zeolites (mordenite, clinoptilolite, ZSM-5...). Starting with a "simpler" and reference matrix from a crystallographic point of view, the type of bonding as well as the siting of the organic molecule within the matrix is to be determined. The SEM X-ray microanalysis is performed in order to check the chemical composition of the zeolites. The samples are also analysed by X-ray powder diffraction in order to study possible changes in the crystalline zeolite structure due to the presence of the organic molecule. Stability tests of the composites are carried out by performing acid attacks of different intensities. The results are analysed in terms of pigments decoloration and destructuration of the matrix lattice, revealed by X-ray diffraction. Thanks to such analogues, we will be able to understand some ancient techniques, and thus better describe the long-term preservation or degradation of the colours. This objective is important for the safeguarding and the restoration of our cultural heritage, in particular for the polychrome statuary, the murals and the easel painting.

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**THE SUITABILITY OF XRF ANALYSIS FOR THE CLASSIFICATION OF
ARCHAEOLOGICAL CERAMICS, AS COMPARED TO INAA.**R. Padilla Alvarez¹, P. Van Espen², P. P. Godo Torres³¹*Centro de Aplicaciones Tecnológicas y Desarrollo Nuclear (CEADEN), Habana, Cuba*²*Micro and Trace Analysis Center, University of Antwerp, Belgium*³*Centro de Antropología, Habana, Cuba*

Chemical ‘fingerprinting’ of archaeological ceramics, when properly interpreted in the associated contexts, has proven to be a powerful tool in solving archaeological tasks of different degree of complexity. Instrumental Neutron Activation Analysis (INAA) has been extensively used for ceramic compositional profiling, due to its capability to analyze a large group of the elements, which are of more usefulness for differentiating ceramic fabric. Although INAA requires a minimal invasion of the sample (only around 200 mg are required for the analysis), sometimes it is difficult to collect even such small sub-samples, especially when dealing with extreme valuable artifacts. Other drawbacks of this technique are the time delay required to allow the decay of part of the activated isotopes prior to the analysis, the high costs and availability. For archaeologists or museum curators would be of great usefulness to account for a technique allowing classifying or determining the provenance of a given ceramic object in an express and completely non-destructive way.

This contribution illustrates the capabilities of using a combination of improved sensitivity polarized x-ray fluorescence (EDPXRF) and ²⁴¹Am analysis for the study of archaeological ceramic fabric. The suitability of this XRF approach is illustrated with the study of a group of Cuban aborigine pottery, which was previously analyzed with INAA.

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**IN SITU XRF STUDY OF THE XV C. MURAL PAINTINGS
IN THE TOWN HALL OF GDANSK**

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The X-ray fluorescence technique has been applied in-situ for non-destructive mapping and identification of the pigments used in religious mural paintings of the Little Christopher chamber in the Main Town Hall in Gdansk, Poland. The original frescos dating from the 15th century were retouched and underwent a partial restoration in the late 1960's. The analysis was completed by the Raman spectroscopic measurements on samples extracted from selected locations of the wall painting.

The measurements were carried out by means of the portable XRF spectrometer completed at the IF-FM PASci in Gdansk. The spectrometer is characterized by the X-ray tube excitation operating up to 60 kV and 1 mA current, and the thermoelectrically cooled Si-drift detector of 10 mm² active area. The resolution of 155 eV at 5.9 keV and low detection limit estimated for a few hundreds ppm makes possible to detect the trace elements, too.

From the XRF data the mapping of elements in the painting was obtained. Basing on the elements detected the presence of calcite, red lead, traces of vermilion, azurite and earth pigments was concluded. In order to obtain a reliable identification of the pigment compositions in case of colors such as brown, green and red the accurate micro sampling has been performed for the additional Raman examination. The comparison of results obtained by both the XRF and Raman techniques allowed to determinate the palette of original pigments applied in the 15th and 16th century as well as the contemporary pigment materials used during the restoration.

A further research to characterize the composition of the organic binding media in order to determine the complete restoration guidelines is in progress.

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**XRF AND MICROPIXE STUDY OF CALCITE SAMPLES FROM THE
PALEOLITHIC ROCK ART CAVE
ARCY-SUR-CURE (YONNE, FRANCE, 24000-28000 BP)**

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Conservation of Paleolithic rock art is a real challenge nowadays. Famous examples of rock art are the Altamira, Lascaux, Chauvet and Arcy-sur-Cure paintings. These paintings are conserved under very exceptional conditions in caves. However, they are threatened by numerous alteration phenomena, among them the formation and interaction with calcium carbonate concretions. The cave “Grande Grotte” of Arcy-sur-Cure (Yonne, France) with prehistoric paintings is particularly concerned by this problem. Paintings are recovered by calcite crystals whose growth process is particularly important in an archaeological, geological and biochemical point of view. Indeed, different translucent and opaque calcites can be observed on the cave walls. While opacity is harmful for the paintings which then are completely hidden, transparent crystals should be favoured since they act as a protection for the paint layers. Understanding of this calcite formation, and particularly of the interaction with pigments, requires the exact knowledge of the calcite composition. Therefore, this study focuses on the elemental analysis of calcite at the surface of rock art paintings by X-ray fluorescence analysis (XRF) and micro-Proton Induced X-ray Emission (μ PIXE) within the frame of a large interdisciplinary research project on the alteration phenomena of Arcy-sur-Cure paintings [1]. μ PIXE is a very well-known method to quantify elements on a major, minor and trace level (used at the accelerator AGLAE in the C2RMF) ; nevertheless, in situ measurements in the cave are impossible by this mean. An alternative method for the quantitative determination of the chemical composition of the calcites and pigments is XRF. Different natural calcite samples from the cave, laboratory samples as well as synthetic samples altered in situ in the cave were investigated. A methodology for quantitative analysis of calcite is established on the basis of this set of samples by comparing XRF and μ PIXE results which can be at a later stage used for in situ measurements in the cave.

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μ-PIXE/PIGE ANALYSIS OF EFFECTS OF DIAGENESIS AND CONSOLIDATION TREATMENTS ON TRACE ELEMENTAL DISTRIBUTION IN PALAEO-LITHIC REINDEER ANTLERS

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Bone materials record as biomaterials information about the ways of life in the past in their structure and in their chemical and isotopic composition. Therefore, it is very important, as far as archaeological and physicochemical views are concerned, to have access to these information by chemical analysis and to preserve these materials.

This study presents a scientific approach of the alteration phenomena (diagenesis) and the effects caused by consolidation treatments on the structure and the chemical composition of Palaeolithic reindeer antler. Previous measurements of diagenetic parameters were performed on each sample by FT-IR spectroscopy, X-Ray Diffractometry analysis and with Scanning Electron Microscopy (SEM-EDX) and Transmission Electron Microscopy (TEM-EDX), to estimate their state of conservation [1,2].

The elemental composition of samples was determined by μ-PIXE/PIGE using the external microbeam line at the particule accelerator AGLAE [3]. PIXE/PIGE measurements were performed for archaeological samples on cross sections to determine trace element profiles. Samples were analyzed before and after consolidation to evaluate their state of preservation and possible modifications of the elemental distribution caused by treatment. Point analysis were carried out on a modern reindeer antler to compare its elemental content with the content of an archaeological reindeer antler.

Thanks to μ-PIXE/PIGE analysis, we noticed that the element content of Ca, P and Mg in the treated samples was unchanged whereas Na content has increased and contents of S or F have decreased compared to the untreated ancient reindeer antlers. Then, as far as elemental distribution was concerned, μ-PIXE/PIGE analysis didn't reveal important modifications in shape of profiles of Ca, P, Mg, Ba, S and F. On the other hand, profiles of Mn, Al, Si, Zn and Na were weakly changed ; they show an homogenisation in their distribution across the section.

So, these results indicate that consolidation treatments modify weakly the chemical composition and the distribution of trace elements in reindeer antler sections. Then, we can consider that consolidation doesn't prevent the reading of archaeological information contained in chemical composition of bone materials like reindeer antlers.

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**ACCESS TO THE LOUVRE IBA FACILITY THROUGH
THE EU-ARTECH EUROPEAN PROGRAM**

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Under the name Eu-ARTECH (Access Research and Technology for the conservation of the European Cultural Heritage) a consortium among most internationally distinguished European institutions operating in the field of cultural heritage has been formed. The objective of Eu-ARTECH project is to create a permanent interoperability among the participating infrastructures and establish co-operations with other infrastructures in the field in the perspective of structuring a common European Research Area. The activities of the project are:

- 1) Networking: exchange knowledge, diffuse good practice and common work-parameter among infrastructures
- 2) Access to AGLAE and to a collection of portable instruments (MOLAB)
- 3) Joint Research Activities: JRA1 (new conservative treatment on out door monuments) and JRA2 (development of methods for in-situ non-destructive non-contact analysis)

The Eu-ARTECH project has entered its “access phase” now in which the call for proposals is open. Proposals can be submitted to obtain access to the Accélérateur Grand Louvre d'Analyse Élémentaire (AGLAE) of the C2RMF which is open to Eu-ARTECH users 46 days per year.

This infrastructure is equipped with an external beam line well fitted to in-air analysis of artworks and has a long tradition in this field of research. AGLAE is serviced by a specialised team with a wide experience in operating and optimising ion beams for archaeometric analysis. Proton beams with energies up to 3 MeV can be produced. IBA experiments which are routinely performed are PIXE and PIGE at various currents and with various beam spot diameters from 20 µm up to 500 µm. µ-PIXE elemental mappings are also possible. Furthermore RBS and NRA are extensively used.

Next deadline for proposals in 2006 is the 15th October.

This project is featured by the Sixth Framework Program of the European Commission.

Detailed information can be found on the internet at:

<http://becu.chm.unipg.it/euartech/HOME.htm> or <http://www.c2rmf.fr>

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ANALYSIS OF THE INVASION PROFILE DUE TO DRILLING FLUID MUDCAKE FILTRATION BY X-RAY MICROFLUORESCENCE USING SYNCHROTRON RADIATION

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The purposes of this study were to identify mudcake invasion profile and track solids compounds of the drilling fluid that invaded the core. In this way, make a distinction between carbonates and polymers, given their concentration and penetration at the porous media will provide information about the potential damage (reducing permeability) caused for each component [1]. The success of such treatments is based on the knowledge of the invasion profile and their composition. Therefore, a better characterization of the invasion profile could improve substantially the clean up procedures and the treatment selection. In this paper, the spatial sensitivity of the μ SRXRF technique [2] was used to evaluate and map the invasion profile of drill-in fluid components in a synthetic unconsolidated sandstone sample, similar to an oil field rock from the Campos Basin.

The measurements were performed at the X-Ray Fluorescence Beamline at Brazilian National Synchrotron Light Laboratory (LNLS), in Campinas, São Paulo, using a polychromatic beam with maximum energy of 20 keV for the excitation, orthogonal slits (200 μ m x 200 μ m) and standard geometry (45° + 45°). The spectrum of fluorescence was recorded with a Si(Li) detector with energy resolution from 165 eV to 5.9 keV at the atmospheric air. To determine the invasion profile in unconsolidated sandstone, the core samples were prepared; cut in thin slices and the surfaces polished was positioned in the holder. In this way, pixels of 200 μ m x 200 μ m were obtained and the counting live-time for each pixel was 60 s/step.

This first study was capable to identify the invasion profile for the major components of a water-based drilling fluid and differentiate bridging agents from polymers inside the porous media. These components are responsible for the majority of the damage caused in the reservoir during drilling operations and the knowledge of the invasion depth and concentration for each component can make the clean up process and the secondary treatments more efficient. It was seen that the damage caused by polymers and bridging agents is not the same along with the well extension and are bigger for higher pressures.

The μ -SRXRF technique using a synchrotron light source demonstrated to be an efficient and powerful tool for petroleum industry applications, because it allows to identify and to map the depth of invasion for bridging agents and polymers commonly used in drilling fluids.

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**ANALYSIS OF ROCK-GEOLOGICAL MATERIAL FROM PLACES IN
TANZANIA BY WAVELENGTH DISPERSIVE
X-RAY FLUORESCENCE SPECTROMETER**

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A number of precious stones and minerals are found just on the ground or unexplored inside the earth of the Tanzanian surface. Principally those found at the surface differ in their source of origin. When others are actually coming from the rocks in their present locations (primary deposits), others are transported from other places (secondary deposits). The mechanism of transportation may be rivers, sea or wind. The distribution of these valuable stones is regionally irregular in Tanzania as a country. In some of the regions the deposits are higher compared than others. At the same time, in some of the places the information is completely unavailable and in many cases unexplored. In order to expose this to the decision makers and investors, Wavelength Dispersive X-ray Fluorescence (WDXRF) Analysis have been used with objective of identifying the composition of some of these stone and rock samples. The samples identified and reported in this paper include: Iron ore, Green Aventurine, Amethyst, Red Garnet, Sapphire nuts, Green Opal, Blue Kymete, Black Tormaline, Ethiopian/Sudanese opal, Aquamarine and Granite. The samples were prepared as pellets after mixing with boric acid or fused as discs for analysis. Typical results for the Iron Ore in % are SiO₂(0.97), Al₂O(0.57), Fe₂O(77.5), MnO(0.35), MgO(0.35), CaO(0.16), Na₂O(<0.01), K₂O(0.04), TiO₂(19.1), P₂O₅(<0.01), SO₃(0.14) and that of the Amethyst SiO₂(97.8), Al₂O(0.11), Fe₂O(1.37), MnO(<0.01), MgO(<0.01), CaO(<0.01), Na₂O(<0.01), K₂O(<0.01), SO₃(0.33). The results imply that Tanzania is a very rich country in minerals but are currently unexplored either because of lack of information or investment capital.

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THE USE OF SMALL-SPOT EDXRF FOR THE STUDY OF CORE SEDIMENTS GEOCHEMISTRY

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During last decade, the use of EDXRF instrumentation for the analysis of sediment drilling cores has been successfully applied both for recent environmental pollution and environmental changes recorded in quaternary sediments. Bearing in mind the fastness of sediment deposition in river stream channels and lakes, many of the geochemical changes occur at millimetre or sub-millimetre scale. Therefore, the chemistry changes should be studied at this dimensional scale and the use of small-spot focus equipments seem a good alternative to classical chemical analysis.

In this study we evaluate the accumulation of metals at short scale in sediment cores by means of small-spot (0.6 mm focal beam) X-ray fluorescence analyser. The technique allows us to obtain simultaneous data of the accumulation of different elements existing in sediments or soil in open-air conditions.

We studied two types of cores collected in contrasted sedimentary environments. The first ones were sampled in river stream sediments from a recent abandoned mining area, (Cartagena-La Unión mining district, SE Spain) which was mined several centuries for Pb and Zn recovery. The second sediment cores were obtained from lake sediments (Banyoles Lake, NE, Spain) an area non-affected by strong mining activities impact.

The study of vertical distribution of heavy metals in mining sediments or mine soil profiles can offer sound basis for understanding the mining processes and also the post-depositional migration of metals for environmental studies.

Acknowledgments : This study has been performed in the framework of a project of the Spanish National Research Programme (ref. CGL2004-05963-C04), entitled "Integrated study of water quality in mining abandoned areas: Assessment on the surface and groundwater impacts and possible attenuation measures".

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APPLICATIONS OF A 10 μM SPOT SIZE LABORATORY MICRO-XRF TO ENVIRONMENTAL SCIENCES

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X-ray spectromicroscopy coupling micro-XRF and X-ray microscopy has been developed on synchrotron source more than ten years ago. At the laboratory scale such techniques were more confidential. Due to recent developments in terms of X-ray source and especially in terms of focalization (capillaries, Zone plates...) laboratory micro-XRF equipment have been commercialized in the last 4 or 5 years (Horiba-Jobin Yvon, EDAX, Shimadzu, COX...). Such laboratory instrument are not only limited to material science but they are known to be very efficient in geosciences and environmental science. In these last domains, the main issue is to assess the transfer of pollutant and/or to localise spatially some element(s) of interest. Elements are often present at low concentration and can not be detected by SEM-EDX. Otherwise, the studied samples are generally disordered, heterogeneous, and/or fragile but X-ray spectromicroscopy is a non destructive method and allows measurements on such samples.

In the present work we will present and discuss the advantages and limitations of micro-XRF/microscope (XGT-5000, Horiba-Jobin-Yvon) equipped with of a 10 μm spot size on different environmental applications. The X-ray beam is generated with a Rh X-ray tube at an acceleration voltage of 15 to 50 keV with a current adjustable up to 1 mA. The X-ray beam is focused with an X-ray guide tube, whose inner diameter is 10 μm , producing a finely focused and high-intensity X-ray beam. The latter is calibrated by measuring the absorption of a tungsten wire of 5 μm thickness, scanned through the beam. X-ray emission from the irradiated sample is detected with an Energy-Dispersive X-ray (EDX) spectrometer equipped with a liquid-nitrogen-cooled high-purity Si detector. The resolution of the detector is 145 eV at the Mn $K\alpha$ emission line. Furthermore, a scintillator enables transmission measurements.

Many scientific topics benefit from the application of our micro-XRF. For example, the impact of waste reuse can be assessed by determining the transfer mechanism of metal pollutants. Recent results concerning by-products from steel industry indicate that vanadium is released from the initial matrix. Lab- installed micro XRF helped to identify the mineral bearing phases of V.

First results concerning the composition of marine sediments are very promising. For example, the ultra-high resolution analysis of a partly laminated sediment core from the Arabian Sea reveals element variabilities at the seasonal scale (100 μm scale). This helps to determine the extend and exact timing of individual phase transitions with respect to past climatic and oceanic changes.

Micro-XRF can also be very helpful to identify and classify extra terrestrial material by analyzing e.g. Fe/Ni and Fe/Si ratio. This technique has been successfully applied to meteorites and micrometeorites. Indeed such materials are rare, fragile and very small (down to a few tens of μm in size for micrometeorites). One needs a non destructive technique. Moreover the surface is generally altered and SEM-EDX failed to discriminate samples. Lab-micro-XRF appears as a very interesting routine tool.

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EVALUATION OF DISTRIBUTION AND BIOAVAILABILITY OF Cr, Mn, Fe, Cu, Zn AND Pb IN WATER OF THE UPPER COURSE OF THE LERMA RIVER.

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Distribution and Bioavailability of Cr, Mn, Fe, Cu, Zn and Pb in water of the Upper Course of the Lerma River (UCLR) were evaluated by means a Total Reflection X-Ray Fluorescence Spectrometry. The UCLR, giving rise to the Upper Basin of the Lerma River, is situated in an area known as the Mexican Highlands. This area is an important center for industrial and agricultural activity, with a high population density and enormous demands for water. The overall balance of the aquifer indicates an imbalance between inflow and outflow, since the outflow is greater than the inflow by 5 hm³/yr. The water quality of the Lerma River has been deteriorating over time as a result of the inflow of both urban and industrial wastewater, which has combined with the effect of a decrease in water volume. This reduction in freshwater volume and the deterioration of the water quality has resulted in an important decrease in lake and riparian life in the region. The surface water samples were collected in 8 sites distributed following the stream flow direction of the river. Four sampling campaigns were carried out in each site in a year period. Water samples were collected by means of a "Grab" device in a depth of 30 cm, after that, water samples were transferred in polyethylene flasks, and they were immediately transported to the laboratory at $\pm 4^{\circ}\text{C}$. The water samples were analysed in triplicate, using an TXRF Spectrometer "TX-2000 Ital Structures" with Si (Li) detector and a resolution of 140 eV (FWHM) at Mn K-alpha. Mo tube (40 kV-30mA) with a 17.4 keV excitation energy was used for a counting time of 500 seconds. Results show that the concentration range of heavy metals in water are the following: Cr, from <5 to 56 $\mu\text{g/L}$; Mn, from 9 to 788 $\mu\text{g/L}$; Fe, from 98 to 8474 $\mu\text{g/L}$; Cu, from 10 to 225 $\mu\text{g/L}$; Zn, from 23 to 189 $\mu\text{g/L}$ and Pb, from <3 to 30 $\mu\text{g/L}$. There are statistical differences in the concentration of heavy metals between the different sampling sites and between different sampling campaigns, it means that sampling zones 1 and 8 are different to others one and there are differences between dry and wet seasons. The Pearson correlation results indicate strong correlation between some heavy metals in the water, this significant correlation ($p < 0.05$) indicate a natural origin or/and a shared contamination source for these metals. Some heavy metals in the water exceed in some sites the Mexican recommended limit for living aquatic resource protection and irrigation water, representing a risk for living organisms around the Lerma River.

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TEMPORAL AND SPATIAL ABUNDANCE OF PARTICLES IN SUSPENDED MATTER OF WATER FROM LERMA RIVER IN MEXICO.

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Elemental composition, morphology and abundance relative of particles has been evaluated in suspended matter of the Upper Course of Lerma River, by means of Scanning Electron Microscopy coupled to Energy Dispersive X-Ray Spectrometer (EDS) in a hydrological cycle. The water samples were collected in 8 sites distributed following the stream flow direction of the river. Four sampling campaigns were carried out in each site in a year period. Water samples were centrifuged by 30 minutes at 5000 rpm and suspended matter was collected on Millipore filters of 0.45 micrometers. 100 particles distributed in 1 cm² of each sample site and sampling campaign were analysed using an EDS "EDAX" coupled to high vacuum scanning electron microscopy "Philips XL30". In general, in all sites and in all sampling campaigns, the aluminosilicate group, iron group and silica group are predominant over the other groups. However, in the site number one, always the predominant group is the sulfur with a particle abundance of 43 %. In wet season, the iron group presents the highest abundance, probably due to natural contributions. The presence of typical anthropogenic elements Cr, Ni, Cu, Zn, Sn, Pb, W and Hg in the intermediate sites and in all sampling campaigns is result from industrial and urban activities. In general, the particle groups decrease in the next sequence: aluminosilicate > silica > iron > sulphur > metals > calcium > manganese > carbonate. The genetic particle types that describe the compositions of the Lerma suspended matter are: authigenic, terrigenous, diagenetic, biogenous, and anthropogenic. The analysis of suspended matter by EDS coupled to scanning electron microscopy is useful in the evaluation of origin and heavy metals transport in surface body waters.

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XRS METHOD AND DEVICE FOR FAST DETERMINATION OF METALS IN USED TIMBER

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An analytical device based on XRS has been developed to perform fast determination of metals and chlorine in used timber. The device consists of two radioactive sources to cover a broad energetic spectrum:

A 109Cd source (ca. 100 mCi) emitting 3 Gamma lines in the range of 21 – 25 keV and a 55Fe source (ca. 250 mCi) with a Gamma line at 5,899 keV.

The X-ray fluorescence photons are accumulated by a Peltier-cooled Si-PIN-Diode, and the obtained spectra are evaluated by an appropriate software (Picotax) using an appropriate spectra deconvolution (Super Bayes).

The following detection limits have been achieved for the elements critical in used timber:.

Element	Threshold value by German regulations mg/kg	Detection limit mg/kg
Arsenic (As)	2	2
Lead (Pb)	30	30
Chromium (Cr)	30	20
Copper (Cu)	20	10
Mercury (Hg)	0,4	2
Chlorine (Cl)	600	350

If desired, more elements are detectable.

Method and Device have been verified with several synthetical and real timber samples and the results are compared with conventional laboratory analysis (AAS, ICP).

It has been shown that the described approach is an useful tool for first on-site analysis and classification of used timber on disposals and deposits.

Of course, the method is also suitable for other environmental materials like soil samples, electronic waste etc.

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**ANALYSIS FOR CLEANING AND PROTECTION FROM VANDALS'
SMEAR ON STONE-LIKE MATERIALS AVALING OF A SPECIFICALLY
ASSEMBLED PORTABLE EDXRF SYSTEM**

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The vandals' smearing on the stone-like materials, the so called "graffiti", is particular form of pollution that has become very heavy because nowadays it is usually used to mark the territory of different groups of "communities" respectless for the artistic and cultural value of the marked object. The media that the vandals use to mark the objects can be of different kinds: ink, ink pads, pens, sprays and so on. It is understood that for any pair of substratum/smearing element there will be an optimal solution for cleaning and subsequent protection. It is therefore important, before the cleaning and protection operation, to characterize the surfaces and pigments to clean, so that to choose the best solvent and removing procedure. This characterization can be made directly in situ in a non destructive way or in laboratory by extraction of a sample to study. It is clear that the study of the materials in an "in situ" way would surely improve the work as far as cost and time are concerned.

An X Ray Fluorescence system has been set up to analyze smearing pigments and substratum to have a quick response directly in situ with a low cost of operation.

In this work we are going to present the specifically assembled EDXRF portable system with his set up case and software. Results of several in situ campaigns are shown.

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ELEMENTAL CONTENT OF PM_{2.5} AEROSOL PARTICLES AT DIFFERENT LOCATIONS IN AND AROUND GÖTEBORG DURING FEBRUARY 2005

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In February 2005 a large air pollution measurement campaign was conducted in Göteborg, Sweden. The Göte – 2005 campaign was managed by the Atmospheric Science group at the Chemistry department, Göteborg University. Its main focus was to study the influence of winter inversions on the air pollution situation in Göteborg. Several measurement sites both urban and rural in and around Göteborg were used. As part of that campaign the elemental content of PM_{2.5} aerosol particles was studied.

Particles were collected on Teflon filters using plastic cyclones with a collection cut off diameter of 2.5 micrometer. Samples were changed at noon every day on a regular basis. The main sampling sites were on the roof of Femman, a commercial complex located in the centre of Göteborg and the Chalmers campus area situated 2 km south of the city centre. Samples were also collected at roof level on the high Lipstick building in the city centre and at the rural site Råö, 35 km south of Göteborg.

The obtained samples were analyzed for trace elements by Energy Dispersive X-Ray Fluorescence (EDXRF), based on three-axial geometry with a Mo secondary target. The spectrometer was operated at 55 kV and 25 mA and the samples were analyzed using a livetime of 1000 seconds.

The concentrations of S, Cl, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, Br, and Pb were evaluated. The results showed that S, Cl, K, Ca and Fe dominated in the sampled atmospheric aerosols, with average concentrations of 1300, 600, 150, 50 and 100 ng/m³ respectively. The average concentrations for the whole measurement period were very similar at the main urban sites, but the concentrations of different elements were highly variable on a daily basis mainly due to different weather conditions. Both the high urban site and the rural site showed lower concentrations of most elements, compared to the urban sites. Especially Zn had a different variation pattern at the high Lipstick site compared to the Femman and Campus sites. One inversion period was identified during the measurement campaign. Although the particle samples are collected during a 24 hour period giving an average of concentrations over the whole day, the inversion period can be seen in higher concentrations of most elements, with the exception of S, Zn and Br indicating differences in sources for the elements.

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**SINGLE-PARTICLE CHARACTERIZATION OF NIST SRM 70A
(POTASSIUM FELDSPAR), USING LOW-Z PARTICLE EPMA**

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A single particle analytical technique, named low-Z particle electron probe X-ray microanalysis (low-Z particle EPMA), employing an energy-dispersive X-ray detector with an ultra-thin window, has been proven to be useful in atmospheric aerosol research since the low-Z particle EPMA allows the quantitative determination of concentrations of low-Z elements such as C, N, and O, as well as higher-Z elements that can be analyzed by conventional energy-dispersive EPMA and many environmentally important particles contain low-Z elements in the form of nitrates, sulfates, oxides, or mixtures including a carbon matrix. Eventually, the low-Z particle EPMA technique can provide size-segregated relative abundances of chemical species observed in aerosol samples, which is valuable for the characterization of atmospheric environmental aerosol samples. However, information on size-segregated mass fractions of chemical species using a single particle analysis could be useful considering that most aerosol analyses are done by the use of bulk analyses that provide data for mass fractions of chemical elements, ions, and/or organic species. By obtaining mass fractions of chemical species from the low-Z particle EPMA analysis, bulk and single particle analyses will provide complementary information on chemical compositions of aerosol samples. In this context, we analyzed a certified reference material of potassium feldspar (NIST-SRM 70a). The measurements were carried out on a Hitachi S-3500N LV-SEM equipped with an Oxford Link SATW ultra-thin window EDX detector in Korea Basic Science Institute Chuncheon Center. Since we know the chemical compositions of individual particles, the densities of the individual particles can be estimated and thus with the combination of information on chemical compositions, densities, and sizes of individual particles, mass fractions of chemical species observed in the CRM sample can be obtained. Weight concentrations of chemical species obtained from a single particle analysis of 500 particles of the CRM sample were found not to be much different from those certified values, in spite of totally different approaches employed between the single particle and bulk analytical techniques. It is necessary to identify the uncertainty involved in the low-Z particle EPMA analysis.

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**SINGLE-PARTICLE CHARACTERIZATION OF SEASONAL AEROSOL
SAMPLES COLLECTED AT A SUBWAY STATION PLATFORM
IN SEOUL, KOREA**

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In general, people spend their time inside more than outside, so that bad indoor air quality can provide an adverse effect on human health. Among various indoor environments, the subway station has unique characteristics, i.e. it is a very much closed space with various sources of aerosols, e.g. due to running-trains, moving-passengers, and shopping activities at nearby underground stores. And thus the aerosol particles might be accumulated in this somewhat closed environment, resulting in the high concentration of particulate matters in the air. A single particle analytical technique, named low-Z particle electron probe X-ray microanalysis (low-Z particle EPMA), employing an ultra-thin window X-ray detector and enabling the quantitative determination of even low-Z elements such as C, N, and O, was applied to characterize samples collected in four different seasons at a subway station in Seoul, Korea. The measurements were carried out on a Hitachi S-3500N LV-SEM equipped with an Oxford Link SATW ultra-thin window EDX detector in Korea Basic Science Institute Chuncheon Center. According to their chemical composition, many distinctive particle types were identified, i.e., for all the samples collected at the subway station platform, the major chemical species are observed to be carbon-rich, organic, aluminosilicates(AlSi), AlSi/C, CaCO₃, SiO₂, and Fe₂O₃. Fe-containing particles that come from the wearing of brake block, subway train wheel, and electric contact materials are the most abundantly encountered both in coarse and fine fractions: the relative abundances of the Fe-containing particles are in the range of about 50 % ~ 70 %. The Fe-containing particles are observed as various types of Fe₂O₃, Fe₂O₃/C, (Si, Fe)Ox, (Si, Fe)Ox/C, and etc. The other abundantly encountered particles are carbonaceous particles (either carbon-rich or organic) and those originated from soil such as aluminosilicates, AlSi/C, CaCO₃, SiO₂. Some of those particles are believed to come from outdoor air. By the application of the low-Z particle EPMA, it is demonstrated that the single particle analytical technique can provide detailed information on various types of chemical species in the indoor samples and there exist no significant seasonal variations in chemical compositions of the samples.

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**SINGLE PARTICLE CHARACTERIZATION OF AEROSOL SAMPLES
COLLECTED DURING AN "ASIAN DUST" STORM EVENT IN 2004, USING
LOW-Z PARTICLE ELECTRON PROBE X-RAY MICROANALYSIS**

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Nearly every spring, usually from March to May, "Asian Dust" originating mostly in Central China's arid areas is transported into Eastern China, over the Yellow Sea to Korea. During the Asian Dust's long-distance travels, it can react with diverse chemical species and/or provide a reaction site for chemicals in the air. For example, it would react with chemical species such as SO_x and NO_x so that the transport of modified Asian Dust to the East Asian region could result in the deposition of sulfate and nitrate, in addition to mineral dust, in this area. Hence, increasing attention has been devoted to the study on the modification of physicochemical properties of Asian Dust particles during long-range transport. A single particle analysis, named low-Z particle electron probe X-ray microanalysis (low-Z particle EPMA), was applied for the characterization of aerosol samples collected in Chuncheon, Korea, during an Asian Dust storm event that occurred on 10-12 March, 2004. Four different samples were analyzed, i.e., those collected just before the Asian Dust storm event, at the peak of the storm event, at the late stage of the event, and at the end of the event. The measurements were carried out on a Hitachi S-3500N LV-SEM equipped with an Oxford Link SATW ultra-thin window EDX detector in Korea Basic Science Institute Chuncheon Center. All the four samples are found to have experienced chemical modifications during long-range transport because the samples contain a significant number of particles composed of chemical species, such as nitrate and sulfate, which resulted from atmospheric reactions of CaCO₃ and sea-salt particles. This finding implies that CaCO₃ and sea-salts particles reacted with sulfur and nitrogen oxide species during long-range transport. The sample collected on March 10 just before the storm event experienced the most extensive chemical modification during its transport. For this sample, the overall relative abundances of reacted CaCO₃ and reacted sea-salt particles are 9.8 % and 44.2 %, respectively. By the application of the low-Z particle EPMA, it is demonstrated that the single particle analytical technique can provide detailed information on various types of chemical species in the samples. Further, it is observed that chemical compositions of the four samples are significantly different, which could provide a clue to how Asian Dust particles can interact with local air pollutants.

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SUSPENDED PARTICLES IN A WATER SUPPLY RESERVOIR: A CASE STUDY OF THE PASSAUNA RESERVOIR AT CURITIBA, SOUTHERN BRAZIL

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Suspended particles, as well as the dissolved substances, play an important ecological and quality role in water by attenuating light, providing reactive surfaces, influencing metabolic activity, and contributing to the net sediment deposition. The composition of suspended particles is based on saturated mineral phases in water columns, sediment re-suspended from bottom deposits, and the input from human activities. The water quality, particularly in reservoirs, is crucial and it is naturally maintained by flushing and sedimentation that remove phosphorus from the water. For instance, in eutrophic reservoirs, these removal processes are countered by recycling of ions and metals from the sediments, which can maintain the eutrophic state. However, if the level of phosphorus loading exceeds the threshold, the eutrophication of the reservoir will become more severe and the water quality will deteriorate substantially. Under such conditions it has been reported that the concentrations of bloom-forming cyanobacteria increase three-to-five-fold. If this is the case, the water reservoir management will become significantly more costly and difficult. Trace and microanalysis techniques can be useful in the context of both acute environmental disasters and long term release of pollutants, as a means of tracing pollution sources by means of a chemical fingerprint of such heterogeneous materials, e.g. suspended particles. The magnitude and patterns of the suspended particles were assessed in one of the Curitiba reservoirs, the capital of the Paraná State, in the South-Eastern part of Brazil. The watercourses that cross the Curitiba metropolitan area are heavily polluted and feed into the Passauna reservoir, one of the three main intakes with a capacity of 1.7 m³/s of water. Data on the chemical composition of suspended particles in the Passauna reservoir are scarce or nonexistent, even though it is important from a health point of view. The objective of this work was to determine the nature of the anthropogenic and crustal particles in the Passauna reservoir. The samples were investigated using both energy-dispersive X-ray fluorescence (EDXRF) and automated electron probe X-ray microanalysis (EPXMA). A recently improved data reduction method was combined with the X-ray analyses and used to determine the chemical and morphological characteristics of individual micrometric-sized suspended particles. Special attention was paid to the phytoplankton community composition, in particular diatoms, due to its controversial ability to remove phosphorus from the water column. The elements could be classified into two main groups on the basis of the variability of the elemental concentrations and the source of origin. In the first instance they originated mainly from crustal re-suspension, and secondly they were related to anthropogenic sources. The chemistry of different groups of suspended particles could be elucidated by the application of EPXMA with subsequent cluster analysis of the results. Results obtained showed that the particles may be divided into three groups, namely those of: (1) mineral, (2) organic, and (3) mixed origin. The contribution of these groups to the total composition of suspended particles was evaluated. According to abundances of the particle groups, two categories of particles in the reservoir have been distinguished and the chemical differences will be discussed.

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CALIBRATION OF AN ENERGY DISPERSIVE X-RAY FLUORESCENCE FACILITY FOR THE ANALYSIS OF ENVIRONMENTAL SAMPLES

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Aim of this work is the calibration of an Energy Dispersive X-Ray Fluorescence facility for the analysis of solid environmental samples such as soil, ashes produced in coal-fired power plants and sediments. The main components of the facility are: a 50 W (4-50 kV, 0-1 mA) OXFORD X-ray tube with Mo target and a CANBERRA Super-SiLi x-ray detector with 160 eV resolution @ 5.9 keV. For the x-ray spectra collection an AMPTEK pocket MCA connected to a PC is used. The x-ray spectra are analyzed with the in-house developed computer code SPUNAL. For the sample preparation a 20 t hydraulic press is used to compress the materials under analysis mixed with a binder additive, inside 40 mm diameter aluminum cups. A thorough investigation has been performed for the determination of the best source-target-detector geometry and the ultimate irradiation conditions - in terms of high voltage, current and filtering - for the detection of the various elements of interest. For the efficiency calibration of the facility several Certified Reference materials were used from NIST (Montana soil nr. 2710, 2711, San Joaquin soil nr. 2709, Coal fly ash 1633b) and from IAEA (Soil nr. 7, Lake sediment nr.1). For each different type of material a response factor (ppm/cps) was determined for each element that was detected. Repeatability and reproducibility experiments were conducted for each Reference material. The calibration allowed for the quantitative determination of the following elements: Ca, Ti, V, Mn, Fe, Cu, Zn, Pb, Rb, Sr, Ba, Cs. Furthermore, Arsenic may be indirectly determined taking into consideration the interference of its $K\alpha$ x-rays with the $L\alpha$ x-rays of Pb. For most elements the detection limit is about 100 ppm.

The facility is used for the determination of the elemental concentration of soil and sediment samples from industrial areas of the Attica district, as well as ash samples from lignite and biomass fired power plants.

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CADMIUM AND CHROMIUM (VI) DETERMINATION BY SMALL-SPOT EDXRF AFTER MEMBRANE CONCENTRATIONClàudia Fontàs¹, Eva Marguí¹, Manuela Hidalgo¹ and Ignacio Queralt²¹*Department of Chemistry, University of Girona. Campus de Montilivi, 17071 Girona, Spain*²*Laboratory of X-ray Analytical Applications, Institute of Earth Sciences "J. Almera". Solé Sabarís s/n, 08028 Barcelona, Spain*

Cadmium and chromium are recognised as toxic elements that can produce many health problems. Therefore they appear in all the Environmental Agencies regulations related to water, soil and biota. The concern for a clean environment has prompted the development of sensitive methodologies for their control and monitoring in the environment surveillance. Whilst the cadmium adverse effect seems to be related to their concentration, chromium hazard is related to its chemical form. Hexavalent chromium compounds are considered 100 to 1000 times more toxic than the most common trivalent ones.

From the experimental X-ray fluorescence techniques two different main problems are related with the determination of Cd and Cr. Cr (VI) need to be carefully isolated from Cr (III) prior to the XRF analysis. On the other hand, Cadmium levels are near the limit of detection for the main XRF instruments. Additionally, for conventional WDXRF systems, based on Rhodium-target tube, the Cd K-lines are situated in the region were the Rh K-lines and Compton appear. The use of tungsten EDXRF systems imply that the Cd K-lines appear in the region where the elemental sensitivity is growing down. Therefore, a selective pre-concentration methodology for both elements seems to be a solution for their precise determination.

For this purpose, we investigated the use of membranes activated with the commercial anionic exchanger Aliquat 336 (a quaternary ammonium salt) for collecting both Cr(VI) and Cd(II) species. Different types of membranes have been investigated, such as the so-called impregnated membranes, where a solution of the extractant dissolved in decaline fills the pores of a polymeric support, and the polymer inclusion membranes, prepared by physical inclusion of Aliquat 336 in a polymeric matrix made of cellulose triacetate or poly(vinyl chloride). The extraction efficiency of the membranes was evaluated analyzing the depleted feed by ICP-AES, and it was shown that short times of contact are needed to achieve high extraction efficiency. Moreover, the analyses of the membranes by EDXRF were done in order to check not only the content of cadmium or chromium but also the homogeneity of the metal distribution along the membrane surface. In the case of Cr(VI), it was shown that polymeric inclusion membranes made of PVC gave better results in terms of homogeneity, and that a good linear relationship between metal content in aqueous phase and fluorescence signal was obtained, indicating the feasibility of using activated membranes for preconcentration purposes.

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**ANALYSIS OF ILLYRIAN TERRACOTTA FIGURINES OF APHRODITE
AND OTHER CERAMIC OBJECTS USING EDXRF SPECTROMETRY**

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The modern scientific techniques and methodologies, developed especially for the study of archaeological objects (archaeometry) can extract important cultural information. For example, the ancient ceramic technology reflects a lot of parameters of a cultural society, such as technological know-how, economy, trade, competition, hierarchy, religious influences and so on.

In this paper we will present the results obtained during the study of some terra-cotta figurines of Aphrodite and related ceramics. The objects were found under water close to the bank of Seferan Lake which is situated about 2 km from the ancient Illyrian settlement of Belsh (central Albania). The discovered objects included about 30 figurines of Aphrodite with different sizes and shapes and 10 ceramic objects, mainly wares. Most of the figurines were covered with a black layer of not uniform thickness. According to the archaeological evaluations the objects belong to IIIrd century BC. No ancient ruins or buildings were found near the lake. It is thought that the site could have been acting as an open sanctuary devoted to Aphrodite where people offered to the deity by throwing figurine votive to the lake.

X-ray fluorescence was used for the determination of the type of raw materials used for the manufacture of the terra-cotta figurines and for the investigation of the objects' provenance. This later objective was based on the comparison of the composition of Seferan objects with the composition of the same period ceramics from the city of Belsh and other areas, such as Durres and Apollonia, which have been the nearest big and developed cities that have had close relations with the ancient center of Belsh. Raw clay samples collected around the lake and also in the areas of Belsh, Durres and Apollonia were included in the comparison. The composition of the black layer that covers some of the figurines was also investigated.

The analytical results obtained from all the samples allow us to conclude that, from the viewpoint of composition, the objects found in Seferan Lake are not similar with the objects from neighboring sites of Durres and Apollonia, which means that they should not be imported. On the other side, the similarities observed with some of the objects from Belsh and two of the raw clays indicate that with much probability these objects should be local products.

The analyses performed on the black cover material showed that this layer was not of organic nature, as was initially suggested, but is made of an iron rich material. It is not clear if the black layer was intentionally prepared during the manufacture of the figurines or was created due to the weathering of the objects under water.

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**ELEMENTAL COMPOSITION OF VEGETABLES IN THE DAR ES SALAAM
MARKET USING WAVELENGTH DISPERSIVE X-RAY
FLUORESCENCE ANALYSIS**

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Several elements and their concentrations were found in vegetables collected from different areas of Dar es Salaam City. The samples were analyzed with Wavelength Dispersive X-ray Fluorescence Spectrometer. 1 gram of fine dried and grinded vegetables were prepared as pellets for analysis for Species of *Vigna Unguiculata* (Kunde), *Amarathus* (African Spinach), *Cucuta maxima* (Pumkin), *Brassica Chinese* (Spinach). The WDXRF SRS 300 operate at 20 kV, 5 mA and 60 kV, 50 mA for the two anodes respectively. In all the sample cases Carbon and Oxygen were found to dominate with high concentrations between 32% and 47%. This paper presents result of elemental concentrations originating mainly from the samples which form an important main meal of the Dar es Salaam residence.

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COMPARISON OF FOUR DIFFERENT FILTER MATERIALS FOR AEROSOL ANALYSIS WITH XRF

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Since several decades, the analysis of aerosol loaded filter has been an important task for XRF and particularly of EDXRF. The choice of the right collection substrate is very important. Still it appears that no overall and systematic comparison has been published on the suitability of different filter materials for XRF. Several aspects such as “filter penetration effect”, pore size, substrate chemical composition, the distribution of the particles on the filter surface should be taken into account. Therefore it is advisable to estimate the quality of the filter materials applicable for XRF analysis. Four filter materials differing in surfaces, internal structure and composition were investigated: Nuclepore, cellulose nitrate, quartz and Teflon® (PTFE). Parallel indoor aerosol samples were collected on the investigated filter materials in the same place. Thickness of layer and penetration effect were estimated during the investigation [1, 2]. For XRF measurement the EDXRF spectrometer Epsilon 5 from PANalytical (Almelo, The Netherlands) was used. The spectrometry has a powerful X-ray tube, 3D polarizing geometry, up to 15 secondary targets and a high-resolution HPGe-detector. The visual examination of the filter substrate surfaces was performed on a Scanning Electron Microscopy coupled with Energy Dispersive X-ray detector (SEM/EDX); type JEOL JSM 6300. A Si(Li) X-ray detector coupled to a PGT (Princeton Gamma Tech, Princeton, NJ, USA) system was employed for acquiring the X-ray spectra. The typical energy of electron bombarding was 20 keV and a beam current of 1 nA was used. From the preliminary results it was found that the deposition on Nuclepore and cellulose nitrate filters give the most homogenous particle distribution over the surface.

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[2] Ron Jenkins, R.W.Gould, D. Gedcke, Quantitative X-ray Spectrometry, Marcel Dekker, Inc., New York-Basel-Hong Kong, 1995, p.484.

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**CONCENTRATION OF SOME ELEMENTS IN THE ADRIATIC COASTAL
SEA SEDIMENTS: CASE STUDY THE KVARNER BAY**Vladivoj Valkovic¹, Jasmina Obhodas², Mladen Crnjar²¹*A.C.T., d.o.o., Prilesje 4, 10000 Zagreb, Croatia*²*Ruder Boskovic Institute, Bijenicka c. 54, 10000 Zagreb, Croatia*³*County Institute for Sustainable Development and Town and Country Plannin
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Maritime transport of goods and people, including nautical tourism, is the most intensively growing activity in the Kvarner bay (Northern Adriatic) consuming considerable amounts of its marine resources. Heavy metals, which are present in the antifouling paints used by cargo, passenger and pleasure boats, strongly impact marine environment diversity, health and vitality of its ecosystem and its productive capacity. The purpose of the study was to systematically investigate the distribution of major and trace elements along the Kvarner bay coast and islands, especially in the most exposed regions, such as marinas, shipyards, small harbours in the villages, ports and other places where ship repairs and paintings are performed.

The elemental concentrations of some 20 elements in the sediment samples were investigated by the use of energy dispersive X-ray fluorescence spectrometry (EDXRF). Contour maps for concentrations of individual chemical elements in the surface layer of sediments were produced indicating the level of sediment contamination from locations of potential pollution sources. Results showed that contents of the toxic elements Zn, Cu, As and Pb in sediments close to the areas closed to marinas or shipyard services were found to be several orders of magnitude greater than background values. The protection and remediation measures could be proposed based on these results. The treatment of waste waters in service areas of marinas and shipyards is one of such measures considered.

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GEOCHEMICAL MAPPING OF CROATIAN SOILS OBTAINED BY GPS-GIS SUPPORTED XRS METHODSJasmina Obhodas¹, Darko Tibljas², Vladivoj Valkovic¹*1Ruder Boskovic Institute, Bijenicka c. 54, 10000 Zagreb, Croatia**2Department of Geology, Faculty of Science, University of Zagreb, Horvatovac bb
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The present study was undertaken as a screening survey on geochemical properties of soils in Croatia. The aims of the study were to determine average concentrations of some minor and major elements in different types of soils in Croatia, to find out their large-scale variability and to determine how their mineral and elemental composition was associated with environmental parameters, such as location (latitude, longitude), rainfall, soil type, land use, rockiness, stoniness, slope, natural drainage, erosion and soil moisture. The survey was conducted as a part of the DIAMINE project (IST-2000-25237) oriented towards investigation of neutron backscattering method as a demining technique. Namely, the geochemical properties of soils are one of the parameters that might influence the field application of the method. Since the information on soil properties is needed in many fields of human activities, the obtained data can be widely used, especially in the advanced environmental system modelling such as climatological, hydrological or soil-water-vegetation-air transfer modelling.

Ninety soil samples were collected in different localities across Croatia. Their mineral and elemental composition was investigated by X-ray powder diffraction (XRD) and by energy dispersive X-ray fluorescence (EDXRF), respectively.

GIS-GPS approach was used to construct regional geochemical maps and to compare obtained maps with geographical, geological and land-use data-basis. Data were subjected to multivariate statistic analysis in order to obtain factors that control variability of minor and major elements.

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EDXRF MONITORING OF ELEMENT TRANSPORT IN COLUMN EXPERIMENTS

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Columns have been designed to monitor the kinetics of heavy metals transport in running experiments. The material for investigation is filled into polyethylene pipes of 80 µm wall thickness, thin enough for emission of x-ray fluorescence of elements heavier than potassium. The columns are connected to an automatic valve to adjust the water table at 10 cm from the bottom of the column. Six columns are mounted on a rotating holder and can be brought within defined time intervals ranging from daily at beginning to monthly basis in the later stage of the experiment into the measuring position.

Measurements are performed with the geoscanner, based on a Mo-long fine focus XRD tube, boosted by a glass slit capillary. The signal is monitored by a peltier element cooled drift chamber detector. Standard operation occurs at 45 kV, 30 mA in 0,25 to 1mm steps and 10 to 30 sec signal acquisition time. The data are processed and results are presented in x-y-graphs. In the water saturated zone of the columns primary minerals are getting dissolved. The solution migrates by capillary transport and reacts on the way up to the top of the column where secondary phases precipitate. Both, transported solution and precipitation provide detectable signals good enough to document the solution and capillary driven element migration in the column.

Element - position - time plots show the chemical changes at on measuring point over the investigated time interval highlighting the difference in behaviour of individual elements such as S, K, Ca, Fe, Cu, Zn, As, Pb, Sr, and others.

The obtained information is highly valuable to understand processes taking place within waste rock dumps responsible for the formation of hardpans and acid mine drainage, and to estimate the kinetics of such processes.

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NON-DESTRUCTIVE X-RAY AND NEUTRON TECHNIQUES FOR ASSESSING ENVIRONMENTAL IMPACT OF URANIUM AT THE PREMISES OF REMEDIATED HUNGARIAN URANIUM MINE

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Uranium ore mining and milling have been terminated in the Mecsek Mountains (southwest Hungary) in 1997. Restoration of most of heap-leaching areas, tailing ponds has been accomplished. The resources of drinking water of the city of Pécs lie in the vicinity area of the remediated Hungarian uranium ore mine, therefore the continuous U monitoring of the water effluents and creeks is important both from the point of view of the chemical cleaning technology and public health. Mine tailings and waste rock piles are the main environmental contamination sources of the territory of the mine. Therefore the chemical state of uranium and other heavy metals is important for assessment of the environmental impact.

In this work, a simple and reliable method for U analysis of contaminated water based on total reflection x-ray fluorescence (TXRF) is presented. The possible leaching of uranium depends on its chemical state and distribution in the tailings sludge. Micro-X-ray absorption near edge structure (μ -XANES) was applied for the determination of U oxidation state in tailings particles enriched with uranium.

Water samples were collected from a spring and creeks with elevated uranium concentration. A detection limit of 17.4 $\mu\text{g/l}$ could be reached with TXRF using a Mo-anode X-ray tube and a KETEK silicon drift detector. Concentrations of the water samples were in a wide range with a maximum concentration of 25 mg/l uranium.

Tailing sludge samples were collected at the ground of tailings pond No. I of the mine. Particles were dispersed on Nuclepore filters that were attached to the surface of a polyallyl diglycol carbonate detector (TASTRAK). After irradiation with fast neutrons for 5 minutes, the fission tracks were recorded in an optical microscope. From the stored images, the positions of particles with elevated uranium content were located on the Nuclepore filters. The oxidation state of U, As and Pb was determined by μ -XANES at HASYLAB Beamline L, Hamburg, Germany. Major fraction of uranium in the tailings particles was present in the less mobile U(IV) form not risking their leaching into the ground water. Arsenic was present mostly as arsenopyrite and arsenate, but significant amount of As(III) could also be detected.

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CAPABILITIES OF MICROANALYTICAL METHODS FOR URANIUM ANALYSIS OF INDIVIDUAL MINE TAILINGS PARTICLES

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Environmental problems caused by mining activities are of high importance all over Europe. Mining and mineral processing operations produce the largest amounts of waste in all industrial processes. Such wastes are deposited in waste dumps and tailings. One uranium deposit exists in Hungary where the radiological monitoring of the site is continuous. The nuclear spectroscopic methods are well established in order to study the problem concerning radionuclides. However, very limited information is available on the distribution and chemical form of uranium in the tailings sludge. In order to solve this complex analytical problem, a combination of different analytical methods is necessary. One of the most applied methods for studying the major elemental composition of particulate samples is electron-probe microanalysis (EPMA). Detection limits of uranium determination by single-particle EPMA were calculated using Monte Carlo simulations, as a function of particle diameter and accelerating voltage. For a 25 kV accelerating voltage, 1 nA beam current and 50 s measuring time, the detection limit of U were calculated as 4 wt.%. However, uranium and its decay products are often present only at trace amounts in the particles, insufficient to detect by EPMA. For most actinides that are long-lived radionuclides, micro beam X-ray fluorescence (μ -XRF) has superior sensitivity to nuclear spectrometry in case of particulate matter. For studying the micro-distribution of uranium and other heavy metals within one particle of a few hundred micrometres, a tomography method based on μ -XRF was used. Micro-Raman spectrometry was applied aiming structural and molecular characterization of individual microparticles.

Tailings samples were collected from the uncovered part of tailings pond No. I of the Hungarian uranium mine, dried in air and prepared on Nuclepore polycarbonate filter as well as on Al foil. Using single-particle EPMA, the abundance of U-containing particles (over 4 wt.%) was found to be around 1 % in all samples. U was mostly associated to Ti-rich aluminosilicate particles. It was possible to identify larger particles with lower U content using laboratory μ -XRF. A particle of 250 μ m diameter identified with μ -XRF was further investigated with micro-XRF tomography resulting in an inhomogeneous U distribution within the particle. Micro-Raman spectra were collected from U-rich particles identified by EPMA on samples prepared on Al foils. From micro-Raman results the occurrence of uranium was considered in the form of pitchblende and pyrochlore.

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POSSIBILITIES OF XRF SPECTROMETRY FOR TRACE ELEMENT ANALYSIS OF VEGETATION SAMPLES IN ENVIRONMENTAL STUDIES

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The use of vegetation specimens as bioindicators of the degree of pollution with metallic elements in monitoring studies is already a widespread approach in environmental research. Commonly, plant analysis has been carried out by means of atomic spectroscopic techniques. However, the use of these techniques involves sample preparation procedures for the total destruction of the matrix by mineralisation, which may lead to problems of contamination or disturbances of the measured concentrations by element losses due to incomplete digestion. X-Ray fluorescence spectrometry (XRF) comply with the desired features for the analysis of vegetation specimens including the multi-element capability, simple sample preparation, a wide dynamic range, high throughput and low cost per determination. However, the use of XRF technique for environmental purposes has been limited due to the poor sensitivity for some important pollutant elements (such as Cd and Pb) and a somewhat worst precision and accuracy compared to other spectroscopic techniques. In this sense, the implementation of suitable quantitative strategies and the recent improvements in XRF instrumentation have been evaluated in the present work to achieve reliable analytical results for plant analysis. Besides, analytical figures of merit such as precision, accuracy and limits of detection have been carefully determined in diverse configurations of XRF spectrometers (EDXRF, WDXRF and Polarised-EDXRF) using different excitation sources in order to assess the capability of XRF for environmental purposes.

Data obtained showed up the benefits of using Polarised beam EDXRF instrumentation since the instrument can be designed to generate a range of excitation and polarisation conditions optimised for different groups of analytes leading to an improvement of the achieved sensitivity. Moreover using this configuration, we reduce the characteristic high degree of scattering of the X-Ray source by organic matrices leading to an improvement of the limits of detection.

On the other hand, the combined use of a gadolinium anode tube and high-energy Ge semiconductor detector allow performing EDXRF analysis using K-lines of high atomic number elements. In this way, the problems of reduced sensitivity and spectral interferences inherent to the choice of L-lines for the determination of some important pollutant elements such as the cadmium is feasible in the low $\text{mg}\cdot\text{kg}^{-1}$ range.

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HEAVY METAL ANALYSIS ON CANDLES

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Candle market is a developing market especially last years, with an estimation of a 10%-15% per year increase and sales of the order of \$ billions. Besides candle aesthetic significance they may be a potential source of indoor air pollution [1]. The main problems are the heavy metal and organic compounds emissions. Heavy metal emissions usually referred in the literature are originated from candle metal core wicks.

As candle production is a high increasing market with numerous producers, a fast and reliable analytical technique will be needed in the near future. In the present work the possibility of direct candle heavy metal analysis with energy dispersive XRF was examined. A ^{109}Cd radioactive source was used for excitation and different types of candles were analysed. Especially high contents of some metals (Cu, Zn, Fe) were detected on the surface of certain type candles (gold color plated candles) while their cores did not show any pollution problem; the surface metal contents were found equal to 0.8 mg/cm^2 in the case of copper. The results show that a more extensive study is needed and the problem of candle surface analysis could have been underestimated.

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ADAPTIVE MATCHED FILTERING OF XRF DETECTOR SIGNALS.

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Matched filtering idea was proposed by V. Radeka and N. Karlovac back in 1967. Several attempts for approximate implementation have been made since then. Matched filtering is extremely efficient in XRF spectrometers due to relatively high detector noise (resulting in resolution degradation). This paper discusses an adaptive procedure for exact coefficient determination of optimal matched filter.

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APPLICATION OF KUMAKHOV'S POLYCAPILLARY OPTICS FOR SYNCHROTRON RADIATION FOCUSINGOleg Mikhin¹, S. Nikitina², A. Priladyshev²¹*Institute for Roentgen Optics, Moscow*²*IRO, Moscow, UNISANTIS, Geneva*

Kumakhov's polycapillary optics is one of the most efficient type of x-ray optics applied for laboratory sources-based instruments used for spectroscopy and diffraction applications. In this research we studied microfocusing properties of half-lenses with various parameters using highly collimated monochromatic synchrotron radiation beam at the ESRF. The Microoptics test bench at BM05 was used to evaluate optical performance of polycapillary lenses in terms of resolution, efficiency and gain. We found that half-lenses allow focusing effectively a parallel synchrotron beam to the focal spot of about 10 microns. As a result the increase of the flux density in the focal spot was more than three orders higher as compared with a direct or unfocused beam. The obtained results show real applicability of the Kumakhov's polycapillary systems in microXRF and other applications where high density of x-ray radiation is required.

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PROPERTIES OF POLYMER X-RAY REFRACTIVE LENSES FOR SPECTROSCOPY

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For spectroscopic experiments like micro-fluorescence analysis, EXAFS, XANES or micro-diffraction micro focused X-ray beams are used. X-ray compound refractive lenses (CRLs) are one of the cheapest and most simple ways to micro focus X-rays. Unfortunately, the focal distance of the lenses is altered at a change of the mono-chromator energy as the refraction index of the material is a function of wavelength. To keep the object, the lens and the image position at a change of the monochromator energy, X-ray refractive lenses generating a large focal depth are required for static spectroscopy experiments. By lithography processing of polymer it is also possible to fabricate lenses with quasi-parabolic profile providing a large focus depth with uniform intensity distribution in the focal spot for a relative energy change of 0.1.

Our SU-8 polymer lenses for photon range from 1 keV to 100 keV have been tested in spectroscopic setups. We have fabricated planar parabolic lenses with focal spot sizes with FWHM $< 0.5 \mu\text{m}$ and an intensity gain of more than 100. Lenses optimized for different wavelengths and with focal lengths of between several millimetres and several tens of centimetres were fabricated on one substrate. The focal length of the lenses can be adjusted to the needs of the experimental setup by breaking away parts of the lens arrays. This can be done independently for the x- and y-focussing direction. By moving the lens substrate as well as the detector in a distance of about 10 cm and stepping from one lens to the next, the whole spectral range can be scanned. The lens apertures are in the range of some tens of micrometers to several hundred micrometers.

In the paper we will present recent results concerning the improved focal spot size of less than 500 nm for circular focal spots and less than 150 nm for linear focal lines.

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**POLARIZATION DEPENDENCE OF X-RAY REFLECTION AND
ABSORPTION SPECTRA OF HEXAGONAL CdS CRYSTAL IN THE
ENERGY REGION OF S L_{2,3} – AND Cd M_{4,5} –EDGES**

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A strong polarization dependence of the reflection and absorption spectra of strongly anisotropic hexagonal BN crystal were early established [1]. Hexagonal CdS crystal is a weakly anisotropic crystal. Moreover this crystal is a cubic crystal from the nearest neighbors point of view. The purpose of this work is to analyze the influence of the spatial crystal anisotropy of weakly anisotropic hex. CdS crystal on the x-ray reflection and absorption.

The reflection spectra were measured in the vicinity of the S L_{2,3}–, Cd M_{4,5}– absorption edges for different grazing incidence angles using s- and p- polarized synchrotron radiation. The absorption spectra were calculated from reflection spectra using Kramers-Kronig relationship. The weak polarization dependence of the reflection and absorption spectra was established in the vicinity of the S L_{2,3}–absorption edge. The orientation dependence of the SK–absorption spectra obtained earlier [2] was used for the explanation of the obtained polarization dependence. Common analysis of the S K– and S L_{2,3}–absorption spectra shows, that the polarization dependence in the vicinity of the S L_{2,3}–absorption spectra is caused by the transitions to the final states of p-like symmetry. According to selection dipole rules, the probability of the transitions from the initial 2p- states to final states of the p – like symmetry is low. The transitions from the initial 2p- states occurs to the final states of the s – like symmetry mixture with the p – like symmetry. The weak polarization dependence of the reflection and absorption spectra is caused by the weak trace of the p- states splitting by the crystal field.

The strong polarization dependence of the reflection and absorption spectra was established in the vicinity of the Cd M_{4,5}–absorption edge. It is shown that the polarization dependence of the absorption spectra in the vicinity of the Cd M_{4,5}–absorption edge is defined by the transitions to the final states of p-like symmetry splitting by anisotropy crystal field. Because the probability of the transitions from the initial 3d- states to the final states of the p-like symmetry is great the polarization dependence is strong in the vicinity of the Cd M_{4,5}–absorption edge.

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**PRESENT STATUS AND UPGRADING PROJECT OF X-RAY
FLUORESCENCE BEAMLINE AT BSRF**

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X-ray fluorescence analysis facility has been developed since 1988 at the Beijing Synchrotron Radiation Facility (BSRF). In 2003 the 4W1B dedicated beamline and its experimental station was set up and commissioned. A recent upgrade with a double crystal monochromator and a K-B focusing mirror improved significantly the beamline capabilities. A single multilayer monochromator was also tested in order to enhance the intensity of monochromatic light for XRF experiments. With the available setup and the K-B mirror a X-ray microprobe with a spot size of $20 \times 20 \mu\text{m}^2$ is achievable allowing with a white beam a minimum detection limit of trace elements down to a few ppm ($\mu\text{g/g}$).

The beamline allows also performing XAFS experiments with the double crystal monochromator and several microanalysis experiments in biomedicine, geology and environmental science have been performed.

A new wavelength dispersive X-ray fluorescence spectrometer with multi-curved crystals system was installed and successfully tested. The instrument is based on three spherically curved Si (220) crystals working with resolution smaller than 1 eV at 6.5 keV and with a large solid angle acceptance. Some experimental results of X-ray emission (XES), resonant inelastic scattering (RIXS) and high-resolution X-ray absorption near edge spectrum (XANES) collected with such device will be presented.

Due to the scheduled storage ring upgrade from BEPC to BEPCII, the electron energy and current will be increased by 2.2 GeV and 120 mA to 2.5 GeV and 250 mA respectively within the next 12 months. As a consequence the upgrading project of the XRF beamline and its experimental facility at BSRF has been approved and should be ready for users at the end of 2006. The new beamline will have a toroidal focusing mirror and a multilayer monochromator. The layout of the new beamline and its characteristics will be presented

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METROLOGY AND TEST BEAMLINE AT SOLEIL

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The objectives of this project is to design and install at the SOLEIL synchrotron radiation source a calibration and metrology test facility for the R&D of optical components and detectors. We propose to build, on a bending magnet, three branches dedicated to VUV, soft x-rays and hard x-rays energy ranges to cover 10 eV to 15 keV. This installation will first address the needs of the SOLEIL experimental groups (Optics and Detectors) and will be used by a large community. This beamline will also be valuable as a general-purpose beamline to prepare, test and set up a wide range of experiments. A complementary important aspect of this installation is the realization of primary standard: the metrology beamline of SOLEIL could become the national primary standard source in collaboration with the Laboratoire National d'Essais (LNE). The beamline has been designed to provide great flexibility. We describe in detail the beamline design, capabilities, and end station instrumentation

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COMBINATION OF MICRO X-RAY TECHNIQUES: THE SYNCHROTRON RADIATION LABORATORY FOR ENVIRONMENTAL STUDIES AT ANKAJörg Göttlicher, Ralph Steininger, Rolf Simon*Institute for Synchrotron Radiation, Forschungszentrum Karlsruhe in der Helmholtz-Gemeinschaft, D-76344-Eggenstein-Leopoldshafen*

Environmental samples are generally complex (e.g., contaminated soils, dump sediments), consisting of mixtures of mineral phases (often with micrometer and nanometer particle sizes), microbes, and in some cases vegetable material. Elemental distribution, spatial resolved speciation, and phase association of trace levels of contaminants are the ideal basis for risk assessment and development of remediation strategies. This problem is best addressed by a combination of microfocussed synchrotron X-ray techniques centralized at the ANKA storage ring in the Synchrotron Radiation Laboratory for Environmental Studies (SUL). It consists of a microfocus X-ray beamline (SUL-X) at a wiggler source that will enable elemental mapping using X-ray fluorescence analysis (XRF), chemical speciation with X-ray absorption spectroscopy (XAS) and mineral phase determination by X-ray diffraction (XRD), successively at the same sample position. Furthermore, the laboratory is supplemented with an infrared microscope (SUL-IR) at an edge radiation IR beamline. A typical procedure of characterizing heterogeneous samples will consist in the first stage of an X-ray fluorescence mapping or profiling to obtain an overview on the distribution of elements and to detect 'hot spots' of contaminants, e.g. arsenic, lead. The beamline can be switched from monochromatic mode to 'white light' to increase the photon flux on, e.g., diluted samples for XRF analyses. The beam position on the sample is thereby preserved. To detect the X-ray fluorescence radiation a solid state Si(Li) detector is available. Subsequently the species of the element of interest can be determined on selected sample locations using ionization chambers for X-ray absorption spectroscopy in transmission mode or for diluted samples in fluorescence mode with the 7 element Si(Li) detector. A CCD detector is available to determine mineral phases on a micrometer scale which helps to assign contaminants to hosts. To meet the increasing demand of speciation of low Z elements like Al, Si, P, S for environmental questions XAS at energies down to the Al K edge (1.5 keV) will be offered after removal of an interim Be-window. Adjustable beam dimensions from about 1mm^2 to $10\mu\text{m}^2$ in combination with automated sample positioning and a precise diffractometer will allow a comprehensive characterization of heterogeneous samples: a need to improve the knowledge on the behavior of pollutants in the environment. The beamline is planned to be upgraded later with a superconducting short-period undulator. SUL-X is currently being commissioned, and examples from first measurements will be shown.

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XSW - X-RAY STANDING WAVES IN SIMULATION AND EXPERIMENT

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XSW (X-ray Standing Waves) is a technique to measure element distributions and thicknesses in thin films and layered samples on a nanometer scale. Unlike other XSW techniques, Grazing Incidence XSW (GI-XSW) utilized in this work does not demand a crystalline or periodic sample structure. Main requirements are monochromatic, coherent radiation and a flat reflecting surface. The technique is suitable for conducting and non-conducting, organic and inorganic samples, metals, nonmetals and semiconductors. Samples need very little preparation, vacuum is only necessary if very light elements are to be observed. Use of synchrotron radiation significantly increases signal intensity and widens the choice of accessible photon wavelengths, and thus the lateral resolution as well as sensitivity for a chosen element of interest.

Several kinds of samples were measured using synchrotron radiation from DELTA synchrotron at Dortmund University. These XSW scans were compared to results of a simulation program developed to analyze XSW scans, as well as to visualize the XSW principle.

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CHEMOMETRICS BASED XAS CHARACTERIZATION OF TITANIUM ON TITANIUM-OXIDE-MODIFIED CHROMATOGRAPHIC SILICA.

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Silica (SiO₂) is a weakly acidic material with high mechanical resistance and is the most widely used support for High Performance Liquid Chromatography (HPLC) [1,2]. Such silicas are porous and amorphous [1] with surfaces that are covered with silanol groups (SiOH) [1,2]. These groups are used to anchor the functional (alkyl) groups essential for reversed phase HPLC applications. Unfortunately, silica also has some disadvantages, limited pH stability [1,2], with most applications being limited to the pH range of 2-8 and the stationary phases (SP) made from silica often show peaks tailing with basic compounds due to residual silanols. This reduces the applicability of silica as a SP or support for many HPLC analyses. One alternative is to place a metallic oxide layer on a chromatographic silica support. Some examples are the preparation of a SP on silica having covered with oxide layers of titanium [3,4] or zirconium [5,6] oxides. Procedures to graft titanium [7,8] and other metals onto silica for non-chromatographic applications are described in literature.

Alkoxides of titanium react readily with silanol groups, forming Si—O—Ti linkages [7]. The proposed stoichiometry of this reaction has two silanol groups reacting for each molecule of titanium alkoxide [7]. These metal oxide layers may give some protection to the underlying silica in acidic or basic media. In this work, different types of silica were modified with titanium alkoxide and characterized by X-ray Absorption (XAS) allied to Chemometrics. The XAS analyses were done at the National Synchrotron Light Laboratory, LNLS (in Campinas, Brazil), and the spectra were obtained with 3-Win DCM software. For comparison, the XAS spectra were normalized and treated with WinXAS 2.3 software to give the coordination number of Ti on SiO₂ and the bond length of Ti-O. Also, with the XAS spectra, a matrix was constructed and analyzed by Principal Component Analysis (PCA) and Partial Least Squares (PLS) chemometric techniques carried out using “The Unscrambler 9.2” software. PCA analyses showed that it is possible to differentiate the type of silica employed in the reactions with the alkoxide, to classify the silica with a layer of oxide of titanium with respect to (a) the Ti coordination number and (b) the bond length. PLS analyses showed that it is possible to calibrate the Ti coordination number and the bond length, making all the calculations of the XAS experiments easier.

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DOUBLE ACCEPTOR LEVELS IN THE BAND GAP OF BORON-DOPED DIAMOND SEMICONDUCTORS ANALYZED BY SOFT X-RAY ABSORPTION SPECTROSCOPY AND DV-XA CALCULATIONS

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Boron (B) doped diamond is a p-type wide-gap semiconducting material, which has promising technological applications such as electron nano-emitters and high-power amplifiers. We have recently observed the electronic structure transition between the semiconducting and metallic states in the band gap of B-doped diamonds by soft x-ray emission and absorption spectroscopy using synchrotron radiation. In semiconducting thinly-B-doped diamonds, the BK x-ray emission spectra, which reflect the B2p density of states (DOS) in the valence bands, are enhanced with a steep-edge-feature near the Fermi level. In addition, a localized x-ray absorption peak, which is interpreted as the acceptor level, is clearly observed just above the Fermi level. However, two absorption peaks, which are regarded as the double acceptor levels, are observed in the CK x-ray absorption spectra. In order to understand the electronic structure of B-doped diamonds from the soft x-ray spectroscopy, we calculated the DOS of B-doped diamond cluster models using discrete variational (DV) $-X\alpha$ molecular orbital (MO) calculations and then compared the measured x-ray spectra to the calculated DOS spectra with an emphasis on the double acceptor levels in the semi-conducting band-gap of the carbon (C) matrix.

In the C matrix, the C atoms have two chemical states. One state is the C atom, which is bonded to dopant B atoms and the other is the major C atom, which is not bonded to the B atoms. From the DV- $X\alpha$ calculations, we did not observe a significant difference in the MO energy levels of the lowest unoccupied C2p orbitals (acceptor levels) between these two C atoms. However, there is a difference in the MO energy of the occupied C1s orbitals between the C atoms. The MO energy of the C atom that is not bonded to the B atoms is deeper than that of the C atom that is bonded to the B atoms. Therefore, it is concluded that the measured double acceptor levels in the band-gap of C matrix is understood by the chemical shift of the inner C1s orbitals due to the chemical state difference of the C atoms in B-doped diamond. One acceptor level in the band gap of the B atoms is reasonable because the B atoms have one chemical state in thinly-B-doped diamond, which is B atom bonding with the C carbon atoms.

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SPECIATION OF CARBONITRIDE NANOLAYERS

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The aim of this work is the determination of the chemical bonds character of novel and technologic relevant layered systems of boron and silicium carbonitrides.

For such carbonitrides a wide application range is predicted. One reason of this prediction is founded in their mechanical properties. They have a high mechanical steadiness and stability, even at high temperatures [1]. Because of their chemical resistance they are inert against a lot of aggressive chemical media. Therefore, in form of layers these carbonitrides are suited for mechanical and chemical protection (wear and corrosion) of a substrate material.

The carbonitrides are often produced by plasma-enhanced chemical vapour deposition processes with precursor materials like hexamethyldisilazane and bis(trimethylsilyl) carbodiimide for SiC_xN_y [2] or trimethylammoniumborane [3,4] for BC_xN_y, respectively. Furthermore, it will be tried to produce complex layers out of reactions of small molecules as acetylene, ethylene, ammonia, hydrogen, nitrogen etc [5].

Furthermore, the conversion of the precursor materials (often a polymer) into an amorphous ceramic material and their conversion at high temperatures (ca. 1000°C) into crystalline components are procedures which are not fully understood [6].

From this point of view it is an important question whether the produced "carbonitrides" are new materials with well-defined bonds or are mixtures of carbides and nitrides.

For the speciation of the carbonitrides methods as TXRF-NEXAFS, XPS, TEM-EELS and Raman spectroscopy should be applied. With samples of SiC_xN_y and BC_xN_y the first TXRF-NEXAFS measurements at the electron storage ring BESSY II were realised. The spectra show partly sharp peaks, which could be identified as defined electron bonds (π^* or σ^*), but partly they are showing also broad bands, which are generated by energetic similar electron levels. The same samples were measured by XPS. The binding energy spectra are showing sharp peaks, which are originating from energetically well-defined core-level electrons.

Both methods are a promising beginning to clear up the chemical bond structure of the given carbonitride samples. Additional measurements by these both techniques and by TEM-EELS and Raman spectroscopy can be expected to solve some of the given questions.

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XANES ANALYSIS OF Ru VALENCE IN La_2RuO_5

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To improve on the electrical characteristics of the conventional perovskite materials for Solid-Oxide Fuel Cells (SOFCs) operating at 1000°C RuO_2 or electrically conducting ruthenates are investigated as electrocatalysts for oxygen reduction. In the La-Ru-O system, a large number of compounds were synthesized: La_3RuO_7 , $\text{La}_{4.87}\text{Ru}_2\text{O}_{12}$, $\text{La}_7\text{Ru}_3\text{O}_{18}$, $\text{La}_8\text{Ru}_4\text{O}_{21}$, $\text{La}_3\text{Ru}_3\text{O}_{11}$, LaRuO_3 , $\text{La}_{3.5}\text{Ru}_4\text{O}_{13}$ and $\text{La}_4\text{Ru}_6\text{O}_{19}$. We prepared a new compound with the formula La_2RuO_5 [1]. The reported crystal structure is not only different from those already reported for the La-Ru-O system but appears to have no equivalent structure in oxides.

The main evidence for the new structure comes from powder XRD studies. Primarily, the symmetry class of the structure is determined: it belongs to the monoclinic system with the space group P21/c. The stoichiometry, however, is not directly determined by XRD: only after a suitable model structure is devised, the true occupation of the unit cell by the constituent atoms can be obtained in Rietveld refinement. At this stage of the study, the results of x-ray absorption spectroscopy (XAS) can be crucial [2,3]: in XANES technique, the effective valence of the investigated atom is determined directly, while EXAFS method yields directly the interatomic distances and coordination numbers which can be used in devising of the model structure and as useful constraints in its refinement. These results will be discussed here. The Ru K-edge absorption spectra (EXAFS and XANES) of the La_2RuO_5 and the reference samples were measured in a standard transmission mode at XI station of HASYLAB at DESY (Hamburg, Germany).

In XANES, a linear relation between the absorption edge shift and the valence state of the investigated atom has been established [2,4] for compounds with the same type of ligand. We calibrated the relation for Ru with La-rutenates LaRuO_3 , $\text{La}_{3.5}\text{Ru}_4\text{O}_{13}$ and $\text{La}_{4.87}\text{Ru}_2\text{O}_{12}$ with known Ru valence states and the same octahedral oxygen coordination as indicated for the new compound. Its energy shift of the Ru K-edge in the XANES spectrum gave the average Ru valence state as 4.0±0.1. This surprising finding strongly supported the stoichiometry La_2RuO_5 as estimated from XRD.

The analysis of the EXAFS signal provided the first information on the Ru atom neighborhood, on which the model for the Rietveld refinement of the unit cell of the new compound was devised. Finally, the local structure around the Ru atoms from the refinement [1] was used in the FEFF6 code to calculate ab-initio the photoelectron scattering paths and hence a theoretical EXAFS spectrum of the sample. The perfect quantitative agreement with the measured EXAFS spectrum proves that the refined crystal structure contains no systematic defects around Ru atoms and confirms the proposed La_2RuO_5 stoichiometry of the new compound.

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X-RAY SPECTROMETRY WITH HIGHLY ORIENTED PYROLYTIC GRAPHITE (HOPG)H. Legall¹, H. Stiel¹, V. Arkadiev², A. Bjeoumikhov³¹*Max-Born-Institut, Germany*²*IAP - Institut für Angewandte Photonik, Germany*³*IfG -Institute for Scientific Instruments GmbH, Germany*

For X-ray spectrometry in the keV range with laser plasma sources highly efficient collecting optics are required. Such optics for x-ray spectrometry can be realized with thin films of Highly Oriented Pyrolytic Graphite (HOPG). These films provide highest integral reflectivity combined with high spectral resolution. The main advantage of these HOPG films in contrast to ideal crystals is the opportunity to realize arbitrary shaped crystal optics with these crystal films. An x-ray spectrometer based on these HOPG films developed for laser plasma diagnostics and EXAFS spectrometry will be presented. The spectrometer was tested for the use in time resolved x-ray spectroscopy with sub-ps time resolution.

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LONG TERM CORROSION MECHANISMS OF IRON IN ATMOSPHERE - X-RAY ABSORPTION ANALYSES OF ARCHAEOLOGICAL CORROSION LAYERS

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Nuclear waste storage is envisaged in France over multi-secular periods: the wastes could be confined in a glassy matrix which could be included in metallic overcontainer ensuring water and air tightness of the whole system. Up to now envisaged metallic material is low carbon steel as it is known to corrode uniformly. Corrosion behaviour of steel is well known and can be predicted for 50 years but for longer periods studies have to be completed. The aim is now to understand the long term corrosion mechanisms to ensure a reliable prediction. Their specificity is linked to the characteristics of ancient corrosion layers whose thicknesses are of several hundredth micrometers. Thus the corrosion layer plays a role in the corrosion processes but their influence is not well determined. Previous studies have shown that some phases present in the corrosion scale could be reactive. They have focused until now on the lepidocrocite (g-FeOOH) that can be reduced during the wetting stage of a wet-dry cycle typical of atmospheric corrosion. The reduced phase formed is supposed to be very active in the corrosion process but it was not evidenced by in-situ Mössbauer experiments [1]. Therefore the aim of this study is to understand the corrosion mechanisms and the role of the phases formed during the corrosion process. The first step consists in analysing ancient corrosion layers formed on archaeological artefacts in order to determine their crystalline organisation.

In this study ten well dated archaeological samples coming from French monuments have been analysed by several complementary microprobes techniques. The samples are prepared in order to carry out the analyses on cross sections. Samples were first analysed by X-ray microdiffraction: goethite and lepidocrocite (a-FeOOH and g-FeOOH), two well crystallised phases are identified. But a doubt subsists on the presence of magnetite (Fe₃O₄) or maghemite (g-Fe₂O₃). Therefore Raman microspectroscopy has been involved because this technique allows to discriminate these two phases: it has been evidenced that magnetite is in fact rarely present in the corrosion products of the artefacts of the corpus. Nevertheless the presence of ferrihydrite, a poorly crystallised compound has been suspected [2]. To confirm these analyses, X-ray Absorption Near Edge Structure microspectroscopy under synchrotron radiation (μ XANES) has been used on the samples and the presence of ferrihydrite evidenced. As this phase could be also highly electrochemically reactive [3], new corrosion mechanisms are proposed based on the reactivity of several phases constituting the corrosion scale.

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ENVIRONMENTAL ANALYSES BY COMBINING TXRF - NEXAFS AND IR-SPECTROSCOPY: SPECIATION OF BROMINE IN ORGANICS AND CHARACTERIZATION OF THE ORGANIC MATRIX

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Many polymers in building materials and consumer products contain flame retardants (FR). The most common organic FR are brominated organic compounds. Due to their worldwide output several FR are now ubiquitous and can be found in sediments, biota, and – moreover - in fine dusts. The major task of FR, reduction of risk of fire, is contrary to possible risks from the toxicity and eco-toxicity of FR [1].

Due to detection limits of conventional methods the analysis of trace constituents in fine dusts is complicated. In order to simulate prospective experiments based on cascade impactors for sample collecting, some polymers containing brominated flame retardants were abraded mechanically on an ultra-pure silicon wafer surface. The chemical speciation of bromine is obtained by use of Total-Reflection X-ray Fluorescence Analysis (TXRF) in combination with Near-Edge X-ray Absorption Fine Structure (NEXAFS) analysis [2]. Synchrotron radiation based infrared spectroscopy (SR-FTIR) in reflection mode is used for the characterization of the polymer matrix. Analysis of the X-ray Absorption Near Edge Structure at K and L absorption edges in the hard x-ray range are employed frequently in the characterisation of element speciation. Due to the small penetration and information depth of only a few nanometers in total reflection beam geometry, self absorption effects are negligible even for the analysis of L edges in the soft x-ray range. In addition, the TXRF method offers drastically reduced scattering contributions and thus lowest detection limits.

In the present investigation monochromatized undulator radiation available at the PTB laboratory at the electron storage ring BESSY II in Berlin, Germany, was employed to probe the Br-L3 and Br-L2 absorption edges of some samples deposited on a silicon wafer surface. For the excitation of the present specimens the plane grating monochromator beamline for undulator radiation provides a spectral resolution of about 300 meV and permits the photon energy to be varied in steps of 250 meV. The PTB provides a reference-free TXRF arrangement providing knowledge of the incident radiant power, of the solid angle of detection and of the detection efficiency.

The initial results demonstrate some potential of the TXRF-NEXAFS method to successfully contribute to the elemental speciation, even of trace elements. The shape of the various TXRF-NEXAFS structures reflects the chemical environment of the element bromine in the different organic matrices. Synchrotron based FTIR spectroscopy in reflection mode provides the classification of different polymers within reasonable measurement times. The TXRF-NEXAFS offers the option for reference measurements without the need for any chemical sample preparation, thus reducing undesired modifications (e.g. GC/MS).

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XAFS STUDIES OF THE LOCAL STRUCTURE OF MN DOPED MAGNETIC SEMICONDUCTORS

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In recent years a rapid development of spintronics is observed. The goal is to create conceptually new devices which will utilize spin of electron. To achieve this goal it is necessary to fabricate effective injectors of polarized spin and to learn how to manipulate the spin and detect it. One expects that integration of magnetic materials with conventional semiconductor technology should be achieved. The key to the spintronics success is availability of suitable materials for device manufacturing.

In this report one of the model semiconductor spintronic materials, namely Mn doped GaAs grown by molecular beam epitaxy (MBE) is considered. GaMnAs can be grown by MBE at low substrate temperatures (between 200 and 300°C, depending on the Mn content). It exhibits paramagnetic to ferromagnetic phase transition for Mn content higher than 0.5 at%. The highest ferromagnetic phase transition temperature (T_c) reported so far in GaMnAs is close to 170 K, for GaMnAs containing about 8% Mn. T_c is proportional to the Mn content and to the concentration of valence band holes. High T_c can be achieved in the material from which compensating defects are removed in the post-growth annealing procedures. The composition of GaMnAs is limited to about 10% Mn due to the Mn segregation into MnAs precipitates observed above this limit.

These precipitations were considered as a drawback up to now. However, since MnAs is a metallic ferromagnet with T_c of about 40°C, the GaAs:MnAs granular system constitutes an interesting material with small ferromagnetic nanoparticles immersed in the semiconductor host lattice. Such composite material could be considered as a good semiconductor (applicable for integrated circuits) filled with small magnets providing built-in magnetic field at room temperature. This field would affect semiconductor band structure, in particular, leading to differentiation of semiconductor spin states, which is essential for a spintronic material.

We have studied the GaAs:MnAs samples with different Mn contents prepared under different conditions. In order to determine the local atomic structure around Mn atoms we analyzed the XANES and EXAFS spectra at the K-edges of Mn for GaAs:MnAs as well as for the reference binary samples, like: MnAs layers and homogeneous GaMnAs alloys. Both techniques are sensitive to the local structure around selected element. This feature makes them effective tools for studying the multicomponent materials. Moreover from analysis of XANES spectra it is possible to distinguish between hexagonal and/or cubic MnAs or metallic Mn inclusions. In the case when several Mn compounds are present in the GaAs:MnAs system the percentage of Mn atoms in the particular compound was evaluated using principal component analysis (using XANDA program). Together with the evaluation of the content of each compound we have considered EXAFS scattering from multiple precipitation phases.

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XAS INVESTIGATION OF Fe IONS IN CHITOSAN COMPLEXES

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The extensive research of metallo-organic chelating compounds is inspired by perspectives of biomedical, ecological and industrial applications. One of these types of metallo-organic materials are transition metal - chitosan complexes [1].

Chitosan is produced commercially by deacetylation of chitin, which is the structural component in the exoskeleton of crustaceans (crabs, shrimp, etc.). It has the ability to form multiple complexes [2]. Both materials are important natural polymers. They easily biodegraded, are biocompatible and bioactive and possess attractive physical and mechanical properties. From the application point of view a very important aspect is their ability to bind metal ions, including heavy and toxic ones [1]. Consequently, chitosan and its derivatives have a variety of current and potential applications e.g. in biomedical products, cosmetics, food processing and removal of metallic impurities in wastewaters. Recently, the iron containing biopolymers have been examined as possible drug carriers and controlled release beads for various model drugs [3]. Different methods are used to increase the sorbent functionality of the chitosan. The crosslinking of polymer chains after complexation with metal ions seems to be a prospective method and is frequently used. Moreover, at the low temperatures the iron crosslinked chitosan (CH-Fe-CL) exhibits magnetic ordering [4]. From the magnetic studies it was suggested that Fe-chitosan are composed of randomly dispersed polymer chains and can be classified as a topologically disordered material in which the distribution of Fe-Fe bond orientations are random. It has already been found that Fe ions can either be penta- or hexa-coordinated and that there are two different Fe sites and more than one polymer chain is involved in formation of these complexes. In spite of wide interest in this class of materials, there is not much reported about x-ray studies of atomic structures of the crosslinked chitosans and many basic questions concerning atomic structure waits for answer.

Two iron chitosan samples were investigated: (1) the Fe crosslinked chitosan CH-Fe-CL with the iron content of 118 mg/g and (2) N-carboxymethylchitosan complexes with Fe ions (N-CMC-Fe) at the concentration of 7 mg/g.

The measurements of XANES (X-ray Absorption near Edge Spectra) and EXAFS (Extended X-ray Absorption Fine Structure) at the K-edge of Fe were carried out at the A1 station. The samples were cooled down to liquid nitrogen temperature and the x-ray fluorescence detection mode was used.

The XANES spectra of chitosan will be discussed in respect to reference samples and magnetic properties. Two investigated samples have different radial distribution of atoms around Fe. The local atomic order was proposed on the base of EXAFS spectra analysis.

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**THE SPECIATION OF IRON IN MINERALS USING THE L_{3,2} EDGES
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Analysis of the X-ray Absorption Near Edge Structure (XANES) at K and L absorption edges in the hard x-ray range are employed frequently in the characterisation of element speciation in geological samples. Electron Energy Loss Spectroscopy (EELS) is also an established method requiring, however, very thin specimens to allow for the electron transmission. For the analysis of L edges in the soft x-ray range on thick bulk samples, either photo and Auger-electron yield or fluorescence yield can be used when performing XANES or Near-Edge X-ray Absorption Fine Structure (NEXAFS) analysis. The detection of electrons ensures a constant information depth, whereas in the fluorescence detection mode self-absorption effects have to be accounted for with increasing concentration of the element of interest. The detection of electrons provides rather surface-sensitive data in contrast to more bulk-sensitive data in the case of photons.

In the present investigation monochromatic undulator radiation available at the PTB laboratory at the electron storage ring BESSY II in Berlin, Germany, was employed to probe the Fe-L₃ and Fe-L₂ absorption edges of various minerals such as clinopyroxenes from eclogites as well as clinopyroxenes and orthopyroxenes from earth-mantle rocks. For the excitation of the specimens the plane grating monochromator (PGM) beamline for undulator radiation provides a spectral resolution of about 150 meV and permits the photon energy to be varied in steps of 125 meV. The PTB set up a completely reference-free XRF arrangement providing knowledge of the incident radiant power, of the solid angle of detection and of the detection efficiency. In addition, a 135 nm thick Mn coating on a 2 µm thick Al foil could be placed into the detection channel to modify the spectral distribution detected in favour of the Fe-L fluorescence lines of interest. Employing radiation of high spectral purity, the transmittance of this Mn coated Al foil was determined at the PGM beamline to correct the detection efficiency in the XRF-NEXAFS experiments. Based on theoretical absorption coefficients and the known sample compositions, self-absorption corrections were performed. Self-absorption was significant for samples with FeO contents > 1.8 wt %. The results will be discussed in view of the determined Fe³⁺/Fe_{tot} ratio of the minerals in comparison to data obtained by other methods.

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EXAFS TECHNIQUE IN USE TO INVESTIGATE LOCAL IRON NEIGHBOURHOOD INSIDE COMPOUNDS APPLICABLE IN CANCER THERAPY.

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The new class of compounds, being diaminoacid derivatives of protoporphyrin IX could serve as photosensitizers in techniques of photodetection and photodynamic therapy (PDT) of malignant tissues, employed nowadays in many clinical applications [1]. Diaminoacid (alanine - Ala, arginine - Arg, serine - Ser, phenylalanine - Phe) derivatives of protoporphyrin IX compounds were produced at the Laboratory of Biochemistry and Spectroscopy at Military University of Technology in Warsaw in Poland and shows features of the ideal photosensitizer, which should have such specificity to be able selectively load in the malignant tissue and produce reactive oxygen species (ROS) upon illumination with definite wavelength of light. ROS are responsible for cells' destruction and death. Particularly derivatives with good water-solubility generate a lot of interest. It has been shown that due to the presence of selected amino acids residues attached to the protoporphyrin ring, these novel compounds penetrate more easily into tumour tissues and also clear from healthy tissues faster than other protoporphyrin-based photosensitizers [1-3]. Nevertheless, the knowledge about chemistry and physical properties of these materials is still not sufficient. The one of open questions is the localisation within the compounds' structure and role of iron ions. Without detail information about new photosensitizers' structure these drugs cannot be officially used in the medical treatment. Therefore the bonding of Fe-ion in several diaminoacid derivatives has been the subject of our investigation. Using EXAFS we tried to determine local environment of Fe-ion in relation with results of previous spectroscopic measurements in range of visible light. The measurements of Fe K-edge of x-ray absorption were performed at the ESRF beamline BM26A in the transmission mode. The samples were cooled down to helium temperature to limit x-ray destruction of biomaterials and reduce temperature structure disorder. The radial distribution of atoms around Fe obtained by Fourier transformation of measure EXAFS spectra averaged from several acquisitions and taken in k - range up to 13 Å⁻¹ will be presented. The radial distributions of atoms around Fe in some of diaminoacid derivatives differ only in details, but some has significantly different shape. From EXAFS chi function adjusting by EXCURVE98 program we postulate that the most common structure of the new class of photosensitizers is protoporphyrin IX with diaminoacid attachments and with iron atom in the centre of protoporphyrin IX ring. The information about the nature of chemical bonding one can get from the XANES (x-ray absorption near edge structure). Judging from the shift of the Fe-edge the ionic state of Fe in measurement compounds is identical or very similar to that in Fe₂O₃. This evidence that the ionic state of iron in the investigated materials is +3.

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TEMPERATURE AND PRESSURE DEPENDENCE OF THE Yb VALENCE STATE OF SOME INTERMETALLIC Yb-TM-Ga PHASES

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The valence state of Yb of the ternary phases YbNiGa₄, YbNiGa₂, YbAgGa₂ and YbAuGa was investigated by means X-ray absorption spectroscopy (XAS) at the Yb LIII absorption edge in dependence of composition, temperature and pressure. Also, measurements of the lattice parameters and magnetic susceptibilities were performed to define the Yb state of the given phases. The spectroscopic data were determined on beamlines A1 and E4 of Hasylab at DESY.

As common structural features of these phases, the Yb cations are situated in a three dimensional transition metal (TM) – Gallium network. Here, the coordination polyhedra of Yb show coordination numbers of 12 and more and can be deduced from capped pentagonal prisms. The environment of Yb is altered at a constant Yb : TM ratio.

Except for YbNiGa₂, the spectra at ambient pressure show two maxima indicating the presence of Yb in the 4f₁₄ (Yb²⁺) and 4f₁₃ (Yb³⁺) states. An almost mono-valente situation is reached at pressure of 25 GPa with a dominating contribution of Yb in the 4f₁₃ state. The divers characteristics of these always continuous transitions are described by means of the occupation of the Yb 4f levels which are calculated by the de-convolution of the two peak absorption spectra..

Temperature dependence of magnetic susceptibilities at ambient pressures agrees qualitatively with the XAS results. Here, the temperature dependence for the YbNiGa₂ phase is similar to a Curie-Weiss law ($\mu_{\text{eff}}/\text{Yb} = 4.4 \mu\text{B}$) and confirms the Yb 4f₁₃ state also found by XAS. Small paramagnetic susceptibilities (< 10-8 m³/mol) with weak temperature dependencies were found for the phases YbNiGa₄, YbAgGa₂ and YbAuGa. The evaluation of the susceptibility data hints at an intermediate valency of the ytterbium atoms.

The influences of the local environment, temperature and pressure on the occupation of the Yb 4f levels determined from the XAS data will be presented in detail and discussed in respect to magnetic behaviour of the investigated phases.

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LOCAL STRUCTURES IN $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ SYSTEMS

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The semimagnetic semiconductor $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ is a good representative for studying processes characteristic for some IV-VI narrow-gap semiconductors, such as variation of the band gap with composition, effects of negative magnetoresistance, long-term non-equilibrium processes and the phonon dispersion anomalies. The off-centering effect (i.e. displacement of the atoms from the regular lattice positions), responsible for the appearance of persistent photoconductivity, and related low-temperature ferroelectric phase transition, are some other interesting features characteristic for these systems. In attempt to provide answers on questions concerned with the exact positions and charge states of both constitutive and impurity atoms, possibilities and features of their ordering and(or) clustering, and configurational and thermal disorder in the systems, we have performed EXAFS measurements (at DESY-HASYLAB) on different edges for different concentrations and at different temperatures. That way an atomic-scale insight in the processes that influence structural, thermodynamical, transport and optical properties of these materials is obtained.

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XAFS STUDY OF NANOCOMPOSITE SYSTEM FOR SYNGAS PRODUCTION

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This work is devoted to the structural study of nanocomposites comprised of doped cerium dioxide and lanthanum manganite for syngas production by the XAFS spectroscopy. Recently, great efforts are devoted to the development of membranes allowing to convert methane into syngas by oxygen supplied from the air side of the membrane via its transport due to the mixed O₂-/electronic conductivity (MIEC). MIEC materials are also of a great interest as cathodes and/or anodes in SOFCs. Nanocomposites comprised of ionic and electronic conductors are considered as a promising option. Design of such membranes is at present among the most important tasks of materials science.

A polymerized complex precursor method (Pechini route) was used for synthesis of ceria doped by Gd or Pr and LaMnO₃. Binary nanocomposites were obtained by addition of doped ceria precursors to a suspension of lanthanum manganite in ethanol followed by evaporation and annealing at 500°C. Powdered samples were pressed into pellets and calcinated in air at temperatures up to 1300°C. All XAFS spectra of the Mn-K, Pr-L3, Gd-L3, La-L3 Ce-L3 edges were recorded at Siberian Synchrotron Radiation Center (SSRC).

It was established that polymerized complex precursor method ensure a homogeneous mixing of components on the molecular level for a given phase. It was found that samples of ceria doped by Gd or Pr have a CeO₂-reference structure (a cubic fluorite-like structure), while the structure of lanthanum manganite is pseudocubic.

Analysis of the XANES and EXAFS La L3-edge spectra revealed no pronounced difference between La environment in pure LaMnO₃ phase and nanocomposites which suggests a minimum (if any) undesirable incorporation of La into ceria.

On the other hand, EXAFS Mn K-edge spectra of nanocomposites annealed at high (1300°C) temperatures strongly resemble those for the nanocrystalline low-temperature samples of LaMnO₃ characterised by decline of the first Mn-Me coordination sphere amplitude along with shift and splitting of peaks corresponding to next spheres. This feature agrees with the disordered pseudocubic structure of nanosized LaMnO₃ domains in composites, extent of their doping by Gd or Pr cations (if any) remaining uncertain.

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STUDY OF CNF SUPPORTED Co(Ni)-Mo CATALYTIC SYSTEM USED FOR HDS BY EXAFS AND XANES

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Currently, a new type of supported catalysts - CNF (carbon nanofibers)-based catalysts excites a heightened interest. As rule, the CNF-based catalysts have improved catalytic activity, selectivity and thermostability as compared with traditional supported catalysts.

This work is devoted to the study of the promising Ni-Mo and Co-Mo carbon nano-fibers (CNF) supported catalysts used for hydrodesulfurization (HDS) reaction by the EXAFS and XANES methods.

The studied Co(Ni)-Mo samples were prepared by methane decomposition over high-loaded Ni-Mo-Al₂O₃ (10 wt. % Al₂O₃) and Co-Mo-Al₂O₃ (25 wt. % Al₂O₃) catalysts at 550 and 500°C, accordingly. It was found that carbon nano-fibers (CNF) containing metal catalyst nanoparticles located on their tips were formed. All EXAFS and XANES spectra of the Mo-K, Co-K, Ni-K edges were recorded at Siberian Synchrotron Radiation Center (SSRC).

The local Mo and Ni(Co) surroundings of the all samples studied were established and the phase composition were determined. It was shown that there are some differences of the molybdenum arrangements for the Ni-Mo and Co-Mo nanoparticles. All possible structural models were discussed. In addition, these samples were studied by the TEM, EDX and X-ray diffraction methods. The data of all methods are in a good agreement.

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XAFS STUDY OF TITANIA AND TITANIA-SILICA SUPPORTED SYSTEMS

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The present work is devoted to the study of the titania and titania-silica supported photocatalysts prepared by grafting, physic, diffusion methods and sol-gel from inorganic precursors were studied by XAFS method. Silica, glass, polyester granules and fibres were used as supports.

All the EXAFS and XANES spectra of the Ti-K edge were recorded at Siberian Synchrotron Radiation Center (SSRC). It was shown that structural lability of the titanium-silicate systems studied and the change of symmetry of the oxygen coordination around the Ti(+4) ions depends on preparation method, calcination temperature, titanium percentage and way of titanium introduction into the silicate matrix. It was found that both formation of distorted titanium oxide nanoclusters and presence of dissolved Ti(+4) ions takes place. All possible structural models of different titanium locations were discussed. In addition, these samples were characterized by X-ray diffraction (XRD), XPS, TEM, UV-Vis methods. The data of all methods are in a good agreement.

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AN IMPROVED GENETIC ALGORITHM AND ITS APPLICATION TO CURVE FITTING IN GEOLOGICAL SAMPLES

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Genetic algorithms can be applied to curve fitting and resolution of overlapped spectra. The main advantage of genetic algorithms over the classic methods is its potential capability of making the global optimum search. However, it does not mean that they can always find out the optimum solution in a certain limited time by a conventional searching strategy. Moreover, to find a global optimum solution takes usually a long time.

A typical genetic algorithm consists of initialization of data, selection, crossover, mutation and evaluation of fitness. As the first step in the algorithm, a suitable fitting object is chosen and the possible solution to the special problem has to be provided. After the data are randomly initialized, they should be restricted within a reasonable range based on the scientific knowledge in x-ray fluorescence spectrometry to speed convergence. An error function is designed to evaluate the qualification of fitness, along with the genetic operations. The fitness value is usually the inverse of the errors derived by comparison of the calculated and the measured values. Every individual is evaluated according to the fitness. A better fitness means better solutions. As a common rule, the best individual is kept to the next generation. The procedure continues until it meets a designed convergence criterion.

A key in the genetic algorithms is the choice of a powerful searching strategy, which determines whether the algorithm can find out the optimal solution without falling into a local minimum. Three searching strategies have been compared in the study.

First of all, a very simple approach is examined by only keeping an individual with the maximum fitness to the next generation. A poor solution was produced by this method. This search process looks like a random walking. There is no evolution, as well as no convergence. Obviously, this approach cannot be acceptable.

On the basis of the survival of the fittest, then, a conventional method was used to search for an optimal solution. By this method, however, not each fitting spectrum was acceptable. It might fall into a local minimum. And a poor searching precision was often obtained. A procedure of performing multiple searches was always needed and the averages of several solutions were then calculated to get the acceptable fitting results.

Now, an improved optimal searching strategy was suggested based on the species evolution principal. In fact, the species evolution optimal strategy was utilized to answer a question about who should or who can survive longer than others. When the species evolution, rather than the fittest individual alone, was used, a real global optimum fitness can be found in a rather easy way. Fitness increases dramatically by using this strategy. The species evolution optimal strategy in genetic algorithms has been applied to curve fitting in geological samples by x-ray spectrometry.

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**FUNDAMENTAL PARAMETER METHOD USING SCATTERING X-RAYS
AND MONTE CARLO SIMULATION**

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A Monte Carlo simulation method has been applied to actual analyses in x-ray fluorescence analysis. When the elements of the base matrix of a sample are not measurable such as in polymers and sediments, the sample can not be accurately analyzed by using conventional fundamental parameter methods. A fundamental parameter method has been developed for estimating such non-measured elements by measuring scattering lines from x-ray tube. A Monte Carlo simulation method is used to calculate the corresponding theoretical scattering intensities of Compton and Thomson scattering lines.

It was found that the influence of the difference of scattering angles caused by the divergence of primary x-rays is large, especially in Thomson scattering lines. On the other hand, this influence is comparably small for fluorescent x-ray lines.

Long computing times have been a weak point of Monte Carlo simulations in practical use for x-ray fluorescence analysis. However, the computing time is short enough when only scattering lines are calculated since no wavelength integration of primary x-rays is required. Accordingly, the regular theoretical intensity calculations for fluorescent lines in combination with a Monte Carlo simulation for scattering line gave reasonable short computing time even in routine analysis. The Monte Carlo calculation is executed in each iteration step.

Good results were obtained in samples such as powders, polymers, and liquids, and results will be presented.

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USE OF THE THEORETICAL SIMULATION IN THE CHOICE OF XRF TECHNIQUE OF ANALYSIS WITH THE SYNCHROTRON RADIATION

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Little attention is given to the specific character of used procedures to convert experimental intensities into concentrations of determined elements in the extensive and, as a rule, good-quality literature on SRXRF. Many important details of the use of the individual classical analytical techniques remain wholly beyond the scope of researchers. Let us also to note that the need is obvious for the further work from the review of publications to improve a methodical supply used for SRXRF.

The aim of the present report is to fill partly this gap and to draw attention to the importance of the correct use and description of applied procedures to convert intensities into concentrations of studied elements.

As long ago as the end of 1960s the theoretical simulation is successfully used to choose the procedure for the conversion of the XRF intensities into the concentrations of the determined elements in the Irkutsk XRF laboratories. The programs were developed and tested for the calculation of analytical line intensities, which took account of the contribution of the selective excitation effect. In these calculations the features were taken into account that were characteristic of the long-wave region of the X-ray spectrum (2-10Å). The satisfactory agreement was obtained between the calculated and experimentally determined intensities for low-Z elements (from Na to Fe, A.G. Revenko, 1970, 1972). The programs were modified during the progress in computers. One estimated the contribution of the radiation scattered from sample atoms (Yu.I. Velichko et al., 1976; A.L. Finkelshtein et al., 1985) and the contribution of the bremsstrahlung from photo- and Auger electrons of sample atoms (G.V. Pavlinsky et al., 1974; V.P. Afonin et al., 1984) to the XRF intensities using their own the software. The calculation algorithms were developed for the case of a divergent beam of the primary radiation (B.I. Kitov et al., 1979, 1981). The investigations were conducted, the aim of which was to determine limits of applicability of idealized models. It is natural that the attention was paid to the effect of errors on the description of the spectral distribution of the primary radiation from X-ray tubes and also to errors in values of mass absorption coefficients (Yu.I. Velichko and A.G. Revenko, 1974, T.N. Gunicheva et al., 1975). The conducted investigations allowed recommending to use the theoretical stimulation for the execution of one of main steps in a process of an XRF technique development, namely the step of the choice of a suitable analytical technique (A.N. Smagunova et al., 1974).

The examples of the theoretical estimates of the interelement effects are presented for different studied materials: rocks, plant materials, and biological tissues. A number of the conventional variants of the fluorescence radiation excitation were estimated. One examined the excitation using the mixed radiation from the Sc-, Rh- and W-anode X-ray tubes, and also using the monochromatic radiation of the different energy (the simulation of the SRXRF variant). The considered approach allows to reduce the time and charges necessary for the development of the analytical technique as well to avoid undesirable errors in choosing CRMs.

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SIMPLE METHOD TO IMPROVE A DETECTION SYSTEM RESOLUTION

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A simple multiplicative iteration method (MIM) is described to improve energy resolution of a detection system when the response function to mono-energetic incident photons is known. It is shown that "hidden" lines can be observed in the experimental spectra collected with relatively poor energy resolution after the procedure of MIM is applied.

The problems discussed are: the dependence of the method efficiency on the statistics in the spectral intervals treated, and validity of the background subtraction procedure. The results are presented for Si(Li), NaI(Tl) detectors and for gas proportional counters.

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APPLICATION OF THE MONTE CARLO METHOD TO X-RAY UNFOLDING: COMPARISON BETWEEN GERMANIUM AND SILICON DETECTORS.

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The characterization of the X-ray spectra is the most powerful tool to perform a quality control (QC) of X-ray tubes. Normally, QC is simplified measuring some parameters such as the half value layer, the fluence, the peak voltage, etc. However, this QC is not completed until the primary spectrum is determined. In previous works, a powerful methodology to assess primary spectrum using a Compton spectrometer has been studied. In summary, this methodology consists of the use of a Monte Carlo model (normally the MCNP code is applied) to reproduce the physical phenomena involving the interaction of photons and electrons with the Compton spectrometer and with a high purity germanium detector (of high resolution). By means of this Monte Carlo model, a response matrix can be built, relating the pulse height distribution (PHD) registered in the detector, with the primary X-ray spectrum. In this work, it is proposed a comparison between the PHD obtained by means of a germanium and a silicon detector. A new response matrix, corresponding to the silicon detector is built. Both response matrices (germanium and silicon) are compared. Subsequently, an unfolding method based on the application of a Modified Truncated Singular Value Decomposition (MTSVD) is applied to these matrices in order to assess the primary spectrum. Finally, primary X-ray spectra obtained by simulation using the germanium and the silicon response matrix are compared. Differences between primary spectra obtained with the germanium and the silicon response matrices are studied and related with the resolution and intrinsic features of both detectors.

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PERFORMANCES OF CALIBRATIONS AND VALIDATION: INFLUENCE OF EDXRF MEASURING TIME

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The minerals K, Ca, Fe and Zn are today commonly analysed in powdered food matrices (milk powders, infant formulae and infant cereals) by Energy Dispersive X-Ray Fluorescence systems.

In order to optimize the measuring time and then increase the samples throughput of the analytical device in factory line laboratories, the influence of the acquisition time (ranging from 30 s till to 300 s) on the calibration and validation performances as well as the number of pellets/sample have been investigated.

Surprisingly, longer acquisition times do not improve performance factors such as Standard Error of Calibration, Standard Error of Prediction, Bias....

Repeatables and measurement uncertainties have also been studied vs acquisition time. An EDXRF PANalytical Minipal 2 with Rh tube was used for this study.

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X-RAY DIFFRACTION FROM CELL WALLS FOR *ESCHERICHIA COLI* G 35 #61 STRAIN

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Although many investigations on commensal bacteria, very little research has been done to understand the structural-functional characteristics of membranes from probiotic strains.

The aim of this work was to investigate the membrane characteristics for *E. coli* G35 # 61 probiotic strain. The cell walls by the X-ray diffraction under small and big angles as well as qualitative and quantitative composition of bacterial phospholipids for G35 # 61 and five other commensal strains from gut microbiota of cancer patients were investigated.

The insignificant increase of concentration of main phospholipids and at the same time also the phospholipids with small size of polar heads- phosphatidylethanolamines in the membranes of *E. coli* from cancer patients were shown. The approximately same concentrations of biosynthetic precursors of phosphatidylethanolamines - phosphatidylserines is also observed.

For clarifying of phospholipids' organization in bacterial cell walls the X-ray diffractions under small and big angles were researched.

It is known, that the reflex with midplanar distance 4,3 Å characterizes a status of hydrocarbonaceous chains of phospholipid molecules in membranes. The absence of diffraction at 4,3 Å points on liquid state of membrane, and the presence of galog points on amorph state, and the presence of circle- on mutual parallel equidistant occurrence of phospholipid molecules in membrane.

It has been shown the reflexes at 4,3 Å as well as at 8 Å and 11 Å on rentgenograms are missed, which points out that the phospholipid molecules in membranes have not cluster character and the phospholipids are in liquid state. On the other hand, the differences between the intermembrane water fractions' tickness from cell walls for probiotic strain and such for strains from cancer patients were shown.

The observed changes can play an important role in regulation of host important physiological processes.

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CHARACTERIZATION OF OSTEOPOROTIC BONE STRUCTURES BY BIDIMENSIONAL IMAGES THROUGH X-RAY MICROFLUORESCENCE WITH SYNCHROTRON RADIATION

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The X-ray Microfluorescence (μ XRF) is an analytical technique based on the local excitation and microscopic analysis of the region of interest, supplying information about the superficial distribution of minerals [1]. The osteoporosis is a pathology that assails the bones, defined as systemic skeletal disease characterized by a decrease in the bone mass and deterioration of the microarchitecture with the increase of the bone fragility and more susceptibility to fractures. The ovariectomized process in female rats has been used frequently as animal model of experimental osteoporosis, because it supplies similar data to those observed in the adult skeleton post menopause [2].

In this context, the aim of this study was to characterize the bone structures of the femoral head, cortical and trabecular regions, from the bidimensional images. There were three groups of animals: control, ovariectomized and ovariectomized with estrogen intake. The ovariectomized process occurred when the animals were four months-old. The measurements were performed in standard geometry of 45° incidence, exciting with a white beam and optical capillary with 20 μ m of diameter collimation in the XRF beamline at the Synchrotron Light National Laboratory (Campinas, Brazil).

It was found ten elements: P, S, Cl, K, Ca, Cr, Fe, Cu, Zn and Sr. The results show that both the concentration and the distribution of the minerals are significantly among the groups, mostly in relation to the calcium element. It can be seen a function inversion in Ca and Sr, that is, in animals with a lesser concentration of Ca occurs an increase in the Sr concentration, beyond an alteration of their distributions in the present sites. Other important result revealed by the images is the thickness of the cortical with the ovariectomized process, there was a decrease in the thickness and it increase again with estrogen intake. The bone mineralization is associated with less calcium excretion as well the estrogen action and lesser bone resorption. Besides others factors, calcium can not be fixed by the bones in the absence of estrogen, making them thin and weak, contributing positively to the appearance of the osteoporosis.

It was concluded that μ XRF with Synchrotron radiation a powerful and alternative technique to characterized bone structures. Through this technique it was possible to observe that the ovariectomized process in a period of four months was able to reduce the percentages of calcium, increasing the strontium levels and the thickness of the cortical femoral head, while the estrogen intake increased again those percentages, defining again more clearly the geometry of the cortical in femoral head.

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ELEMENTAL CONCENTRATION BIDIMENSIONAL MAPPING IN THE BRAIN OF WISTAR RATS BY X-RAY MICROFLUORESCENCE WITH SYNCHROTRON RADIATION

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Implication of trace metals (Fe, Cu and Zn) in some neurodegenerative diseases (Freidriech's ataxia, Parkinson's disease, Alzheimer's disease, Wilson's disease and Multiple Sclerosis) by oxidative stress implication is now well admitted [1]. Considering that, the aging is a potential factor of risk to develop these diseases, the aim of this work was to map the elemental concentration in brain sections of Wistar females rats as function of aging. The elemental distribution and the elemental concentration were performed by X-Ray Microfluorescence with Synchrotron Radiation (μ SR-XRF). Wistar young (14 days old), adults (60 and 100 days old) and middle-aged (20 months old) rats (n=12) were analyzed. They were sacrificed by decapitation and their brains were carefully dissected and quickly removed. They were immediately frozen by submerging in isopentane, which was cooled in liquid nitrogen, in order to avoid ionic mobility until cryosectioning. To perform the coronal section (2.0 mm thickness), the brain was positioned on a manual tissue slicer inside the cryostat at -25°C. The samples were lyophilized during 36 hours and they were fixed in resin for SR-XRF measurements. These measurements were carried out at the XRF beam line at the Synchrotron Light National Laboratory (Campinas, Brazil). The characteristic X-rays produced were detected with an HPGe detector with a resolution of 165 eV at 5.9 keV. The sample was positioned on the image plane within an accuracy of 0.5 μ m with a 3 axis (x, y, z) remote-controlled stage. The measurements were carried out using a conventional system of collimation (orthogonal slits 300 μ m X 300 μ m), white beam and a geometry 45°/45°. A two-dimensional scanning was performed in order to study the tendency of elemental distribution variation. The counting live-time for each pixel was 10 s/step and the step size was 300 μ m/step in both directions. There is a pattern in the iron and zinc distributions throughout the brain, independently of the age. It was observed that the iron distribution was more conspicuous in the thalamus and hypothalamus. On the other hand, iron, copper and zinc levels were different in relation to the age. All of these elements levels increased with advancing of age. Aging is a potential factor of risk to develop Alzheimer and Parkinson's diseases. This study efforts the idea that these elements are involved in the chemical mechanisms of the brain, which lead these neurological diseases, due these elements also present high levels in specific areas of the brain, such as the hippocampus and the substantia nigra of patients with these disorders.

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THE INVESTIGATIONS OF IRON LOCAL ENVIRONMENT IN HUMAN BRAIN TISSUE USING XAFS TECHNIQUE – PRELIMINARY RESULTS

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Iron-mediated processes in human brain are subject of numerous studies. As is known this element may participate in some pathological mechanisms e.g. via production of free radicals in the Fenton's reaction. For this reason, studies of iron sites in human brain tissue are of great importance. One of the methods providing this kind of information is X-ray Absorption Fine Structure (XAFS) spectroscopy.

The investigations were carried out for samples from selected areas of human brain i.e. substantia nigra (SN), white matter (WM) and grey matter (GM). The specimens were taken during an autopsy. SN sample was cut using cryomicrotome (20 micrometer thick), then placed on ultralene foil and afterwards freeze-dried. The tissue of GM and WM was lyophilized for 24 h at temperatures from $-40\text{ }^{\circ}\text{C}$ to $35\text{ }^{\circ}\text{C}$ at a pressure of 200 Pa. Then, each sample was homogenized in an agate mortar and approximately 250 mg of it was pressed into a 1.3-cm-diameter pellet without any additions.

The measurements were performed at the bending magnet beamline E4 at HASYLAB equipped with two mirrors and a double-crystal Si(111) monochromator.

The absorption spectra were measured at the Fe K-edge in the fluorescence mode in the energy range from 7050 to 7700 eV.

The spectra have been elaborated with the ATHENA/FEFF software. The Fourier transforms of the EXAFS functions show that the distances of the first coordination shell (Fe-O) are almost the same in the grey and the white matter ($\sim 1.80\text{ \AA}$), whereas the Fe-O distance in substantia nigra is larger ($\sim 2.13\text{ \AA}$). Further investigations are in progress.

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TRACE ELEMENTS IN HUMAN BRAIN

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This work is a contribution to better understanding the heavy metals accumulation in human brain tissues in the aging process.

Cerebrum, cerebellum and brainstem samples were collected from the same individual and sampling for different ages was performed, in order to find some relationship between the elemental concentrations in the different tissues and the age of the individual. Samples were collected post-mortem and frozen until analysis. Age, sex, origin of dead and specific diseases were registered.

Quantitative analysis was performed for K, Ca, Mn, Fe, Cu, Zn, Rb and Pb. A few of these elements, K, Ca, Zn, Fe are essential to life, however Pb is toxic. Cu and Zn can become toxic in high concentrations.

All samples were analysed by X- Ray Fluorescence spectrometry without any chemical preparation.

Different concentrations for a few elements can allow distinguishing brainstem tissues from the cerebellum or frontal lobe tissues. A similar behaviour for age dependence was observed for some elements in the different brain regions. A decrease of K and Rb with age was observed for the three studied regions while an increase of Fe, Cu Zn and Pb was observed.

Very low concentrations for Pb were found in the whole the analysed samples.

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BROAD BEAM- AND MICRO-PIXE ANALYSIS OF NORMAL AND IN VITRO DEMINERALIZED DENTAL ENAMEL

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Dental enamel has been widely studied by PIXE and μ -PIXE [1], but less attention was paid to its demineralization, which leads to caries formation [2]. Studies of incipient demineralization by classical methods showed that a surface layer some tens of μm thick seemingly remains unaffected, while removal of mineral substance takes place below it producing a 'gap' of similar width [3]. Broad beam PIXE can analyze enamel down to 15-30 μm near the surface, while deeper layers can be explored in sectioned teeth by microprobe measurements. Here we report investigations by broad beam PIXE and by μ -PIXE of normal and *in vitro* demineralized enamel. For broad beam PIXE, clinically sound enamel from adults and children was studied both before and after demineralization. For microbeam analysis, a caries free inferior molar was cut in its four cusps of whom two were demineralized, then all were sectioned and polished. In all cases demineralization was done for 3 days in lactic acid solution (0.09 M, initial pH 4.5). Broad beam PIXE was performed at Bucharest using 3.0 MeV protons from a van de Graaff accelerator, and μ -PIXE measurements were done at the Rossendorf nuclear microprobe with 3.1 MeV protons. The microbeam was focused to a $\sim 3 \mu\text{m}$ spot and areas of 64×128 and 128×128 pixels were mapped at $\sim 4 \mu\text{m}/\text{pixel}$ size and at 1,7-2,8 μC per map. Broad beam PIXE detected P, Cl, K, Ca, Mn, Fe, Cu, Zn, Br, Sr, Y and Pb in enamel and evidenced an apparent increase of Fe/Ca, Cu/Ca, Zn/Ca, Sr/Ca and Pb/Ca ratios at the surface. The demineralizing solution evidenced increases of P, Ca and Zn, of pH up to 4.9 and of conductivity by 11 %. In enamel, the increase of Fe, Cu, Zn, Sr and Pb vs. Ca relative intensities seem to evidence mainly an unmasking effect in the outer superficial layer, by a more accentuated removal of Ca than of the trace elements. The μ -PIXE maps of Ca and P evidenced relatively little changes in a surface layer about 180-200 μm thick except its outermost region of up to $\sim 20 \mu\text{m}$, with an abrupt and almost linear decrease of Ca towards the exterior. The latter supported the broad beam PIXE results. Down to 180-200 μm , the relative intensity of Ca decreased by 25-30 %. However in the deeper 'gap' zone from 180-200 μm on the Ca level dropped dramatically, to 15-25 % of its maximum. Thus apart of giving multielemental information and of not requiring (semi)thin tooth sectioning as the classical methods, the combined approach of broad PIXE and μ -PIXE provide structural insight of the *in vitro* dental enamel demineralization, partly not accessible to the former.

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**MICRO-XANES INVESTIGATIONS OF Cu AND Fe OXIDATION STATE
INSIDE SINGLE NEURONS FROM SUBSTANTIA NIGRA OF
PARKINSON'S DISEASED PATIENT**

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The most characteristic feature of Parkinson's disease (PD) is the loss of nerve cells in the area of substantia nigra (SN). In most cases the causes of cellular atrophy and death are enigmatic, however according to the leading theory oxidative stress triggers a cascade of events resulting ultimately in the death of neurons [1-4]. Oxidative stress occurs when the generation of reactive oxygen species in a system exceeds its ability to neutralize and eliminate them [2]. Transition metals like: Fe, Cu, Mn can promote the generation of free radicals in Fenton's reaction. The determination of their oxidation state in the nerve cells representing PD and control case may shed some new light on the problem of neuronal degeneration in case of the investigated neurological disorder.

X-ray absorption near edge structure spectroscopy (micro-XANES) was applied in order to examine differences in iron and copper chemical state between neurons from SN representing PD and the control cases. Autopsy samples cut using a cryotome, neither fixed nor embedded in paraffin were investigated.

The comparison of the absorption spectra near Fe and Cu K-edge measured in melanized neurons from SN of PD and control samples did not show significant differences in the oxidation state. Measurements of inorganic reference materials containing Fe(II), Fe(III), Cu(I) and Cu(II) indicated that most of both Fe and Cu occurred in neuromelanin rich neurons in the oxidized form. The least-square fitting method was used for the analysis of the XANES spectra in order to avoid the problem of their normalization.

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TRACE ELEMENT ANALYSIS OF BIOLOGIC SAMPLES USING ENERGY-DISPERSIVE X-RAY FLUORESCENCE AND TOTAL REFLECTION X-RAY FLUORESCENCEAnnemarie Wagner¹, Johan Boman¹, Michael J. Gatari²¹*Department of Chemistry, Atmospheric Science, Göteborg University, SE-412 96 Göteborg, Sweden*²*Institute of Nuclear Science and Technology, University of Nairobi, P.O. Box 30197 Nairobi, Kenya*

X-ray fluorescence is an excellent tool for the elemental analysis of environmental samples, since it combines multi-element capacity with an extensive analytical range. For most chemical elements, the sensitivities of EDXRF spectrometers are in the low microgram range. In the TXRF mode, the peak to background ratio is improved by the highly reflected exciting photons, resulting in a better monochromatization of the excitation beam and negligible scatter from the reflecting surface. Consequently, detection limits are in the picogram range for some elements. This technique, however, requires an elaborate sample treatment. To produce a thin homogeneous sample with a representative composition, organic material is often chemically digested in a tedious and time-consuming procedure. Biologic tissue usually contains numerous trace elements in varying concentration ranges embedded in a sample matrix that may enhance the signal to background ratio. In such samples, a high background and an overlapping of the spectral lines of interest may cause a considerable deterioration in detection limits as compared to the optimum which can be achieved in single element standards.

In the present study, detection limits and detectable concentrations of trace elements in environmental samples are compared for a home-made EDXRF and a TXRF spectrometer placed at Göteborg University, Sweden. The instrumental setup of the spectrometers is similar. The EDXRF is equipped with a W X-ray tube, whereas the TXRF has a high-power rotating Mo anode achieving a higher effect than the EDXRF. Both instruments have a 80 mm² KeveX Si(Li) detector with a resolution of 173 eV FWHM for 5.9 keV. In both spectrometers, the pulse processor and multichannel analyzer system are of the same type. For spectral analysis and quantitative calculations, the AXIL/QXAS package has been used. Certified Reference Material (NCS ZC78005 Mussel) has been chosen to compare the accuracy of elemental analysis and the detection limits of the instruments. Before analysis with EDXRF and TXRF, the standard reference material was pressure digested with nitric acid in a microwave oven. Additionally, it was analysed by EDXRF without any previous sample treatment. The detection limits for the untreated standard material were generally poor compared to the digested material. For the digested samples, detection limits were lower for the TXRF, albeit for some high-Z elements such as Se and Pb, they were of the same order of magnitude for both instruments. The analysis of different volumes of the digested reference material in the EDXRF suggested that for some applications the inferior detection limits of this instrument can be compensated by using a higher total sample mass than in the TXRF mode.

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**DETECTION OF MERCURY IN THE KIDNEY VIA SOURCE-EXCITED
X-RAY FLUORESCENCE**

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Mercury is a toxic heavy metal that accumulates in the kidney and can cause adverse health effects upon exposure. Chronic occupational exposure can lead to kidney impairment and even loss of function. A non-invasive form of detection is required in order to monitor the total mercury organ burden of workers. Previously, the McMaster University in vivo prompt gamma neutron activation system was used to determine the minimum detection limit (MDL) of mercury in the kidney to be 315 ppm. This MDL remains far too high to be suitable for detection of mercury at any conceivable occupational levels. Börjesson et al (Phys. Med. Biol. 1995; 40: 413-426) and O'Meara et al (Appl. Radiat. Isot. 2000; 53: 639-646) obtained kidney MDL levels of less than 30 ppm through polarized x-ray fluorescence, however improved sensitivity is required for successful in vivo measurement. In order to lower the detection limit further, source-excited x-ray fluorescence with a Cd-109 source was used to determine the MDL. Cadmium-109 emits 88.0 keV gamma rays; this energy is slightly greater than the mercury K-edge energy of 83.1 keV. Following excitation, emitted K x rays were used to measure the concentration of mercury in the kidney. The in vivo x-ray fluorescence system consists of a Cd-109 source in a backscatter geometry, an HPGe germanium detector and torso and kidney phantoms. Two detectors were compared: a 25 mm radius planar HPGe detector and a cloverleaf HPGe detector, which consists of four separate 8 mm radius crystals. Phantom calibrations were performed using both systems to obtain the MDL, leading to improvements over the neutron activation MDL by more than an order of magnitude, and a reduction in the MDL achieved with polarized x-ray fluorescence.

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SEMI-QUANTITATIVE ANALYSIS OF Fe, Cu AND Zn CONCENTRATION IN BREAST CANCER

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Each year more than one million women are diagnosed with breast cancer around the world. Early screening and diagnosis can certainly improve cancer survival rates. Analysis of some trace element usually present human breast has gained great interest over the last few years, due to the increase in knowledge on the role of these trace elements and the possible correlations between abnormal concentrations and pathological conditions.

In this work Fe, Cu and Zn concentrations present in healthy as well as in neoplastic breast tissues were evaluated by Synchrotron Radiation X-ray Fluorescence analysis (SR-XRF). Eighty samples of breast tissues coming from biopsies, mastectomies or breast reduction surgeries were analyzed. Pathological information was available for all samples. The experiment was performed at the XRF beamline of the Laboratório Nacional de Luz Síncrotron (LNLS), in Campinas, Brazil. A monochromatic beam of 11 keV was used to excite the samples. The samples were placed at 45° from the incident beam whereas the energy dispersive solid state HPGe detector was placed at 90° from the incident beam, on the plane of the electron storage ring, in order to benefit from the strong polarization of the synchrotron beam thus improving the signal to noise ratio. Metal concentrations in breast tissues specimens were determined by using calibration curves obtained from aqueous and ethanolic solutions with inorganic salts of well-known concentrations.

The Fe, Cu and Zn were significantly higher in the neoplastic breast tissues (all $p < 0.001$). It was also observed from the results that Zn showed the highest alteration in the pathological tissues, followed by Cu and Fe. As a conclusion of this work it is remarkably important to point out that a significant alteration of the concentrations of some elements can indicate the presence of neoplastic in breast tissues.

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X-RAY SCATTERING PROFILES OF SOME NORMAL AND MALIGNANT HUMAN BREAST TISSUESD.M. Cunha¹, O.R. Oliveira¹, C.A. Pérez², M.E. Poletti¹¹*Departamento de Física e Matemática – FFCLRP – Universidade de São Paulo, Ribeirão Preto
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Recent studies have been shown that X-ray scattering experiments (X-ray diffraction and small-angle scattering) give detailed information of structures within tissues providing an alternative means of distinguishing pathology. In this work the scattering profiles (or X-ray diffraction patterns) from normal (17) and malignant (14) human breast tissues were measured in the interval of momentum transfer $0.2 < x < 6.2$ nm. The experiments were performed with a powder diffractometer apparatus (Siemens D-5005) operating in reflection mode, equipped with a graphite monochromator in the scattering beam. The X-ray tube was equipped with a Cu anode and Ni added filtration. The sample was located on the central axis of the goniometer system, inside a sample holder with thin plastic wall. The number of scattered photons was measured varying continuously the scattering angle between 5° and 150° and the acquisition time was chosen in order to keep the statistical uncertainty below 5%.

Results from the diffraction system have been compared with histological analysis for each individual sample. The preliminary results of this work show that the majority of malignant breast tissues analyzed presents different scattering profiles that normal breast tissues, being significantly different in the region of low momentum transfer, due to intermolecular correlations present in the elastic scattering. A multivariate statistical analysis has been used to classify breast tissues on the basis of the scattering profile. The results suggest that scattering profile may be an effective marker to be used in the diagnosis of the breast cancer.

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MONITORING PLASMA AND SKIN IRON CONCENTRATIONS IN HUMAN METABOLIC DISORDERS

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Total body iron overload due to uncontrolled increase in iron absorption as occurs in hereditary hemochromatosis affects multiple organs, such as liver, heart and skin. The determination of plasma iron concentration is relevant as it may constitute an additional indicator of therapy efficacy, and of its availability to tissues. Also, skin, as an accessible organ affected by this disease, can be used to monitor body iron status, eventually reflecting what occurs in other organs.

The objective of the on-going project is to assess iron body status in haemochromatosis. Routine iron metabolism indicators, such as serum ferritin concentration, total iron binding capacity and transferrin saturation were assessed in sixteen patients with primary haemochromatosis along the phlebotomy therapeutic programme. Also iron hepatic deposits were determined using nuclear magnetic resonance. Nuclear Microscopy techniques were used to quantify and image iron in vivo at the epidermis and dermis skin layers.

Plasma iron concentrations were carried out using Total Reflection X-ray Fluorescence (TXRF) preceded by acid digestion in closed Teflon bombs. To provide reliable and accurate results in blood trace element determination that can be useful in biomedical studies, quality assurance schemes were implemented and uncertainties were estimated. Using plasma data gathered from haemochromatosis patients and controls the measurement uncertainty and the accuracy evaluation for iron was improved, as this study provided sufficient statistics for the repeatability and recovery results.

At the initial phase of the disease a strong relationship between iron concentrations in plasma and skin, as well as with serum ferritin, was found. However, at maintenance phases of the therapy programme, the observed decrease of iron concentration in plasma and skin reflects the marginally high liver iron deposits in opposition to the sharp decrease exhibited by ferritin concentration and transferrin saturation in serum. These observations point out an interesting role for plasma and skin iron evaluation using X-ray spectrometry methods, in the disease progression and therapy efficacy.

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QUALITY CONTROL OF REFERENCE, GENERIC, SIMILAR AMOXILLIN AND DICLOFENAC BY X-RAY SCATTERING AND CHEMOMETRICS

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The production and commercialization of generic drugs is becoming a common practice in Brazil. So, it is very interesting that simple, fast, non-destructive, non residue generation, of low cost and efficient methods be developed to guarantee the quality of the product in the market and, mainly, the authenticity of the formulation presented in the label.

The objective of this work was the use of X-ray spectroscopy to control the quality of reference, generic and similar amoxicillin and diclofenac, common drugs encountered in the market and consumed by Brazilian people. Amoxicillin and diclofenac, acquired with no receipt in the local market, in three distinct physical states and from different trademarks were irradiated with no pretreatment. The equipment was a bench-top Energy Dispersive X-ray Spectrometry (EDX 700, Shimadzu). The irradiation conditions were: irradiation time-100 s, beam collimation-10 mm, X-ray source-Rh tube, voltage-50 kV and 25 % of detector dead time. The spectra were treated by Principal Component Analysis, considering mainly the Compton and Rayleigh scattering regions, which are susceptible to variations in sample content, morphology and structure.

A clear separation was observed among the reference, generic and similar drugs, independently of the presented form (tablet, capsule, liquid or powder for suspension). It was also observed for the two drugs that one of generic sample has been grouped together with the references, evidencing the possibly of this sample is presenting similar characteristics with the reference group.

One of the samples of the amoxicillin generic drugs showed a high content of Ti, possibly in the form of TiO_2 . This composition is usually added to alter some properties of drugs, but with maximum allowed content of 1% w/w (according to FDA, Food and Drug Administration). In this sample, the %Ti was of $2,6 \pm 0,2\%$ (w/w), well higher than the allowed concentration.

By conclusion, X-ray Spectrometry allied to chemometrics is a new possibility to perform the quality control of reference, generic and similar drugs.

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STUDY OF THE EFFECTS OF CHRONIC ARSENIC POISONING IN RAT ORGANS BY MEANS OF SYNCHROTRON MICROSCOPIC X-RAY FLUORESCENCE ANALYSIS

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Arsenic is a naturally occurring element widely present in the environment. It is known that groundwater contamination represents a major source of exposure of human and animals to toxic levels of arsenic upon utilization of such ground waters for irrigation purposes. Chronic inorganic arsenic exposure in humans is causally associated with development of malignancies in various tissues (skin, urinary bladder, lung, prostate, kidney and liver)[1,2,3]. There are reports of elevated cancer risks at multiple countries where subsets of the population are exposed to arsenic-contaminated drinking water [1,4]

Synchrotron microscopic X-ray fluorescence analysis (μ -SRXRF) was applied to determine the two-dimensional distributions of Cl, K, Fe, Cu, Zn, As and Br concentrations in slices of different rat organs. Mapping of x-ray fluorescence intensities in freeze-dried organs sections were done at DO09B beam line[5] of the Synchrotron Light National Laboratory (Laboratório Nacional de Luz Síncrotron, LNLS). The bulk elemental analysis of mapped samples were done using the BRUKER SRS3400 XRF spectrometer located at CEPROCOR in Córdoba, where also were prepared the samples and standards. The animals received drinking water containing 100 ppm of sodium arsenite ad libitum for 30 and 60 days. Animal handling and experimental procedures were executed in agreement with the Guidelines for the Care and Use of Laboratory Animals approved by the Animal Care Committee from 'Universidad Nacional de Córdoba', Argentina. Lyophilized samples sectioned from normal and diseased rats were scanned with a collimated white synchrotron spectrum (300 μ m x 300 μ m pixel area). A correlation study between spatial distributions of the elements was performed for kidney, brain and pancreas of rats. The results allow us to formulate interesting hypothesis which are reasonable well founded by biophysical principles. Antioxidant effects or electrostatic attraction explain some correlation patterns under arsenic exposure. In particular, the accumulation of arsenic and copper in rat kidney induced by arsenic exposure was corroborated and the spatial distributions of these elements were studied in detail. While copper was restricted to renal cortex, arsenic shown changes in its spatial distribution suggesting nephrotoxicity.

Synchrotron microscopic X-ray fluorescence analysis, due to intrinsic characteristics of SR, is able to implement multielemental spectrochemical analysis with spatial resolution on the micrometer scale. It shows high efficiency for trace element determination and short time of analysis requirements. The results show that μ -SRXRF is a very well-positioned and precise technique to study the effects of arsenic contamination on the spatial distributions of elements in mammal tissues.

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TWO-DIMENSIONAL ELEMENTAL MAPPING BY μ -SRXRF IN LIVER SLICES WITH CONTINUOUS SCANNING MODEGerald Falkenberg¹, Romana Höftberger², Friedrich Wrba³, Wolf Osterode⁴*1 Hamburger Synchrotronstrahlungslabor HASYLAB, Deutsches Elektronensynchrotron DESY**2 Medizin Universität Wien, Klinisches Institut für Neurologie**3 Medizin Universität Wien, Klinisches Institut für Pathologie**4 Medizin Universität Wien, Univ. Klinik für Inner Medizin IV*

To compare elemental mapping with biological structures in histological slices large areas in the millimeter range, but with microscopic resolution are often required. To test whether two-dimensional scans can be performed in an appropriate time with sufficient results we investigated normal liver tissue and liver tissue from patients with genetically disturbed iron metabolism (haemochromatosis, HC) in a continuous scanning mode by μ -SRXRF.

Methods: μ -SRXRF measurements were performed at beamline L of the DORIS III storage ring at HASYLAB/DESY in Hamburg. Slices 10 μm of thickness - imbedded in paraffin - were fixed on trace element free Ultralene foil for investigation. The white beam of the bending magnet was monochromatized by a double multilayer monochromator (NiC). The energy of the incoming beam was set to 17.5 keV for all measurements, and the monochromatic X-ray beam was focused by a polycapillary half-lens to a cross section of 15 μm providing a flux of 10^{11} photons/s. A Silicon multi-cathode X-ray Spectrometer VORTEX-EX (Radiant Detector Technologies) was employed in combination with a CANBERRA 2060 digital pulse processor. The system provided an excellent energy resolution of 160 eV (5.8 keV) for all count rates up to 80 000 cts/s.

Results: In normal liver tissue, after fixation and imbedding in paraffin, mean Fe, Cu and Zn concentrations were 152 ± 54 , 20.1 ± 4.3 and 88.9 ± 19.5 $\mu\text{g/g}$ sample weight, respectively. No substantial, characteristic differences in their distribution were found in the two-dimensional scans. In slices from patients with HC mean Fe, Cu and Zn concentrations were 1102 ± 53.9 , 35.9 ± 14.6 and 27.2 ± 6.7 $\mu\text{g/g}$ sample weight, respectively. Additionally, a significant decrease in phosphorus and sulphur concentrations existed. An increased Cu around cirrhotic regenerations nodules is mostly associated with a lymphocytic infiltration in this region. Analyzing Fe in different sample regions reveals negative dependencies between Fe and Cu, Cu and Zn, but a positive one between Fe and Zn.

Conclusion: In the continuous scanning mode elemental distribution in a near histological resolution (20x light microscope) can be achieved in due time providing additional metabolic features.

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THE EFFECT OF CORRELATION BETWEEN THE K-ALPHA AND THE K-BETA LEAD PEAK CONCENTRATIONS ON THE UNCERTAINTY IN THE RESULT OF IN VIVO ¹⁰⁹Cd KXRF BONE LEAD MEASUREMENT

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The effect of covariance between the K-alpha and K-beta lead peak concentrations on the uncertainty in the result of the ¹⁰⁹Cd K X Ray Fluorescence measurement of lead in human bone will be addressed. It is commonly believed that this covariance arises as a result of the mutual dependence of the amplitudes of the K-alpha and K-beta Pb peaks on the amplitude of the coherent peak. Crude estimates of the uncertainty have explored this mutual dependence and concluded that the effect of covariance on the measurement uncertainty is small. A refinement to the method of estimating the covariance between peak concentrations will be discussed which is based on the correlation coefficient between the K-alpha and K-beta peak amplitudes and on their uncertainties based on repeated measurements performed on lead phantoms. The revised uncertainties following this method exceed the uncertainties estimated by the accepted method by 40 %, which suggests a much stronger effect of covariance on the measurement uncertainty than previously reported.

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**CHARACTERIZATION OF CATARACT IN DOGS: TRACE ELEMENTS
CONCENTRATION FOR MATURE AND IMMATURE CATARACT**

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The present investigation is a multidisciplinary study aiming to clarify the relationship among essential trace elements and the levels of opacity in canine cataract lenses. The role of some trace elements, especially metals, in the pathogenesis of aging diseases is not completely known. Cataract is an aging manifestation of multifactorial etiology. In this study, the monitoring of trace elements in cataract is presented. The first step was the definition of lens characteristics according to its progression. Clinical cases of mature and immature cataract were selected by age from 2 to 15 years old. Cataract grades were assessed by the ophthalmologists through a slit-lamp biomicroscope before surgery. This exam was considered for quantification of the degree of cataractogenesis. Concentrations for Ca, Fe, Cu, Zn, and Sr were carried out by direct analysis of dried 100 canine lenses by X-Ray fluorescence spectrometry. Distinct values of trace elements were obtained to each cataract type. These results suggest a possible influence on Ca, Fe and Cu lens content to distinct levels of lens opacity. Considering the average values, the Ca, Fe, Cu and Sr concentration were higher in mature cataract than in immature cataract. The Zinc concentration showed similar average values for both types of cataract development. A negative correlation was found between Ca-Fe and Ca-Cu concentrations to mature cataract; and a positive correlation for immature cataract. A positive correlation was observed for Zn-Fe to mature cataract and a negative correlation for the elements in immature cataract. Positive correlation was obtained for Zn-Cu and Zn-Sr for both cataract progressions.

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X-RAY NANOPHOTONICS FOR MATERIAL STRUCTURES ON BASE OF THE PLANAR WAVEGUIDE-RESONATOR

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Development of the material structure nanotechnology is defined in great part by possibilities of its dimension, structure and element diagnostics. Possibilities of conventional methods based on the visible light and ultraviolet radiation using are objective limited by effect of the diffraction satellites appearing. The implementation of a nanosize object testing by standard X-ray technique application is awkward owing to the reliable systems absence formed nanosize radiation beams. Significant hitch in the nanophotonic development was designated by discovery of the specific mechanism for X-ray flux passing through nanosize cavities in material – the mechanism of its waveguide-resonance propagation or the radiation superstream mechanism [1]. This mechanism is characterized by lower attenuation of the radiation flux at its propagation through nanosize extended slit clearance in comparison with the flux multiple external total reflection. It allows to form X-ray filiform fluxes with a nanosize width, its being not accompanied diffraction satellites. Moreover, the waveguide-resonance mechanism gives an opportunity to influence with high efficiency on X-ray flux by the mediate manner [2]. The simplest device functioned on base of this mechanism is the planar X-ray waveguide-resonator (PXWR) constituted the air narrow extended slit with width 20-200 nm which is formed by two planar polished dielectric reflectors [3].

The work presents the detail information about space X-ray intensity distribution for the characteristic component of fluxes formed by waveguide-resonators with a diverse design. There are adduced data shown that the waveguide-resonator radiation transport properties is very faintly depended from magnitude of the reflectors material absorption factor. X-ray flux transport features of the composite planar waveguide-resonator (CPXWR) [2] are discussed, too. Results of the features study allows to maintain that it is possible to operate with its emergent beam properties by influence on the uniform interference field of X-ray standing wave excited by initial radiation in its slit clearance space. Some attention is devoted to discussion of the waveguide-resonance conception principles. There are presented results of PXWR practical using for diffractometry and for X-ray fluorescence analysis. Main directions and methods for the waveguide-resonance conception development are pointed.

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APPLICATIONS OF TWO-WAVE X-RAY REFLECTOMETRY IN STUDY OF NANOSTRUCTURES

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Reflection/transmission and energy-dispersive properties of thin film semitransparent monochromators (SM) are analyzed. Results of experimental investigation of highly oriented pyrolytic graphite films ranging from 5 to 100 μm are presented. It is shown that freely suspended SM 35-50 μm thick (3 cm^2) have typically a mosaic spread down to $20'$, and its reflectivity is nearing that of bulk graphite monochromators. High SM transmission coefficient (0,8-0,9 at $E\sim 10\text{ keV}$) provide effective opportunities of spectral line selection and spectral line mixing in collimated X-ray beams.

As an example of practical application the scheme of the multi-wavelength

X-ray reflectometer is described. Its basic feature is a beam-splitter with SM, bulk monochromator, rotation stages, and corresponding number of scintillation detectors connected to registration channels. The beam-splitter is placed in the position of an analyzer and every monochromator can be tuned to a predetermined spectral line. This scheme offers unique device capabilities:

1 – simultaneous measurements of reflection and refraction angle dependences in different spectral bands;

2 – ratio reflectometry mode and ideal calibration of reflection curves,

3 – regulation of the spectral band width in the analyzed beam.

Examples of reflecto- and refractometry investigations of surface layers and multilayer nanostructures with a new device are presented.

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X-RAY FLUORESCENCE ANALYSIS OF STEEL USING VERBA-XRF CONCEPTION

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Analysis of iron based allows which contain (besides iron) 15 chemical elements: Mo, Nb, Zr, W, Cu, Ni, Co, Mn, Cr, V, Ti, S, P, Si and Al. For each of these elements the range of the determined content is from 0,001 to 50 % when the contents of other fourteen elements vary from zero until 50 %. It should be underlined, that the program reliably determines the content of S and P in samples with significant amount of Mo, Nb, Zr, and W. This is a big problem for traditional XRF analysis methods.

The contents of fifteen above-mentioned elements are determined by X-Ray spectrometers with wavelength dispersion and using Fe15v computer program. The content of the base – iron is calculated by the program as the difference between 100% and the sum of the contents of these 15 chemical elements. Analysis mode is the external standard by VERBA-XRF conception with the registration of radiation of analytical lines of all 15 elements except the analytical line of iron. Each analytical line is assigned a single external standard - Benchmark Reference Material (BRM). One benchmark sample could be a BRM for several or all-analytical lines. Fe15v computer program contains corrections of intensities of each analytical line on the influence of each other fifteen elements of the sample which is caused by the processes of interaction of primary X-Ray radiation with the sample. Corrections connected to the operation of the device (dead time of detector, line overlap and etc.) are determined with the help of the group of certified reference materials (CRM), which should be available at any laboratory for estimations or determination of its competence according to ISO/IEC 17025 standard.

BRM is the object of information transfer from a group of CRM to the sample during routine analysis with the help of Fe15v program. During the preparation stage to routine analysis, the virtual content of elements in BRM is determined using analysis of all groups of CRM. The obtained virtual content provides the absence of significant discrepancy between the results of the analysis and the data of certification of CRM. Simultaneously, Fe15v program calculates the magnitude of the "dead time" of the detector, and computes the coefficients for corrections on line overlap and the magnitude of the background.

The experiment was held using spectrometers: ARL 72000 S and SRM-25 (Russia). There were analyzed 149 CRM produced by different manufacturers. There were allows starting from pure iron to high-doped alloys with the iron content of 40%. Thus, the whole range of all content variations, which happen in practice, were covered. The results of the analysis had no systematic errors. At the same time, it was discovered that CRM of some manufacturers had incorrect data of certification of content of some elements, which was later confirmed by the manufacturers of these CRM. The competence of the laboratory to produce technically valid data was demonstrated.

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ANALYSIS OF ALTERNATIVE FUEL IN THE CEMENT INDUSTRY

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Years ago cement industry has started using alternative fuels in the cement kilns to reduce the use of natural fuel resources. By doing this, the cement kiln is used as a very versatile incinerator, whose main product is Portland cement. In some countries regulatory limits for these alternative fuels have been set, in others cement manufacturers use their internal limits for the elemental composition of these materials. The analysis of alternative fuel is one of the standard applications for XRF. As many elements have to be monitored, energy-dispersive XRF (EDXRF) instruments show a benefit from the simultaneous determination of a wide range of elements. Two international standard test methods already have been established for this in the past. With the implementation of the latest generation of polarization- and secondary target excitation into these EDXRF instruments, detection limits can be reached, which are fit-for-purpose for the application. In comparison to conventional analysis techniques as ICP-OES and AAS, XRF requires less sample preparation and offers by this naturally a fast analysis of the alternative fuel sample.

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ANALYSIS OF HONEY BY X-RAY SPECTROSCOPY ALLIED TO CHEMOMETRICS

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The importance of honey has been recently upgraded because of its nutrient and therapeutic effects. Thus, studies of honey have increased exponentially in terms of both geographic and botanical origin. Therefore, the need for more effective quality control methods aiming at detecting adulteration has arisen. Several novel, fast, and accurate methods like AAS, HPLC, GC-MS, direct ES-MS, TLC, HPAED-PAD, NMR, FT-Raman, and NIR have enriched the arsenal of analytical tools for this purpose [1]. However, apart from these methods, the application of multivariate analysis and, in particular Principal Components Analysis (PCA), has proved to be extremely useful for grouping and detecting honey of various origins. In this work, the analytical procedure involves no sample pre-treatment: the honey is weighed directly in an X-ray cell and irradiated for 100 seconds in a conventional EDXRF equipment (Shimadzu EDX 700) equipped with a Rh tube as X-ray source and a Si(Li) detector. A power of 50 kV was applied in the tube operating with a current of 100 mA. For the classification model the spectra collected in the equipment are processed by PCA. For calibration Partial Least Squares (PLS) is employed to treat the data. In this case the collected spectra are treated against the pH values for different honey samples. The results obtained showed a good classification model to identify different kinds of honey and, at the same time, a good calibration model to predict the pH value of the sample. It is interesting to point out that the pH value is important to evaluate the authenticity of the honey. Samples of honey with pH values between 3-4 are considered samples of good quality while pH out of this range can indicate some addition of sugar cane syrup to the honey. Methods for detection of adulteration of honey with cane sugar syrup have been studied lately [2] and the technique proposed in this work can be considered very powerful and useful to identify the nature of the honey samples as well as to detect their authenticities at very low cost and with a very simple method.

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**X-RAY SPECTROSCOPY AND MULTIVARIATE ANALYSIS IN
INVESTIGATING COUNTERFEIT COINS.**

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In March 1994, the Brazilian government decided to change its currency from the Cruzeiro to the Real and, to do so, the Brazilian Central Bank was forced to substitute, in a short period of time, all the bills and coins that were in circulation throughout the country. Real coins did not present adequate quality parameters, mostly caused by the choice of inappropriate raw materials for coin production. This fact has stimulated countless falsifications of these coins, mainly these with a value of one Real, being registered as police cases in several areas of the country. In these cases the determination of counterfeiting were based exclusively on the comparison of some visual characteristics of impression and relief that diverged when confronted with true coins. In that way, looking for a more critical analysis applicable for this kind of investigation, this work proposes the use of a non-destructive technique, to rapidly identify counterfeit coins at very low cost using a bench-top EDXRF equipment coupled with chemometric tools. Six groups of counterfeit coins seized by the Federal Police from Foz de Iguaçu-PR in 2002 were donated for the work and ninety-two R\$ 1 counterfeit coins were randomly chosen for the analysis, while ten not falsified (real) coins were also evaluated for comparison. The procedure involved no sample pre-treatment: it was based only in attaching the samples onto the holder with adhesive tape and irradiating them for 75 seconds in conventional EDXRF equipment (Shimadzu EDX 700) equipped with an Rh tube as source of the X-rays and a Si(Li) detector. A power of 50 kV was applied in the tube operating with a current of 100 mA and the spectra were collected. Typical XRF spectra of counterfeit and true coins showed that the major elements are Fe, Cr, Si, Tl, Ni, Zn and C in both samples while Nb was detected only in the counterfeit coins. These same spectra processed by Principal Component Analysis (PCA) supplied a convenient classification model used to identify the counterfeit coins since two groups were formed. In this way the technique proposed in this work is seen to be very powerful and useful to rapidly identify falsified samples at very low cost and with the possibility of performing measurements for this kind of investigation in situ with a portable instrument.

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**DETERMINATION OF VARNISHES NONVOLATILE MATTER
USING XRS AND PLS**

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In quality control of paints and/or varnishes, some standard test methods are used for evaluation and determination of their physical and chemical properties [1]. The procedures for these test methods (nonvolatile content of varnishes, for example) are established by ASTM (American Society for Testing and Materials) [2]. The application of these tests is relevant for paint quality control. However, some of the procedures involved, which should be done routinely, consume a lot of samples, time, equipment (ovens, viscometers, glossmeters, among others) and operator effort. These characterizations can lead to high cost routine analysis, also generating great volumes of industrial waste. Therefore, the objective of this study is to offer an alternative for the determination of nonvolatile matter in varnishes. The proposed methodology is based on the use of X-ray spectrometry (XRS) [3] and multivariate calibration, using partial least squares (PLS) for correlation with values obtained by the ASTM test method. For this study, 14 XRS spectra from commercial varnishes were obtained. The equipment conditions were: measurement time of 100 s; spectra obtained from 0 to 40 keV region, with spectral resolution of 0.02 keV. The X-ray source was a Rh tube with voltage of 50 kV and collimator of 10 mm. Each varnish (around 2 g) were placed in special Teflon cells and analysed at least 3 times. The nonvolatile matter was determined according to ASTM D 1644 and the values varied from 34 to 54 %. With these data and the XRS spectra, a PLS model was proposed using Matlab version 6.5 and PLS-Toolbox version 2.1. In order to help the selection of samples for the calibration and validation sets, a principal component analysis (PCA) was performed (the spectral data were mean centered). The calibration set was composed of 10 varnishes (with nonvolatile matter varying from 34 to 54 %) and the other samples composed the validation set (with nonvolatile matter varying from 42 to 47 %). The most appropriate number of latent variables (LV), according to PRESS (predictive residual error sum of squares) values, was 2. The values for RMSEC (root mean square error of cross-validation) and RMSEV were 7 % (calibration set) and 1 % (validation set). The model presented a good prediction for both sets and the relative errors varied typically from -10 to 11 % and from -1 to 2 % for the calibration and validation sets, respectively. The proposed methodology shows an alternative for nonvolatile matter determination using fewer amounts of samples and the results quality were equivalent.

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**CALIBRATION AND CLASSIFICATION OF SUGARS USING
CHEMOMETRICS TOOLS AND X-RAY SPECTROMETRY**

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Carbohydrates are organic compounds which include sugars, starch and cellulose and they are defined as polyhydroxyaldehydes, or polyhydroxycetons, or substances that, after hydrolysis, produce such compounds. Carbohydrates are divided in three main classes, depending on the number of simple sugar unities produced after their hydrolysis: (i) monosaccharides are simple sugars that can not be transformed in simpler sugars, (ii) disaccharides are double sugars that produce two simple sugars, and (iii) polysaccharides are complex sugars and that produce several simple sugars after being hydrolyzed. It is known that sugars may present stereoisomery, showing two optically actives forms. When polarized light crosses through a solution containing an optically active substance, the plan of the polarized light suffers rotation, according to the Theory of Van't Hoff, due to the presence of one or more chiral carbons [1].

In this work, two studies were done; the first one proposes a new method for classification of five distinct types of sugar (manitol, glucose, fructose, lactose and sucrose), that belong to the classes of mono or disaccharides. The second study verifies the sucrose inversion, where the calibrations of the rotation angle and the inversion kinetics are reached. In both studies the acquired spectra (in an EDXRS) were organized in a data matrix, treated and submitted to Chemometric Analysis by Principal Component Analysis (PCA) or Partial Least Squares (PLS). In the first study, the use of PCA showed the existence of five groups according with the type of sugar, classifying them. In the second study, a polarimeter was used to obtain the rotation angle from the sucrose inversion at each min after the addition of a HCl solution. In parallel with the polarimeter readings, the X-ray spectra were obtained. Good calibrations were obtained for angle rotation (with correlation coefficient = 0.955167) and inversion times (with correlation coefficient = 0.925091).

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**PREPARATION AND CERTIFICATION OF THE NEW REFERENCE
MATERIALS; PLASTICS (DISK FORM, JSAC 0621 – 0625) FOR
DETERMINATION OF MERCURY USING X-RAY FLUORESCENT
ANALYSIS**

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The Japan Society for Analytical Chemistry has developed the new certified reference materials (CRMs) for the analysis of hazardous elements of mercury in polyester disks using X-ray fluorescent analysis. These CRMs (named as JSAC 0621 – 0625) were prepared as follows; Raw material of polyester mixed with organometallic compounds and hardener was casted in disk type molds. The disks were removed from the glass base plates after 12 h hardening at room temperature, and both face of the disks were ground by milling machine to control their thickness in 4.0 mm. Concentrations of the five levels of mercury were ranged from 0 to 250 mg/kg. Homogeneity test of prepared disks had shown excellent results. Interlaboratory comparison study for the certification was performed by 21 laboratory's participants. The z-scores in robust statistical method was applied for the evaluation of outliers. The certified values were assigned after discarding outliers. The uncertainties of certified values were determined as the confidence levels of 95 %. The presented CRMs are expected to be useful for the quality assurance and quality control of mercury in the plastics.

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SAIME: STUDY AND DEVELOPMENT OF INNOVATIVE ANALYSIS METHODS FOR DETERMINING GOLD IN PRECIOUS METAL ALLOYS BY EDXRF.

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The SAIME project is a research project aimed at studying innovative analysis methods for determining gold in metal alloys employed in jewelry. This kind of research is motivated by the request of certification of the product coming from the markets, especially from the foreign ones. In order to satisfy this request appropriate analyses aimed at determining the composition must be performed by authorized personnel on the goldsmith alloys, both at the level of raw material and of final products.

Regarding EDXRF analysis, the aim of the project is the development of an analysis system based on X-ray fluorescence, that must achieve an accuracy better than 1 % on the final products, and better than 0,1% on the laboratory samples; the minimum expectation is for this system to enable a preliminary screening of the products, so as to allow the selection of those that need further and more precise analyses of a destructive type.

First of all, we considered different commercial EDXRF instruments and compared their performance in order to determine which was the most suitable for our application. To allow an accurate comparison of the instruments, we assessed a protocol of analysis taking into account only hardware performances, being the development of a software specialized in precious alloys one of the objectives of the project.

The instruments were compared based on the following characteristics:

- Stability;
- Linearity;
- Minimum Detectable Limit, MDL;
- Energy resolution;
- Usability.

To guarantee homogeneous results, the analyses were performed on samples expressly realized for this purpose and the spectral deconvolutions were performed through the same software (WinAxil, Camberra Inc.).

We compared six instruments (three of which were portable), and in this work we will show the protocol of analysis assessed and the results obtained.

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**DEVELOPMENT OF TWO ANALYTICAL METHODOLOGIES FOR
QUANTITATIVE DETERMINATION OF TOTAL Cd, Cr, Hg, Pb IN
FLUORINATED MATERIALS BY MEANS OF WDS-XRF SPECTROSCOPY**

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In the last decade the European Union's vision of the environmental impact of industry has moved its focus to the entire lifecycle of the products. An emphasis on the persistence in the environment of the toxic heavy metals Pb, Cd, Hg and Cr(VI) has been put by two important European Directives already effective on the automotive and the electronic equipment sectors [1, 2].

Solvay Solexis provides both the automotive and the electronic equipment industries and all the three main categories of Solvay Solexis products (Perfluoropolyether derivatives, Fluorinated Elastomers and Plastomers) are required to be supported by conformity declarations based on the two Directives.

In the last years the Elemental Analysis Laboratory had to develop analytical methods able to accurately determine the residues of the mentioned heavy metals.

The typical procedure used for the total metal determination on the very stable Fluorinated Polymers, which includes an incineration step, can't be used because of analyte loss of the volatile elements Hg, Cd and Pb. Alternative methodologies typically used in inorganic analysis are generally not suitable for fluorinated polymers matrices. Decomposition at high temperature in the presence of inorganic acids and with microwave energy assistance is virtually impossible because of the intrinsic chemical stability of these polymers and their non-wettability. Both properties increase with the Fluorine content in the molecule and for these reasons the closed vessel itself for microwave decomposition is generally made of fluororesin.

Different approaches were developed either working on liquid solutions or on cold-pressed pellets of the polymers, using appropriate metal standard sources.

Two methodologies are presented for the analysis of total Pb, Cd, Hg and Cr on different kind of Fluorinated Plastomers and Elastomers by means of WDS X-Ray Fluorescence Spectroscopy.

[1] Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on End-of Life Vehicles (ELV)

[2] Directive 2002/95/EC of the European Parliament and of the Council of 27 January 2003 on the Restriction Of Hazardous Substances in electrical and electronic equipment (ROHS)

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**QUANTITATIVE AND STANDARD-LESS ANALYSIS OF HIGH ALLOY
STEEL BY WAVELENGTH DISPERSIVE X-RAY FLUORESCENCE
SPECTROSCOPY (WD-XRF)**

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The XRF spectroscopy is widely used for the qualitative and quantitative elemental analysis in environmental, geological and biological industry. The X-ray spectrum during the XRF process reveals number of characteristics peaks. The energy of the peak leads to the elemental identification i.e. qualitative analysis, while the peak intensity provides the relevant or absolute elemental concentrations i.e. semi qualitative or quantitative analysis. In the metallurgical/steel industry, quantitative analysis are the core requirement, however certified reference materials (CRM's) for the calibration of ferrous/non ferrous materials are very expensive and rarely available for high alloy steels. In the present study, alloying elements (Ti, Cr, Mn, Co, Cu and Mo) are analyzed in commercially available certified reference materials (CRM's) by WD-XRF, SEM-EDS and ICP-AES assuming to be unknown samples. In addition, all the alloying elements are analyzed by standard-less qualitative program by WD-XRF. A comparison is made between the elements analyzed by quantitative WD-XRF, ICP-AES and SEM-EDS with the qualitative analytical program. The study provides that qualitative WD-XRF can be utilized as a potential technique for the quantitative analysis of alloying elements where there is non-availability of CRM's for high alloy steels in metallurgical/materials industry.

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**ACCURATE ANALYSIS OF LIGHT ELEMENT SAMPLES BY
EVALUATION OF THE COMPLETE SCATTERED BACKGROUND
SPECTRUM**

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In EDXRF mainly fluorescent and scattered primary beam radiation contribute to the radiation detected. The scattered radiation is mostly regarded as an added distortion to the fluorescent spectrum. To get accurate analytical results, different models for background correction are employed. The scattered radiation itself however can not only be regarded as noise, but it also yields useful information about the matrix of the sample under investigation. The newest version of the WinFTM® software uses a model to calculate the scattered radiation for a given primary x-ray source and hardware configuration (detector type, geometry) . The software uses this information in the evaluation of the measurement results. The model takes into account the elastic and Compton scattering not only for the characteristic lines, but also for the Bremsstrahlung continuum of the x-ray tube. There are two main advantages in this kind of evaluation: on the one hand the spectrum evaluation is automatically corrected due to the inherent calculation of the background and on the other hand the software yields additional information on the mean mass density or the mean atomic number of the matrix.

The benefit of the calculation and evaluation of the scattered radiation is presented for two applications:

1. Measurement of hazardous substances in plastic material (RoHS). When measuring small amounts of Pb, Hg, Cd, Cr or Br in plastic, the spectrum is dominated by scattered radiation. With the new software it is now possible to measure the correct concentrations of the listed elements independent of thickness (from several 10ths of μm to some mm) and geometry (plates, granulate, cables, etc.) of the sample.
2. Thickness measurement of plastic foils. Evaluating the scattered radiation it is possible to measure the thickness of plastic foils without using fluorescent lines in the range from μm to cm.

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THE EFFECT OF NONHOMOGENEITY OF GOLD AND PLATINUM ALLOYS USING ED-XRF ANALYSIS

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It is the specific advantage of energy-dispersive X-ray fluorescence analysis (ED-XRF) that only a very small volume can be analyzed. Depth information is limited mainly by the attenuation of the detected fluorescence radiation. It is in the order of only a few microns. The lateral extension of the analyzed area runs from centimeters (handhelds) over millimeters and finally reaches down to micrometers using x-ray optics.

For some applications improved lateral resolution tends to become a disadvantage. In particular, the characterization of precious metal alloys is only directed to the average composition. The typical user in the jewelry industry only wants to know the total gold or platinum content of the specimen.

The perception of a homogeneous elemental distribution is an idea of perfection which in reality normally does not hold true. On the other hand, (most) evaluation software assumes this “ideal specimen” – and most of the users do the same; this leads to complications when results are compared from different measurement techniques. Often the effects of nonhomogeneity are small and can be neglected. However, in jewelry applications they must be taken into account.

Characterization of nonhomogeneity

Scans and mappings yield an impressive visualization of the lateral element distribution. Regions of maximum or minimum concentration can be easily localized.

Scans and mappings require flat surface specimens – and are time consuming. Often it is not possible to scan a sample (e.g. if a sample has to be measured in different orientations). Single measurements at random positions which are representative for the whole sample can be evaluated quantitatively with respect to the well-defined distribution parameters such as mean value and standard deviation. The inherent repeatability variation due to counting statistics has to be taken into account.

Design of experiment

The random (statistical) measuring uncertainty can be reduced by increasing the measuring time. The nonhomogeneity of the sample causes an independent random variation of the readings when different positions are analyzed. Therefore it is not practical just trying to achieve a high precision using long measurement times. On the other hand, too many single measurements with extremely short measurement times does not solve the problem because of a loss of time between the measurements. A guideline is developed to optimize the measuring strategy which takes into account both the typical nonhomogeneity and the statistical measuring uncertainty. Obviously, a homogeneous sample can be analyzed much more accurate within a given time budget.

A simple sample preparation diminishes the effect of nonhomogeneity

A nearly perfect homogenization of the sample material can be achieved by a new preparation technique which consists of chipping the metal and pressing the chips to a pellet. The chipping tool can be a drill or a milling head. Only a few 10 milligrams are needed for one pellet sample. The pellets can then be analyzed afterwards by other (destructive) techniques, of course.

The analysis of different types of platinum alloys demonstrates the principal of this homogenization technique. Standard reference material can be produced in this way as well.

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OPTIMISED PROCEDURES FOR TRACE ANALYSIS IN (LIQUID OR LOOSE POWDER) SAMPLES OF LIGHT MATRICES

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Wavelength-dispersive XRF (WD-XRF) has become a powerful tool in the hand of analytical scientists especially for the accurate trace analysis in hydrocarbon matrices. Due to specialized preparation techniques, contaminations and severe matrix effects typical the industrial routine use has been limited to specialists.

With the development of PETRO-QUANT, a powerful and easy-to-use evaluation tool for all hydrocarbon matrices, like lube oils, any kind of fuels, greases, plastics and polymers, WD-XRF for trace analysis has now become available for daily routine.

Beginning with special strategies for preparation and measurements of liquid or loose powder samples, new implications on the hardware design are presented. But sample preparation and new advances in instrumentation are not the only keys for success; the most important one is matrix correction.

The XRF analysis of light matrix elements H to O is difficult (poor count rates and very small information depths) up to impossible (H to Li, and even worse H to F, when analysing liquids or loose powder samples in liquid cells). The compensation of different matrix absorptions based on the respective compositions of these matrices is essential for good results. The benefits of the application of a simple quadratic algorithm up to the sample specific calculation of individual matrix coefficients based on fundamental parameters (“variable alphas”) are presented.

The application of full matrix correction approaches requires the knowledge of matrix compositions. Especially for light matrices these compositions may be not known and at least very hard to determine by XRF. Understanding the physics and transfer this knowledge to a new software, dedicated for trace analysis in petrochemical application is making trace analysis available for daily routine use.

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STRUCTURE AND PHYSICO-CHEMICAL PROPERTIES OF METAL CONTAINING NANO-COMPOSITES BASED ON POLYMER AND POROUS GLASSES

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This contribution considers the structure, and properties of novel materials: metal-polymer nano-composites, and metal/semiconductor clusters incorporated in porous glasses.

The metal-polymer nano-composites are produced by the chemical vapor deposition technique which bases on low temperature co-condensation of metal and monomer vapors followed by solid-state polymerization of the resulting co-condensates. The primary advantage of this technique over other conventional methods is the opportunity for stabilization of very small particles without any specific coordination bonds between the surface of the particle and the polymer environment or without any stabilizing compounds. Stable metal clusters of varying size were obtained also inside the porous glass matrix. Such materials are fabricated by leaching of initial sodium borosilicate glass with phase separation in an acid solution. These porous glasses are capable to sorb metal salt from solution and so they are efficient sorbents. The following reduction of metal ions can be performed under action of UV- or γ -radiation, as well as by various chemical reagents. So produced metal atoms aggregate forming metal nanoparticles bounded weakly to substrate.

Unlike other analogous systems, composites obtained by chemical vapor deposition technique demonstrate a marked increase in the content of small crystals with increasing metal content. The measurements show that in semiconductor PbS - poly-p-xylylene (PPX) composites the contribution of PbS-crystallites of approximately 30 Å size increases from 20 to 80% with an increase in the overall PbS-content from 4.7 to 10 vol.%. At the same time, the high PbS loading favors the formation of rather large crystals in the 70 Å size range. For this reason the mean size of crystal determined from the half-width of the X-ray diffraction line does not change significantly and remains in the range 40-50 Å. The size distribution of metallic Ag-nanocrystals in Ag-PPX composites shows the same behaviour mainly.

It is probable that the observed effect may be related to composite morphology. Our data show that an increase in the metal content decreases the polymer matrix crystallinity. It is believed that this process is accompanied by the formation of a large number of local defect sites where the crystals nucleate in the polymer matrix. This might explain the observed increase in the concentration of small crystallites, which partially aggregate in regions of polymer with more free volume to give small number of larger metal crystals.

The analogous investigations of nanocomposites structure based on porous borosilicate glass were carried out by use the electron microscopy and X-ray scattering. The samples containing nanoparticles Pd were prepared with Pd concentration 4-6 weight %. The SEM photograph of the porous glass sample containing Pd particles shows the average porous size is equal to 18-20 nm. The corresponding average diameter of Pd cluster which gives the small angle scattering is 16 nm.

These samples containing metal or semiconductor nanoparticles demonstrate interesting sensor, catalytic, sorption, optic and dielectric properties.

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ASPHALTENE DETERMINATION IN CRUDE OIL BY X-RAY SCATTERING SPECTROMETRY ALLIED TO CHEMOMETRICS

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Asphaltenes are petroleum constituents formed mainly by polycondensed aromatic rings and side aliphatic chains and, to a less extent, by acid groups and complexed metals. They are considered natural surfactants and so able to produce particles during several steps of petroleum refining. These particles may be adsorbed on the reservoir rock or otherwise, may form stable emulsions between oil and residual water. The asphaltene adsorption on the rocks may result in alterations in rock wettability, which can affect drainage in extraction processes. Also, in deep waters, the oil is subjected to low temperatures, producing blocking of rock porosity. In these cases, the non easy access may cause even the well loss. The determination of asphaltene content is of course a very significant matter. A fast and reliable method for this determination is of urgency.

X-ray Fluorescence (XRF) is a versatile multielementar technique, being applied to solid and liquid samples, without requiring a previous complex sample preparation. Data treatment can be processed via univariate calibration, when spectral peaks corresponding to elemental emissions are integrated and correlated to their respective known concentrations on standards. Nevertheless, XRF intensities are not always linearly proportional to the respective concentrations, when several effects may be operative, as matrix effects, interelemental effects and spectral interferences. Correction mathematical methods may be applied (e.g. Influence Coefficients Method and Fundamental Parameters Method), as well as chemometrics. In this last case, a multivariate handling of data is performed.

This work proposes a successful alternative to the standard methods that are based on laborious and delayed procedures, IP 143-01 and/or ASTM D6560-00, both equivalent methods based on the gravimetric determination of n-heptane insoluble fraction of crude petroleum. The X-ray scattering processes visualized in crude oil spectra can be treated by multivariate calibration and correlated with asphaltene concentrations obtained through the standard methods mentioned above, an unusual way to use XRF conventional equipments. This work shows this possibility, turning the determination fast, reliable, non-destructive of low application cost and showing the possibility to be applied on line.

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MICROSTRUCTURAL CHARACTERISATION OF EUTECTOID AND TRIP STEELS BY EDS, EBSD XRD AND THERMOELECTRIC ANALYSIS

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There are presented the investigations of unalloyed eutectoid steel strips. The tempering of strips was performed on continuous hardening and tempering lines which was preceded by cold rolling and annealing. The microstructure of the tempered strips a fine mixture of ferrite and cementite. It can also contain residual austenite, which amount decreases by plastic deformation or fatigue. Both the morphology of the ferrite and the cementite and the amount of the residual austenite considerably affect the mechanical properties of the tempered strip, especially the resistance to high cycle fatigue. The amount of residual was determined by X-ray diffraction (XRD) and electron backscattered diffraction (EBSD) analysis.

Measuring of thermoelectric power (TEP) is based on the Seebeck-effect. Those phase transformations, where the diffusion of interstitials, the change of dislocation structure is important can be described with this measurement well suitable. TEP measurement is also sensitive to precipitations and segregations. XRD, EBSD analysis and mechanical testing were aimed at the determination of differences, which are caused by the fabrication process. Fine differences of the same steel type – CK75 steel – characterized by the TEP measurements of many hundreds steel sample. The most important differences were investigated by different mechanical and microstructural measuring methods are the followings: the strain to fracture, the inhomogeneity of annealing temperature and the different quantity of residual austenite, which was stabilised at the tempering phase of processing.

The microstructure of TRIP steels is composed of ferrite, bainite or/and martensite, and austenite. The examined TRIP steels were produced in Hungary. The microstructure providing mechanical properties transforms by the effect of plastic deformation, heat treatment and welding. XRD, EBSD analysis TEP measurement, which concern TRIP steels, shows the connection between the thermoelectric power and the phase transformations affected by plastic deformation, heat treatment and welding. It could be find quantitative relations between the measured thermoelectric property and the inner characteristics of the phase transformation for TRIP steel.

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USE OF WDXRF AND XRD TO ASSESS THE CONTENT AND CHEMICAL FORM OF METALS IN AUTOMOTIVE SHREDDER RESIDUES (ASR)Oscar Gonzalez¹, Ignacio Queralt¹, Jordi Soler², Manuela Hidalgo³*¹Laboratory of X-ray Analytical Applications, Institute of Earth Sciences "J. Almera"
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Shredder wastes or shredder residues (SR) are generated from business that recovers metals from waste materials, such as automobiles and house appliances. Ferrous alloys and other valuable non-ferrous metals (which are approximately 75 per cent of vehicle weight) are recovered for recycling and the rest has been historically sent to landfill. The European Directives for End-of-Life-Vehicle (ELV) and the Landfill Directive strongly recommend minimising wastes and landfill lands.

ASR is placed at landfills but its metal content should be evaluated before being definitely disposed. These analyses must be very fast and easy to do because the volume of wastes is very big. Although the residue should be treated to eliminate all the metal pollutants, sometimes the metal content of ASR overpasses the requirements and regulations for landfill disposal. Traditional techniques for detecting metals like the different kinds of atomic absorption or emission spectrometry require a previous digestion of the sample with strong acids, not always efficient for residual materials, composed by very stable oxides.

In this study we evaluate quantitatively the total metal content in different grain-size fractions of ASR by WDXRF (Wavelength Dispersive X-ray Fluorescence). We check also the availability of metals by the official leaching tests, required by landfill regulations. To solve discrepancy between anomalous high total content of some metals and the poor content of leaching extracts, we use X-ray diffraction (XRD) spectrometry to recognize the crystalline chemical form in what the metals are found.

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DETERMINATION OF TRACE ELEMENTS BY TXRF ANALYSIS IN TOBACCO SAMPLES FROM MEXICAN CIGARETTES

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Cigarette smoking and tobacco chewing account together for a large number of deaths every day. Numerous studies have identified an important number of inorganic toxic elements along with organic carcinogen and radioactive elements in tobacco [1]. It has been long suspected that, apart from organic and radioactive carcinogens, some inorganic elements may also be the cause of tobacco toxicity, altering the metabolism thus provoking the growth of tumors. In this work we have analyzed 9 different brands of cigarettes sold in the Mexican Market. Macerated tobacco samples after dried, were weighted, placed into the microwave vessel and digested in a mixture of suprapure nitric and hydrochloric acids. The vessel was then sealed and placed into the microwave digester for dissolution and digestion following the ramp of temperature and pressure. When digestion was completed, the vessels are removed from the digester, allowed to cool, and transferred to volumetric flasks where they were taken to a volume with de-ionized water. Aliquots of the digestate were analyzed in a Total X-ray Fluorescence Spectrometer Model TX-2000. At the same time and in the same way were treated NIST 1573 "tomato leaves", NIST 1572 "citrus leaves" standards and a blank, the former to check the elemental recovery and the latter to correct elemental concentration of samples. Results show the presence of some toxic elements such as Pb, Cr, Ni as well as essential elements such as K, Ca, etc. Results were compared with available data on some foreign brands tobacco [2, 3]; the probable reason for the difference in the contents of some of the elements found in Mexican brands are discussed.

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TXRF ANALYSIS ON ACTIVATED REFLECTORS

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Quartz reflectors were activated after acidification and 1,1'-carbonyldiimidazole attachment on their surface as well as with other activating substances. Various complexing reagents were attached on the surface of the activated quartz reflectors with special ability to react with mercury. The activated reflectors were immersed in high purity and drinking water solutions, containing low concentrations of mercury and selective mercury collection took place. After immobilization process reflector irradiation was performed by TXRF. Different complexing reagents were tested showing different collection capabilities, much higher than the blank samples (no activated reflectors). The impact of various experimental parameters and especially the coexistence of other metals were examined. A very good selectivity of Hg compared to numerous other metals was measured. The immobilized reagents were easily removed and the reflectors can be re-used for many times without any degradation. Very good linearity was achieved in a wide concentration range and the minimum detection limit was equal to 5 ppb (200 s measuring time).

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EVALUATION OF THE CONTAMINATION AND BIOAVAILABILITY OF HEAVY METALS IN LAKE SEDIMENTS USING SR-TXRF

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The analytical technique Total Reflection X-Ray Fluorescence (TXRF) was used to evaluate the contamination and bioavailability of heavy metals in lake sediment samples collected at different depths. The samples were collected in one of the lakes located next to ceramic industries in Santa Gertrudes, São Paulo State, Brazilian Southwest region, during the rain season. In order to determine the bioavailable fraction (weak linked or mobile fraction) and residual fraction (representative of the geological matrix) in sediment samples, procedures of acid extraction were implemented [1]. All the measurements were performed in the Brazilian Synchrotron Light Laboratory (LNLS), located in Campinas, São Paulo State. A polychromatic beam of the approximately 2 mm width and 0.3 mm height was used for sample excitation and for X-ray detection a Si(Li) detector was used [2]. The net areas of the X-ray peaks were obtained using the Quantitative X-ray Analysis System software. Elements as Al, Si, P, K, Ca, Ti, Cr, Mn, Fe, Co, Cu, Zn, Rb, Sr, Zr and Pb were determined in lake sediment samples. The elements V, Cr, Co, Cu, Zn and Pb which can be considered as environmental contaminants showed high availability. The concentrations of these elements are above the reference values recommended by Environmental Sanitary Technology Company (CETESB) [3] for protection of soil quality and underground waters of São Paulo State. So, the concentrations obtained in this work indicated a possible contamination of the studied area.

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**DETERMINATION OF TRACE ELEMENTS IN TREE-RINGS BY
SYNCHROTRON RADIATION TOTAL REFLECTION X-RAY
FLUORESCENCE ANALYSIS (SR-TXRF)**

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Urbanization and industrialization have introduced various harmful substances into the atmosphere. Environmental pollution is one of the main causes of life deteriorating. The analysis of chemical elements is the most frequently method used as monitor pollution. Various plants have been used as bioindicators like lichens, agricultural crops, ornamental plants and some species of trees. In temperate regions trees usually produce one growth ring every year and it is possible to date rings accurately. Trace metals are deposited in the rings and accumulated in the wood [1].

This study was undertaken to determine the levels of heavy metals pollution as an indication of the levels in plant tissues and to prepare a pollution distribution map for the study area. *Caesalpinia peltophoroides* (“Sibipiruna”) was used as bioindicator plant. The samples were removed of 34 years old species, planted in an avenue with great flow of vehicles. The samples were obtained through a method classified as no destructive [2]. In the sheets obtained after polishing were identified the growth rings in the period from 1971 up to 2003. The samples were crushed and the powder material was submitted to a acid digestion procedure. In five microliters of each sample was added Gallium as internal standard and so transferred onto a Perspex support and it was evaporated with infrared lamp producing a thin film in the substratum. Multielemental standards solutions, for the system calibration were prepared containing Al, Si, K, Ca, Ti, Cr, Fe, Ni, Zn, Se, Sr and Mo (K series) and Mo, Cd, Ba, Sb, Pt, Tl and Pb (L series) in different concentrations. All the measurements were performed in the X-Ray Fluorescence Beamline at the Synchrotron Light Source Laboratory (LNLS), located in Campinas, São Paulo State, Brazil. A polychromatic beam with energy ranges 4-22 keV and operating under total reflection conditions was used for sample excitation. For X-ray detection a semiconductor Si(Li) detector was employed [3]. Phosphorus, potassium, calcium, titanium, iron, barium and lead were determined. For Ti and Ba higher values were found between 1969 and 1970 and for Fe between the years 1974 and 1976. Lead concentration varied from 12 and 46 micrograms/gram for the period analyzed. Our study confirmed the usefulness of *Caesalpinia peltophoroides* (“Sibipiruna”) as bioindicator of the environmental pollution.

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STUDY OF THE HEAVY METAL REMOVAL IN WETLANDS BY SR-TXRF

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Among the countless systems developed for the treatment of liquid residues, the decantation ponds, sand filters and more complex systems as activated mud, we can emphasize the wetland system. A simple system, that with the aid of macrophytes (also known by the term hydrophytes) they promote the purification of the water, eliminating good part of the organic and inorganic residues, such as: match, nitrate and fecal coliforms, aiding in the decrease of the organic load thrown in the rivers. The wetlands represent an emergent technology, of cost low energy, efficient and aesthetic, indicating a good alternative to the conventional systems in the treatment of wastewater. The used system of wetland was installed in FEAGRI and it possesses two compartments of square superficial area (2x2m), with the adoption of two you cultivate of different macrophytes: *Typha* sp and *Eleocharis* sp. The samples of wastewater were weekly collected, for 16 weeks, in the entrance and in the exit of the system. Besides, samples of leaves of the macrophytes mentioned above with the purpose of verifying the degree of absorption of heavy metals were also collected. For the element P the system was shown efficient because the maximum text in the entrance of the system was of 249 mg.L⁻¹, while in the exits of the system the concentrations were the same to 18 mg.L⁻¹ and 16 mg.L⁻¹ for *Eleocharis* and *Typha*, respectively. The same fact was observed for S, even so the reduction in the concentration in the exit of the system it went inferior to have observed for P. Being compared the two macrophytes species the *Typha* presented a better efficiency, being verified a text of 12 mg.L⁻¹ in the entrance and 5 mg.L⁻¹ in the exit, while for *Eleocharis* the concentration in the exit was of 8 mg.L⁻¹. The concentrations of Zn in the leaves of *Eleocharis* varied of 7.6 to 44.3 mg.L⁻¹ and in the leaves of *Typha* of 2.9 to 46.5 mg.L⁻¹ and they are higher than in the entrance of the wastewater in the system where the concentrations are in the strip of 0.2 to 1.7 mg.L⁻¹. On the other side, in the exit of the system the concentration strip went from 1.2 to 7.9 mg.L⁻¹, indicating that Zn detected in the plants is not coming of the wastewater. In the entrance of the wastewater the text of Cr varied of 70 to 100 µg.L⁻¹, while, in the leaves of the macrophytes the concentrations varied of 2 to 48 µg.L⁻¹. Besides these elements they were also detected Cl, K, Ca, Mn, Fe, Br, Rb and Sr. This project was performed at XRF Beamline D09B (Project 3549).

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STUDY OF THE REMOVAL OF HEAVY METALS IN A SLOW FILTRATION SYSTEM BY SR-TXRF

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The slow filtration is nothing else that the removal of impurity physical, chemistries and biological through the passage of the water for a granular middle. It is a process relatively simple of treatment of water where high technology equipments are not used, nor chemical products, and it is not needed labor qualified for its monitoring.

The system in study is fed by the coming wastewater of the Agricultural Engineering College (FEAGRI/UNICAMP) and it uses a low cost operational technology and of easy handle, turning it attractiveness for use in rural communities of low purchasing power and that need a better quality of treated water.

The objective of this project went evaluate to removal of heavy metals and the degree of efficiency of that removal in a pilot system of slow filtration.

The collections were weekly accomplished for 16 weeks, in the period of January until march it of 2005. The samples were collected in the entrance and exit for verification of the system efficiency.

The elements were detected: P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb and Sr in practically all the samples.

The concentrations of P stayed practically constant along the treatment, and the same behavior was observed for Mn and Fe.

For S, the minimum concentrations in the entrance and in the exit they didn't vary, being the same to 1.0 mg.L⁻¹. But the difference among the maximum concentrations in the entrance and in the exit it was of approximately 3 times. The maximum concentrations of Ni were the same to 185 µg.L⁻¹ in the entrance and 254 µg.L⁻¹ in the exit, and for the Zn they were the same to 728 µg.L⁻¹ in the entrance and 1677 µg.L⁻¹ in the exit.

In the case of K, the variations in the entrance and in the exit they were the same to 48 and 33 mg.L⁻¹, respectively, showing the efficiency of 68% in the removal of this element.

The element Cr was detected in most of the samples and the concentrations varied of 18 to 125 µg.L⁻¹.

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**ULTRA-TRACE ANALYSIS AND SPECIATION BY TXRF-NEXAFS IN THE
SOFT X-RAY RANGE**

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Using undulator radiation at electron storage rings, very high photon fluxes of linear polarized radiation for the excitation in total-reflection x-ray fluorescence analysis (TXRF) for the contamination control on semiconductor surfaces can be achieved. At the 1.7 GeV electron storage ring BESSY II in Berlin, photon energies of undulator radiation range from the VUV well into the soft x-ray regime, up to about 1,86 keV. The Physikalisch-Technische Bundesanstalt (PTB), Germany's national institute for metrology, operates a plane grating monochromator (PGM) beamline for undulator radiation. Here, the absolute lower levels of detection for TXRF of light elements such as C, N, Na, Mg and Al range between 100 fg and 1 pg with respect to a measuring time of 1000 s. Transition metals can be likewise analysed through their L-fluorescence radiation, sometimes needing absorption filters in the detection channel to modify the spectral distribution in favour of the fluorescence lines of interest. For the explicit purpose of the semiconductor industry, PTB has TXRF instrumentation that can handle 25 mm through 75 mm as well as 200 mm and 300 mm silicon wafers. Routine analysis of wafer surfaces involve TXRF spectra deconvolution based on both detector response functions and physical modeling of background components such as resonant Raman scattering. Furthermore, reference-free quantitation is ensured by calibrated components of the instrumentation employed.

Near-edge X-ray absorption fine structure (NEXAFS) investigations in conjunction with TXRF are able to contribute to the speciation of low Z and organic compounds. The PGM beamline is an appropriate source for TXRF-NEXAFS experiments, which require the tunability of the excitation radiation and a relatively high resolving power while ensuring both a sufficient photon flux to allow for trace analysis of low Z elements and a high spectral purity. Reference contaminants were diluted and deposited as droplets on wafer surfaces. These droplets have been examined by tuning the incident photon energy over the K absorption edges of C, N and O and the L absorption edges of transition metals.

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**APPLICATION OF THE TXRF FOR ANALYSIS OF THE PLANTS
CULTIVATED ON POST INDUSTRIAL ZINC WASTES**Beata Ostachowicz¹, Katarzyna Turnau², Teresa Anielska²¹*AGH University of Science and Technology, Faculty of Physics and Applied Computer Science,
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The aim of the work was to analyze the influence of arbuscular mycorrhizal fungi on elemental composition of the plants growing on the substratum collected from the post industrial zinc wastes. Symbiotic fungi are an important component of soil microbiota. Properly developed mutual symbiosis enhances the survival of plants by e.g. improving nutrient acquisition and water relations. The effectiveness of the bioremediation technique depends on the appropriate selection of both, the plant and the fungal partners. In the present study *Medicago sativa* was used as a model plant. The plants were analysed by Total Reflection X-ray fluorescence method. Shoots and roots were dried, digested and analyzed separately. Following elements were analyzed: K, Ca, Cr, Mn, Fe, Cu, Ni, Pb. Mycorrhizal fungi were found to play an important role in the survival of *M. sativa* on the polluted substrata. Fungal strains either increased or decreased heavy metal uptake by the plant depending on the origin of a fungus. Strong influence of the pre-adaptation of the fungus in polluted soil on the ability of the plant to avoid uptake of potentially toxic elements was found. This results in a better performance of the plant and limited the risk of increasing the levels of these elements in the food chain.

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UNCERTAINTY EVALUATION IN SEAWATER ANALYSIS BY TXRFC. Ralheta¹, M. A. Barreiros¹, M. A. Trancoso¹, M. F. C. Camões²¹*LAACQ/INETI, Az. Lameiros, 1649-038 Lisboa, Portugal*²*CECUL/DQB, Faculdade de Ciências da Universidade de Lisboa, 1749-016 Lisboa, Portugal*

A monitoring program to assess the water quality of the western coast of Portugal, near Lisbon, is carried out for more than 10 years in our laboratory in what concerns elemental analysis of estuarine and seawater. Quantitative determinations have been performed by Total Reflection X-ray Fluorescence (TXRF) preceded by pre-concentration of metals as dithiocarbamates using ammonium pyrrolidinedithiocarbamate (APDC). In order to achieve lower detection limits the method developed by Prange et al. [1] had to be implemented. In the establishment of this analytical methodology, in-house validation and Quality Control was the main process to estimate the overall uncertainty, which conveys reliability to the measurement.

TXRF is a well-accepted technique for ultra-trace determinations. Nevertheless, the seawater analysis implies several steps of chemical sample preparation to remove the salt matrix, all responsible for additional sources of uncertainty. The trace elements are separated from the salt matrix by chelation with sodium dibenzylidithiocarbamate (NaDBDTC), selective chromatographic adsorption (reverse-phase) of the metal complexes and subsequent elution of the metal chelates using a chloroform/methanol mixture, which is the analysing solution. This work reports on results of repeatability, reproducibility, recovery and accuracy studies. They are the main sources of measurement uncertainty, besides instrumental calibration and spectra fitting components.

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ANALYSIS OF LOW Z ELEMENTS IN BIOFILMS DIRECTLY CULTIVATED ON THE TXRF QUARTZ CARRIER PLATESH. Hoefler¹, C. Strelí¹, P. Wobrauschek¹, M. Óvári², G. Záray²¹*Atomintstitut, Vienna Univ. of Technology, Stadionallee 2, 1020 Vienna, Austria*²*Dep. of Chemistry, Eötvös Lorand Univ., Budapest, Hungary*

One of the advantages of TXRF is the need of very small sample amount. This seems to make the method applicable for the analysis of biofilms directly grown on polished quartz plates.

Biofilms (periphyton communities) are complex associations consisting of bacteria, algae, fungi, and their secretions, building up a mucous cover on all immersed surfaces in the aquatic environment. The secretions, the so called extracellular polymeric substances (EPS) contain various organic compounds, which are highly capable to bind various trace elements. Since the biofilms are important nutrition for many organisms in the aquatic ecosystem, the trace elements bound by them can be directly introduced into the food chain.

Concentration of various trace elements can be carried out by almost all of the commercially available atomic spectroscopic methods (e.g. AAS, ICP-AES, ICP-MS). However, in case of biological materials it is often difficult to collect appropriate amounts of samples which are needed for these analytical techniques. TXRF is a suitable micro-analytical method to investigate even very low sample amounts (as low as 50 µg or less) with rather good detection limits. The most important drawback of this method is the limitation, that elements with atomic numbers less than 13 cannot be measured with commercial equipments. However, the use of a soft X-ray source, airless beam pathways, and special detectors, this range can be extended to Z=6, to make it possible to determine low Z elements e.g. carbon or chlorine.

For the complex understanding of biofilm formation and to judge better the effects of pollution on biofilms, it is necessary to determine not only the polluting trace elements but also the major biogenic elements (C, N, P, S) in biofilms.

In this work a method is presented for the determination of low Z elements in biofilms which were directly cultivated on the quartz carrier plates of the TXRF to avoid additional sample preparation like lyophilisation followed by pressure digestion as done in previous investigations.

As excitation source an X-ray tube with Cr anode was used, a monochromatic primary beam of 5 keV was produced by a multilayer monochromator. The internal standardization was made in two steps: 100 ng of Ag (as nitrate) was pipetted onto the centre of the plate. The Ag-La line was used for determination of Ti via its Ka line, and this latter was the internal standard for the other elements (C to Ca). The plate was measured in five different positions: the middle and four outer spots.

On the basis of the results it can be established that this type of biofilm cultivation can be used for monitoring purposes. It is suggested to carry out the direct exposition of the plates not longer than about 6...7 days. The biofilm distribution on the plate has been found before this time to be quite homogeneous, afterwards, however, the inhomogeneity has increased. This was also visible in form of depositions.

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WATER-POLYSACCHARIDE MACROMOLECULES: COMPETITIVE INTERACTION ONTO GLASS MICROSPHERES

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Equilibrium properties of a polymer solution in the vicinity of a solid-liquid interface are locally altered relative to the properties in bulk. Discrepancies between porous media and conventional rheology appear when both the pore wall is attractive or repulsive for the polymer adsorption. These local alterations have manifestations in practical situations, such as filtration, dissolution, purification, chromatography of polymers, and various membrane permeations situations. Theoretical models for both flexible and rod-like polymers were published.

The present work was performed with aqueous scleroglucan solutions up to 0,05% concentration range, on 400 to 600 μm glass micro spheres. The study of the adsorption behavior of the macromolecules was managed marking them with iodide by means of a chemical reaction. Iodine was then detected by Total Reflection X- Ray Fluorescence Spectrometry. An advantage to point out is the direct measurement of the sample; this ensures the preservation of the polymer structure and minimizes the contamination possibilities. The experimental results show that Freundlich dependence is observed for concentrations higher than 0.1%. It is interesting to point out the anomalous behavior for diluted scleroglucan solutions. The time to reach the equilibrium state increases with the scleroglucan concentration up to 0.1% and it is constant for highest concentrations

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**HONEY CHARACTERIZATION BY USING TOTAL REFLECTION
X RAY FLUORESCENCE: EVALUATION OF THE ENVIRONMENTAL
QUALITY AND RISKS FOR THE HUMAN HEALTH**

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Honey is the food produced by bees genus *Apis Mellifera* from the nectar of the flowers and other sweetened plants, transforming, enriching and depositing them in the cells of the wax honeycombs. Honey has important nutritious properties due to its chemical composition mainly fructose and glucose (75 to 85%), proteins, mineral salts, group B and C vitamins and metals. For their elaboration, areas near 10 km² are crossed by bees, representing, from an analytical point of view, a true sampling of the sucking zone. Since this consideration, honey characterization reveals the environmental quality of the zone.

In this work, honey is used as pollution indicator of toxic metal in an extensive Center-West area of Argentine Republic. X-ray Fluorescence with Total Reflection geometry (TXRF) was used for metals identification and quantification due to its sensitivity, low detection limits and multielemental information. Different sample preparation procedures in order to obtain reproducible results are discussed. Levels of contamination are evaluated comparing obtained data against Argentine Nourishing Code values. Chemometric tools were used for matching chemical composition and environmental contamination.

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MICRO TOTAL REFLECTION X-RAY FLUORESCENCE (MICRO-TXRF)

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Total reflection X-ray spectrometry (TXRF) is a powerful tool for trace analysis of impurities on the surface of semiconductor wafers. Usually, the primary x-ray beam in the TXRF has a dimension of 10 mm wide and 0.01-0.1 mm thick. Since primary x-rays irradiate at small incident angle, averaged information in a large area is obtained by TXRF. Recently, however, it has been important to analyze a small single particle on the wafer.

Therefore, we have studied to improve the TXRF instrument, which was combined with micro-XRF analytical technique. We investigated two experimental configurations, where a polycapillary x-ray lens was used for excitation of small region or for detection of micro region. In the first experimental setup, x-rays emitted from a sealed type Mo tube were focused in a beam size of about 40 micro meters. In order to satisfy the total reflection condition, the micro-x-ray beam over the critical angle of the total reflection was cut by a slit. X-rays were successfully focused on a single particle. Using this instrumental setup, we applied to analysis of a single particle on a flat Si substrate. In the second setup, the polycapillary lens was attached to an EDX detector that is used for TXRF analysis. Instead of polycapillary x-ray half lens, (conical) apertures were also applied. Some experimental result will be presented.

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TRACE ELEMENT ANALYSIS OF FINE AEROSOL PARTICLES WITH HIGH TIME RESOLUTION USING SR-TXRF

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Air pollution monitoring is a transboundary issue involving co-ordinated environmental policies among neighboring countries, especially for aerosols that can be strongly related to the health of the citizens. In this work a multielemental analytical technique is presented that allows a very high temporal resolution (<10 min) for the total aerosol. The method is based on direct synchrotron radiation total reflection X-ray fluorescence (SR-TXRF) measurements of particles collected on silicon wafers. Because of its natural collimation, high intensity and low background, SR-TXRF allows detection of trace and ultra trace amounts of most elements. The detection limits achieved are ranging from $\mu\text{g/g}$ (ppm) for the light elements (Al, Si) to pg/g (ppt) for the medium Z elements like Rb and Sr in the present matrix.

Aerosol samples have been collected using a seven-stage May cascade impactor, at different background and urban locations in Hungary and Austria. In order to investigate the fine aerosol fraction exclusively, aerosol collection was performed only at stages 5, 6 and 7 with aerodynamic cut-off diameters of 1, 0.5 and 0.25 μm , respectively.

Measurements were performed at HASYLAB Beamline L using the TXRF vacuum chamber. The synchrotron radiation was tuned to 17.5 keV by means of the NiC multilayer monochromator. A Vortex Radiant SDD detector in use was equipped with a collimator with a 1.5-mm wide slit made of Mo. The beam had a dimension of 1 mm so the samples were scanned over a length of 6 mm in 6 steps. Cr standards having a known mass in dimensions identical to the deposited aerosol particles could be used as external standards for the measurements. Using the sum spectra of the 6-mm scans and the results of the Cr standards, the elemental composition of the deposited aerosol samples could be calculated. Detection limits in the pg/m^3 range could be reached for a 20-min sampling time in the 0.5–1 μm aerosol fraction.

Using the SR-TXRF results, the daily temporal variation of elemental concentrations in the 0.5–1 μm aerosol fraction could be reconstructed. Fe and Zn concentrations in the Hungarian background samples show anticorrelation with the mixing layer height that was expected from aerosol mass measurements at different sites.

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ANALYSIS OF GEOMETRIC-DEPENDENT EFFECTS ON TXRF MEASUREMENTS BY MONTE CARLO SIMULATION

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In this work, we used MCNP4C running on Pentium-based PC to simulate the geometric conditions of total reflection X-ray fluorescence (TXRF) measurements. We have considered an ideal detector, a monochromatic beam (28 keV) and an x-ray spectrum (the tube voltage was assumed to be 30 kV). The use of the Monte Carlo method to simulate radiation transport has become the most accurate means of predicting the x-ray spectra even in complex geometries owing to more accurate physics modelling and incorporation of appropriate interaction cross section data. The procedure of x-ray production consists of tracking a large number of electrons incident on the target until they are absorbed or emerge from it, and calculating the number of bremsstrahlung and characteristic photons produced by them during their travel within the target. The simulations were carried out considering a 90° geometry. Standard solutions with Zn as internal standard were prepared for calibration system. The sensitivity was determined by simulating standards containing the elements Al, Si, K, Ca, Ti, Cr, Fe, Ni, Zn, Se, Sr, Mo and Ag for the K-lines and Sr, Mo, Cd, Ba, Sb, Pt, Hg, Tl and Pb for the L-lines. A small aliquot of 5 mL of the standards were simulated. The sample can be considered as a thin film and therefore, for the analysis by X-ray fluorescence, it is not necessary to apply a correction for matrix effects. Our main aim in the present study was to investigate the geometric-dependent effects (incident and detection angle and incident beam) on concentrations of trace elements measurements. In this way, a sample, which is a mixture of various elements (Al, K, Fe, Ni, Ga, Kr, Sr, Nb, Tc and Ag) with different concentrations was also simulated. Ten ml of the mixture, containing the internal standard, were deposited on a suitable sample carrier of quartz. The concentrations have been calculated and all the results show that MCNP Monte Carlo code was able to identify trace elements with percentual error smaller than 5%.

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ARSENIC SPECIATION IN CUCUMBER (CUCUMIS SATIVUS L.) XYLEM SAP BY K-EDGE TXRF-XANES

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X-Ray Absorption Near Edge Structure (XANES) combined with Total Reflection X-Ray Fluorescence (TXRF) acquisition was adopted for the arsenic speciation in cucumber (*Cucumis sativus* L.) xylem sap. Plants were grown in nutrient solutions containing 2 mmol/dm³ arsenate or arsenite, respectively. Xylem sap was collected, deposited on quartz reflectors and dried.

K-edge XANES measurements have been carried out at the bending magnet beamline L of HASYLAB, Hamburg, using a Si(111) double crystal monochromator and a Si Drift Detector.

Arsenate and arsenite standards diluted to 10 ppm, nutrient solutions containing arsenic in the two above mentioned species in concentrations of 150 ppb, and xylem sap containing arsenic in concentrations in the 30-50 ppb range were analysed and compared.

The arsenite contained in the nutrient solution was found to partially oxidise to arsenate and a quantitative measure of the phenomenon could be obtained with a linear fitting of the spectrum of the nutrient solution with the spectra of the standards.

Analysis of the sap showed that the arsenate contained in the nutrient solution was reduced to arsenite before being transported to the periphery of the plant. Quantitative results in this case could not be obtained due to the poor signal/noise of the spectra.

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DIGITAL DATA READ-OUT BY GLANCING ANGLE INCIDENCE X-RAY REFLECTION

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A new ultrahigh-density x-ray optical data storage media named X-ROM is proposed in the papers [1, 2]. Digital data reading procedure in considered readout systems is based on x-ray diffraction optics. Further progress is based on increased understanding of the phenomena, which are presently limiting applications, as well as developing new materials, which are promising for applications. Material refractive index n decreases while the value of the extinction coefficient increases with increasing photon energy. The change in refractive index of nanostructured materials enables these materials to be used in x-ray optical data storage and data readout devices. New complex materials are designed using known materials as the starting point. An increased data density of 500 Tbit/inch² is the goal to be reached for 0,15 nm – 0,45 nm wavelength operating x-ray optical data storage media.

The scientific objective of presented theoretical paper is the further consideration of nanostructured materials for x-ray optical data storage. Data reading procedure from nanostructured semiconductor X-ROM also can be performed using the glancing angle incidence x-ray reflection (GIX). X-ROM system detects data by measuring the changes in x-ray micro beam intensity reflected from the various surface points of data storage media. In the proposed data handling system the positions of the ultrahigh-density digital information carrier and of the grazing-angle incident x-ray micro beam are fixed, unlike the conventional optical data readout systems. GIX configuration allows data readout from large area of the ultrahigh-density x-ray optical data storage media. Consequently, the data readout speed is much faster than in the optical data readout systems. Digital data reading procedure from the proposed X-ROM would be very effective if it will be performed by the fast charge-coupled device (fast-CCD) based x-ray area detector – a detector, which can display and detect 2-D pages of data (of course, the mentioned fast-CCD must have sufficient resolution to resolve speckle and sufficient speed to keep up with the x-ray laser repetition rate).

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**HIGH ENERGY RESOLUTION X-RAY FLUORESCENCE
MICROANALYSIS BY ENERGY DISPERSIVE SPECTROMETER WITH
SUPERCONDUCTING DETECTOR.**

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We present compositional analysis of materials obtained by a novel turnkey instrument: a superconductor/based - energy dispersive spectrometers (S-EDS) mounted on a scanning electron microscope. The complete SEM and S-EDS system provides morphological and compositional analysis. The use of superconductor technology for the detector and signal preamplification allows to achieve energy resolution one order of magnitude better than semiconductor based EDS. The working detector temperature is $T=110\text{mK}$ and is obtained with a cryostat which uses a combination of a pulse tubes and a two-stage adiabatic demagnetization refrigerator. Nevertheless the configuration is user friendly and there is no need of liquid coolants during the cool down operation. The high sensitivity permits to work at low excitation energy of the electron beam thereby enabling the analysis of nanostructures as well as the identification of L and M characteristic lines with potentiality for quantitative analysis of elements in trace. The results presented here have been obtained on a wide range of specimen from cultural heritage to microelectronics and demonstrate the great potentiality of this novel instrumentation.

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**X-RAY FLUORESCENT ANALYSIS AT SAMPLE EXCITATION BY
SECONDARY TARGET RADIATION**

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In the paper we present a scheme of an x-ray spectrometer with exchangeable secondary targets and investigation results of its characteristics. A high-voltage power source with the voltage up to 75 kV and x-ray tubes up to 2.5 kW power are used in the spectrometer for generation of a primary x-ray radiation. The exchangeable secondary targets make it possible to obtain a monochromatic radiation with high enough degree of a spectrum contrast. Use of the tubes with different anode materials (chrome, tungsten and rhodium) and different secondary targets provides effective analysis in a wide range of elements concentrations having atomic numbers $Z=13-92$. In this case it is possible optimize the sample analysis for definite groups of the elements, reaching the values of the detection limits of $1 \cdot 10^{-9}$ g in thin-layer samples and 10^{-6} g/g in massive samples.

This device slightly yields to spectrometers with total external reflection of the primary beam (TXRF spectrometer) in sensitivity, however, its design is simpler, it has higher aperture ratio, has simple and convenient setup and high productivity.

Samples of this device application for determination of heavy metals content in aqueous solutions are presented in the paper.

The work is fulfilled at financial support of ISTC (Project № 2708).

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ENERGY DISPERSIVE X-RAY DIFFRACTION IN CONTRADISTINCTION TO ANGLE DISPERSIVE METHODS

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Many portable XRF instrumentations have been developed in the past decade from different groups of Research, institutions and companies [1] to characterise materials from the cultural heritage.

Often when analysing museum artefacts with XRF technique, some x-ray diffraction (XRD) peaks appear in the spectra and interfere with the XRF ones. By analysing these XRD peaks, information about the mineral phases could in principle be retrieved. Combined measurements have been already carried out on ancient Egypt wall paintings [2].

We aim at investigating on the possibility to perform X-ray diffraction measurements by using the energy dispersive technique to develop a new portable device.

Usually, in laboratory instrumentation, the angle dispersive XRD is preferred to the energy dispersive approach. Angle Dispersive methods rely on the identification of the angles θ corresponding to constructive interferences, once the incident x-ray wavelength has been fixed. Laboratory equipments are then provided with a monochromatic x-ray source and a linear (multidimensional) detector or a punctual detector located on a goniometer to change the angle θ . On the other hand the energy dispersive method is extensively used in synchrotron radiation experiments.

In this work, we investigate various issues including concrete advantages and disadvantages of the energy dispersive x-ray diffraction with laboratory and portable (Cu or Ag X-ray source from Moxtek) instrumentation. The energy dispersive technique is less complicated from the mechanical point of view and then suitable to a portable device: no movements or rotations are required and the x-ray source is a conventional polychromatic x-ray tube. On the other hand, with this method, x-ray fluorescence (XRF) peaks appear on the spectra and interfere with the x-ray diffraction ones. A system provided with an Al filter has been investigated in order to reduce the intensity of XRF peaks when performing XRD.

The results obtained with conventional x-ray tubes on different kinds of materials are presented and critically analysed. Finally, we methodologically evaluate of the ratio between the intensity of XRF and XRD peaks.

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DIAMOND PRISM X-RAY SPECTROMETER

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An X-ray optical scheme of the diamond prism X-ray spectrometer is described. The prism was manufactured from the natural crystal and had a 15-mm² refracting plane. The scheme includes two goniometers set along the path of the primary X-ray beam, crystal analyzer, and two detecting systems placed on both goniometers. The crystal analyzer is positioned between goniometer axes and serves for prism adjustment at a chosen spectral line. The distance between goniometer axes is variable, and the maximum spacing equals 1 m. The angle diagram of dispersed radiation can be registered either by a scintillation counter with a narrow entrance slit or by a CCD detector with scintillation layer. Influence of energy gaps in analyzed spectrum due to diffraction on diamond crystal lattice is minimized by a proper choosing of the angle divergence in the plane of an incident beam.

Results of measuring polychromatic emission and absorption spectra by the prism method in the energy range 5-40 keV are presented. Energy resolution $\Delta E=90-100$ eV was experimentally achieved at photon energy about 10 keV.

It is shown by computer calculations that for a parallel beam the minimum value of ΔE is determined by the diffraction limit, and at $E=8-10$ keV it's possible to achieve ΔE 10-20 eV. This is an order of magnitude better than the theoretical limit of cooled Si and Ge semiconductor detectors. Combination of a CCD matrix with an X-ray prism spectrometer provides correct measurements of ultra-short pulse spectra in collimated beams from high-brightness sources.

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NEW HIGHLY EFFECTIVE X-RAY COMPLEXES (XRF+XRD) ON THE BASIS OF KUMAKHOV'S POLYCAPILLARY OPTICS

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The multipurpose small-sized instrument intended for the express analysis as for powder samples, and large-sized products with complex form has been developed. Diffraction and spectrometry channels are combined in the instrument that is perfect for the control of technological processes on line. Kumakhov's polycapillary optics is used for creation of parallel initial and diffracted beams.

The instrument is developed in two modifications: portable (weight of goniometer is not more than 7 kg) and desktop with semi-automatic submission of powder test. The portable instrument is applied to nondestructive control and established directly on the researched object. The instrument finds wide application in various fields of science and technical equipment.

X-ray spectral channel allows to carry out the qualitative and quantitative analysis of the chemical elements contained in a sample. It is possible to analyze elements from Al13 up to U92

Usage of X-ray-diffraction and X-ray-fluorescent analysis gives additional opportunities for research.

Results of examination of silver coins are demonstrated in this work. It is shown, that though the diffractogram of the coin surfaces specifies the high cleanliness of silver (> 98 %), but energy-disperse analysis points to the significant contents of copper that approves copper basis and thick enough silver covering of a coin. The opportunity of examination of paintings is based on the analysis as chemical and phase structure of the mineral dyes included in paints. Identifying mineral structure of paints, it is possible to define time and a place when the picture has been painted. Portable diffractometer allows to analyze any part of picture without surface destruction.

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KUMAKHOV'S POLYCAPILLARY X-RAY OPTICS IN MANUAL X-RAY-FLUORESCENT ANALYZER

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Hand Spectrometer has been created for the first time with built-in color CCD camera, multi-
itemed discrete diaphragm and Kumakhov's polycapillary half-lens, transforming X-ray
radiation of a tiny three-electrode controlled x-ray tube into almost parallel beam directed to
the researched object. X-ray beam is accompanied by laser beam.

Advantages: polycapillary half-lens and a diaphragm allow carrying out measurements from
the area in diameter from 0.1 mm up to 10 mm, presence of a video camera enables to be
adjusted precisely on area of measurement.

Hand Spectrometer will find numerous applications in industries, geology, archaeometry,
environment, etc.

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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. Ther are described some examples of applications of these optics in laboratory and on synchrotron the BAM-line at BESSY.

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APPLICATIONS OF CAPILLARY OPTICS FOR XRF AND XRD

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

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RING ANODE X-RAY SOURCE FOR THE IMAGE X-RAY FLUORESCENCE SPECTROMETER (IXRF) COMBINED WITH MULTI-CHANNEL PLATE (MCP) OPTICS

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Following by the previous work, the Imaging X-Ray Fluorescence Spectrometer (IXRF) with Kevex source has been proved to be a feasible image spectrometer combined with Multi-Channel Plate (MCP) optics. To focus on the low Z elements fluorescence analysis, the signal to noise ratio will be improved as the X-ray energy decreased to prevent exciting unwanted elements. But the significantly dropped emission current is the problem coming out. Long filament source is our basic idea to solve this problem. In this paper, we introduce a novel ring anode (9cm diameter) source for the IXRF with the MCP optics. A long (30 cm length) round Tungsten filament is adopted and suspended above the ring anode. Furthermore, by using this ring anode source, we could have a better normal angle projection for the sample table to CCD compared to the 45 degree with Kevex source. The performance of the spectrometer has been tested and measured throughout the emission current up to 100 mA and the high voltage up to 4.5 kV applied on the ring anode. The spatial X-Ray flux profile projected on the sample plane has been obtained. To extend the aim of the low Z elements detecting capability, we describe the preliminary images and spectrum of MgF₂ powder sample on the silicon wafer with the ring anode emission current 50 mA produced at 1.7 kV.

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**PORTABLE MICRO-XRF EQUIPMENT WITH A POLYCAPILLARY
CONIC COLLIMATOR**

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The irradiation and X-rays detection in Energy Dispersive X-Ray Fluorescence Analysis generally involves macro areas, typically of the order of cm^2 . This is not a problem when the sample is sufficiently large and homogeneous. In other cases, when the sample is small or inhomogeneous, the irradiated area must be reduced. In many cases this may be done by simply reducing the irradiated area with pinholes, in other cases, when the irradiated area should be of the order of 10^{-4} mm^2 or less (micro-EDXRF), special collimators are needed. When using X-ray tubes, X-ray microanalysis may be carried out by using capillary collimators. Glass capillary Optics is used for collimating, focusing or parallelizing X-ray beams. Monocapillary or polycapillary collimators are used. Polycapillary lenses consist of many hollow channels which capture divergent X-rays and guide them to form small focal spots. Generally, a microfocus X-ray tube is required to focus the X-ray beam on a micrometric sample area. However, in this case the distances tube-capillary collimator-sample are not well compatible with a compact and portable EDXRF-equipment. An alternative solution for a portable EDXRF-equipment is to irradiate a relatively large area but to concentrate the secondary radiation emitted by only a micrometric area into the detector by using a conic capillary collimator directly located at the detector window. In this paper micro-EDXRF analysis with a portable XRF-equipment with a CCC collimator is described, with particular reference to analysis of small fragments and details, in the case of works of art.

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**ACCURATE EFFICIENCY CALIBRATION OF A LOW-ENERGY HPGe
DETECTOR USING MONOCHROMATIC X-RAY SOURCE**

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In the frame of the French Metrology Institute, the Laboratoire National Henri Becquerel performs accurate characterization of semiconductor detectors that are in use in a number of applications. Their efficiency calibration, energy resolution and the detailed shape of their response function are parameters of interest for accurate processing of low-energy X-ray spectra to be applied to elements identification and fundamental research studies.

In the low energy range ($4.5 \text{ keV} < E < 20 \text{ keV}$), efficiency calibration is usually performed using radioactive standard sources (^{51}Cr , ^{55}Mn , ^{55}Fe , ^{241}Am , etc.). For lower or others energies not covered by the classical x-ray standards, this characterization can be carried out by using an artificial monochromatic photon source (synchrotron or X-ray tube + monochromator). Since 2001, the SOLEX source (Source Of Low Energy X-rays) have been installed at Laboratoire National Henri Becquerel for the purpose of providing tunable monochromatic radiation in the 1-20 keV energy range. With this instrument, the French metrology institute calibrates detectors and also develops metrological studies in this energy range. The efficiency characterization of detectors requires accurate determination of the photon flux of the artificial x-ray source. Moreover, the tunable monochromatic beam can also be used to measure the relative amplitude of the K or L binding edges of typical detector components (electrical contact, infra-red shield, dead layer, etc...). These results allow approximation of the thickness of each component, thus the efficiency calculation by Monte Carlo simulation becomes possible.

The present study is an example of the efficiency calibration of a HPGe detector by using three complementary approaches: radioactive x-ray standard sources, SOLEX artificial source for the binding edges characterization and Monte Carlo calculations.

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X-RAY FLUORESCENCE MEASUREMENT WITH A SMALL GLASS X-RAY TUBE FOR PHOTOIONIZER

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X-ray fluorescence spectrometer was assembled using a Si-PIN detector and an X-ray generator for photo ionizer (Hamamatsu photonics) which was used in semiconductor industry. Whole system was constructed within one day which had interlock mechanism to protect X-rays. The spectral background was too strong because of strong X-rays from the X-ray tube, though the glass X-ray tube was very small size such as 15 mm in diameter and 30 mm in length. The X-ray tube voltage was limited up to 10 kV, but if this limit was made to be a little bit higher, the present X-ray generator will be a useful optical element for next generation X-ray fluorescence analyzer.

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**THE ADVANTAGES OF USING DIGITAL SIGNAL PROCESSING IN
POLARIZED X-RAY FLUORESCENCE ANALYSIS**R. Padilla Alvarez¹, P. Van Espen², J.R. Estévez Alvarez³¹*Centro de Aplicaciones Tecnológicas y Desarrollo Nuclear (CEADEN), Havana, Cuba*²*University of Antwerp, Belgium*

Improving the specificity and productivity of XRF is of great relevance for the analysis of trace elements in samples of diverse origin. The advantages of using digital signal processing (DSP) in energy dispersive polarised x-ray fluorescence analysis (EDPXRF) are demonstrated by comparing the achieved instrumental sensitivities with those obtained by using a conventional analogue signal processing (ASP) based spectrometer. A compact geometry secondary target (ST) arrangement was designed to enlarge the effective solid angles and to reduce the distances between secondary target, sample and detector, thus achieving larger x-ray fluxes for both the excitation and detection process resulting in improved instrumental sensitivities. The performance of both spectrometers was evaluated for two different detectors: a Si(Li) detector and a thermo-electrically cooled passivated-implanted planar silicon detector (X-PIPS). The achieved uncertainties and accuracy are illustrated for the analysis of a group of sediment and organic-origin certified reference materials (CRM) using two different quantitative procedures.

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QUANTIFICATION USING A PORTABLE MILLI - BEAM XRF SPECTROMETER

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The implementation of a portable XRF spectrometer in the analysis of a wide range of materials requires primarily the optimal integration of available X-ray components (Low power X-ray tubes, Peltier cooled detectors) into an effective and lightweight instrument. The task involves a fine mechanical construction along with an experimental study of the various components characteristics. Nevertheless, a carefully designed spectrometer is only the first step towards a successful quantitative XRF analysis, requiring subsequently the development of reliable FPA algorithms.

For portable XRF spectrometers, utilizing mostly direct excitation, FPA algorithms have as starting point the descriptions of filtered or unfiltered anode emission spectra. However, for the novel low power X-ray tubes there is a lack of measured tube spectral distributions and a rather restricted assessment of the validity of the existing semi-empirical theoretical descriptions. In the present work, a portable XRF spectrometer developed at the Institute of Nuclear Physics of NCSR "Demokritos" is applied in the quantitative analysis of different types of reference materials (metal alloys, geological samples). The individual characteristics as well as the performance of the spectrometer is thoroughly presented while the quantification procedures based on either the fundamental parameters approach or in experimental methods are discussed, compared and evaluated in terms of the agreement obtained between measured and certified concentrations of the reference materials.

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**QUANTITATIVE IN-SITU XRFA: MONTE CARLO APPROACH IN
VALIDITY EXAMINATION**

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Many techniques of quantitative evaluation have been already developed for determination of element concentration in laboratory XRFA. Now, quantitative or semi-quantitative analysis of in-situ measurements is more and more discussed because of rapid progress in construction of portable systems. In contrast to laboratory analyses, in-situ ones are usually done without sample preparation, and therefore the measurement conditions may be different for standards and samples under investigation. The aim of this work was to evaluate the correctness of quantitative in-situ XRFA that could be affected by various disturbing effects.

Disturbing effects are related to inaccurately defined experimental arrangement (e.g. variation in source-sample-detector distances or sample tilting), surface effects, and presence of heterogeneities. Code MCNPX, a software utilizes Monte Carlo simulation of X-ray transport in matter, has been used to classification of these particular effects in quantitative in-situ analysis. The main advantage of MCNPX code lies in predicting measurement results for a selected geometric arrangement and specimen composition, without any restriction posed on the source configuration, the X-ray spectrum, and the specimen shapes, structure, and position.

Firstly, the influence of disturbing effects on X-ray spectra were demonstrated with the MCNPX code for the representative and frequently used EDXRF systems. Mainly the variations of X-ray count rates were studied. Secondly, the variations of count rates were taken into account in determination of element concentrations. The calculated count rates were recalculated to element concentrations by means of fundamental parameter method.

The results made us possible to draw conclusions on disturbing effects in quantitative XRFA. It has been shown that some of them do not affect the acquired X-ray spectra and the results of quantitative analysis as well. In the other cases, the element concentrations or the element concentration ratios are wrongly determined and could significantly differ from the correct ones.

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SOME CONSIDERATIONS TO QUALITY CONTROL AND METHOD VALIDATION IN EDXRF ANALYSIS

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The x-ray laboratories face an urgent need for Quality Assurance System implementation, due to the demands from the society for reliable / certified results. The implemented QS should comply with the general requirements for the competence of testing and calibration laboratories of the latest approved quality assurance ISO standard, in particular with the ISO/IEC 17025:2005.

The specific features of energy dispersive x-ray fluorescence techniques require of a careful interpretation of some concepts related to quality control of the results and to method validation.

This contribution presents some thoughts on how to assess the traceability of the results, as well as to evaluate the characteristics of performance of the methods, in particular linearity, working range, precision, trueness and detection limits providing some typical examples of EDXRF analytical methods for illustration. Recommendations are provided to quantify the uncertainty of the results.

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SECCOX, A NOVEL X-RAY CHARACTERIZATION BENCH FOR CRYSTALS

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Laser programs require the using of a great number of calibrated X-ray crystals implemented inside spectrometers and microscopes diagnostics. In this context, a new apparatus was designed in collaboration with CELIA laboratory, Saint-Gobain Crystals (SGC) and CEA, to characterize X-ray Bragg SGC crystals. SECCOX (Station d'Etude et de Caractérisation des Cristaux pour les Optiques X) is based on a micrometric x-ray source and an automated spectrometer equipped with a CCD camera. Properties as homogeneity, resolution, radius of curvature and reflectivity are measured to guaranty diagnostics performances on laser-plasma physics shots. We will present the experimental device, techniques and results of calibration obtained. This work was supported by Aquitaine Regional Council under contract 20030205003FA.

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RECENT DEVELOPMENTS OF POLYCAPILLARY X-RAY OPTICS AND ITS APPLICATIONS IN X-RAY SPECTROMETRY

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Polycapillary x-ray optics has undergone significant development in the past decade and the technology has been widely used in x-ray analytical instruments. Recent research and development efforts have been focused on further improving key features of the optics and extending the applications of the technology. These include, but are not limited to, the achievement of smaller focal spot size, improvement of transmission efficiency at high energies, minimization of performance variation at different energies, reduction of high-energy x-ray penetration effect, and the achievement of larger collection angle. We will report in this paper the technical progress in each of the area and associated applications, including a polycapillary focusing optic that generates a less than 10 micron focal spot size. Experimental results will be presented and the future outlook of the technology will be discussed.

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X-RAY DETECTOR DESIGN BASED ON SILICON THERMISTORS FOR SPACE ASTRONOMY MISSIONS OF THE NEW GENERATION

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X-ray Astronomy in space provides unique information on a wide variety of astrophysical phenomena. The presently operating X-ray observatories Newton / XMM (ESA), Chandra (NASA) and Astro-E (Japan / US) have provided a significant improvement in X-ray spectro-imagery capabilities with the use of X ray CCDs.

A great experience has been acquired on Infra-Red bolometer arrays by the CEA-LETI (Grenoble) in collaboration with the CEA-SAp (Saclay). From this basis, we are undertaking a development of an X-ray detector for space Astronomy missions of the next generation, using a MESA technology (Implanted diffused thermistor) on silicon-on-insulator (SOI) wafers.

This detector will be an array made up of 32*32 pixels or microcalorimeters. Each pixel is made of a Tantalum absorber bound, by Indium bump hybridization, to a Silicon thermistor.

We discuss the design of the link between the absorber and the thermal sensor by Indium bump hybridization, the tuning of its thermal conduction parameters at working temperature (50-100mK) and the development of the thermal sensor starting from the present PACS experiment design on the HERSCHELL satellite. This sensor is an implanted and thermally diffused silicon MESA structure on a simple SOI substrate. In order to gain an insight into the mechanisms at the origin of different implanted profiles in our silicon thermistor, the implanted area of the thermistor has been simulated with the 2D simulator ATHENA (SILVACO International) based on the tool SUPREM3. We have studied the effects of the implants and their thermal treatment on both vertical and lateral dopant distributions at the edges of the thermistor.

We hope, by optimizing the implantation and diffusion process, to obtain the thermistor required parameters (1-10M Ω at 50-100mk) in association with a negligible excess noise.

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CHARGE INDUCTION IN SEMICONDUCTOR DETECTORS WITH PIXELATED STRUCTURE

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Recently the considerable interest is attracted by next generation of compound semiconductor detectors with pixelated structure for usage in X-ray and gamma - astronomy, nuclear spectroscopy and particularly in nuclear medicine.

The spatial resolution of this type of detectors is mainly determined by the charge induction by carriers in electrode with pixelated structure, In this case Ramo-Shockley's theorem that use only the conservation-of-energy argument is not applicable with segmented electrodes, since it gives only the total current that flows in the external circuit, not the fraction that flows through a single pixel.. This work shows how to calculate the current distribution in detectors with pixelated structure.

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ELECTRICALLY COOLED SiLi DETECTORS FOR APPLICATION IN X-RAY EQUIPMENT

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In spite of considerable success attained in the development of Si drift detectors [1], SiLi detectors remain the preferable type of sensors for X-ray fluorescence analysis, diffractometry and other scientific spheres due to high registration efficiency in the energy range of 0.5-60 keV.

In the present work, electrically cooled SiLi detectors (EISiX) have been made as OEM product for applications in X-Ray equipment. SiLi detectors EISiX were developed on the basis of a small-sized electric cooler with Klimentko cycle. The compressor unit with sizes 140x160x300 mm and the weight of 7.0 kg operates from an AC 220V/50Hz power supply, consuming less than 60W. We have paid our great attention at the development to minimization of mechanical vibration, microphone effect and high long time reliability of the cooling system.

The cooler is made on a flange with a diameter of 80 mm, which is vacuum-tightly connected with the casing of a cryostat with sizes 80x135x150 mm and a weight of 1.7 kg. Inside the casing on the cold holder providing the cooling temperature of 110-120K there are placed a SiLi detector with the head section of a preamplifier and a sorption pump for the maintenance of working vacuum in the cryostat. The developed design versions of the detection unit can be easily installed in various equipment for registration of X-ray radiation without liquid nitrogen.

We tested EISiX-20 detectors based on a circular detector crystal with the sensitive surface area of 20 mm² and EISiX-60 detectors based on a rectangular detector crystal with the sensitive surface area of 15x4 mm² as parts of a standard spectrometer.

For EISiX-20 devices the value of energy resolution on 5.9 eV made up 135 eV at the shaping time constant $\tau = 16 \mu\text{s}$ and the input count rate of $n=1000$ cps instead of 164 eV under the same conditions with Peltier's coolers [2]. At the shaping time constant $\tau = 1 \mu\text{s}$ the energy resolution was 197 eV at the input count rate of $n=1000$ cps and 214 eV at the input count rate of $n=100\ 000$ cps. The energy resolution on 59.6 keV made up 415 eV at the shaping time constant $\tau = 16 \mu\text{s}$ and the input count rate $n=1000$ cps.

For the EISiX-60 detector used for diffractometry the energy resolution on 5.9 keV made up 151 eV at the shaping time constant $\tau = 16 \mu\text{s}$ and the input count rate $n=1000$ cps instead of 170 eV under the same conditions with Peltier's coolers [2]. At the shaping time constant $\tau = 1 \mu\text{s}$ the energy resolution was 238 eV at the input count rate of $n=1000$ cps and 275 eV at the input count rate of $n=100\ 000$ cps.

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DEVELOPMENT OF MAGNETIC CALORIMETERS FOR X-RAY METROLOGY APPLICATIONS

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We are developing detectors to improve accuracy on the determination of the emission probabilities of X and gamma rays. For certain radionuclides which emit photons of very close energies, an excellent energy resolution is required.

And in the case where small peaks corresponding to low emission probabilities have to be distinguished from background, we need to improve the detection limit.

Conventional detectors (semi-conductors, scintillators...) have reached their fundamental limit concerning the energy resolution. Hence it is necessary to introduce a different principle of detection for better performances.

Low temperature detectors have demonstrated very high energy resolution for low energy X-rays with different technologies. Our applications cover a large energy range (100 eV – 200 keV). This implies a larger absorber volume compared to existing X-ray cryogenic detectors. Among the different technologies we have chosen magnetic calorimeters which offer the advantage of a linear response over a large energy range. The absorber can be made in gold, allowing high detection efficiency. It is coupled to a magnetic thermometer which is made of gold containing a few hundred ppm of erbium. The thermometer converts the temperature rise upon the absorption of a photon to a variation of magnetic moment. The latter is read by a DC SQUID magnetometer and a second stage SQUID as a preamplifier. This setup makes it possible to reach very high signal to noise ratio.

Two detectors have been built. One is dedicated to photon detection in the energy range 1 – 20 keV. Its thermometer is directly placed in the SQUID loop. The absorber has a diameter of 250 μm and a thickness of 40 μm which corresponds to detection efficiency larger than 99 % for 20 keV photons. The second detector is developed for few ten keV to 200 keV photons. The thermometer with a diameter of 420 μm and a thickness of 340 μm is used as an absorber. The detection efficiency is close to 97 % for 100 keV photons. The magnetic moment is read by the SQUID via a flux transformer.

First measurements with a ²⁴¹Am source are presented.

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NOVEL HIGH SPEED, HIGH RESOLUTION X-RAY CCD CAMERA

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We will refer on the novel high speed, high resolution X-ray CCD camera designed and developed in our laboratories. Our aim was to reach resolution down to 1 μ m. The performance of the camera as well as the results obtained on various biological samples (*Drosophila melanogaster*, *Prorhynoterme simplex*), integrated circuits and on a Au mesh grid (the bar width 8 μ m, the bars pitch to pitch distance 63.5 μ m) will be presented and briefly discussed together with possible applications.

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DEVELOPMENT OF HIGH RESOLUTION X-RAY MICROCALORIMETERS

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Future X-ray experiments require a combination of high energy resolution, high quantum efficiency, high speed, wide energy range, and sometimes imaging capabilities. In the last few years X-ray microcalorimeters have reached the maturity to meet these requirements and are becoming the detectors of choice in a wide variety of fields. Additional advantages of microcalorimeters include no branching of the incident energy and no inherent statistical limitation to the resolution. Moreover the detection of phonons means that the choice is no longer restricted to materials with good electron transport properties, such as germanium or silicon, but different materials, more desirable for the particular experiment can be used. The University of Miami has recently started a program to fabricate fully integrated microcalorimeter arrays using iridium thin films as Transition Edge Sensors (TES) and tin absorbers. A new simpler and cheaper readout scheme to replace the cumbersome Superconducting Quantum Interference Devices (SQUIDs) with transformers is also being investigated. In this paper we will present a general overview of microcalorimeters and details on the progress at the University of Miami.

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**SUPERCONDUCTING HIGH-RESOLUTION X-RAY DETECTORS FOR
MATERIAL SCIENCE APPLICATIONS**

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We are developing superconducting X-ray detectors for material science applications that require higher energy resolution than conventional semiconductor Si(Li) or Ge detectors can offer. For high speed soft X-ray spectroscopy at the synchrotron we develop Nb/Al Superconducting Tunnel Junctions (STJ) spectrometers. For highest resolution hard X-ray spectroscopy, we build Mo/Cu Transition Edge Sensor (TES) microcalorimeters. Our TES X-ray detectors have achieved an energy resolution of 5 - 15 eV for energies below 10 keV, and an energy resolution of 50 - 90 eV for energies below 100 keV. We discuss the use of these spectrometers to study ion-surface interactions with highly charged ions from an electron cyclotron resonance source, and to study the isotopic composition of nuclear materials.

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A MODEL TO INVESTIGATE THE POTENTIAL APPLICATION OF SYNCHROTRON X-RAY SCATTER IMAGING ON BMD REDUCTION

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The increased porosity of bone resulting from a reduction of bone mineral density (BMD) is generally known as osteoporosis, which tends to manifest itself more significantly in regions with a greater surface area. Bone may be classified as one of two types, cortical or trabecular. Trabecular bone consists of a mass of bony struts that form a strengthening structure within the hard outer shell of cortical bone. Trabecular bone has a far greater surface area per unit mass than that of cortical bone and so is far more likely to sustain a significant manifestation of osteoporosis [1]. Non-destructive techniques for investigating the internal structure of samples have been developed by many scientists all over the world. The transmission x-ray tomography reconstruction is one of the most popular methods, which provides the spatial distribution of the total absorption coefficient inside the sample. Other complementary techniques have been developed, based on the detection of the scattered photons. At low values of the momentum transfer argument, the x-ray differential coherent scatter cross-section includes molecular and intermolecular interference effects which rise to a unique and characteristic profile, also referred to as a diffraction pattern or scattering signature [2]. The signature of trabecular bone shows the presence of the mineral and non-mineral bone component. We have related the scattering intensity from mineral and non-mineral bone to the bone mineral density (BMD) reduction. Different mineral concentrations were mixed with fat in order to simulate a possible range of BMD. A detection limit was found to the set-up proposed at the X-Ray Diffraction (XD1) beamline at the LNLS, Campinas, Brazil. Otherwise, aluminum cylinders (simulating cortical bone) containing different bone mineral densities were imaged at the characteristic angle for adipose tissue. Transmission and coherent scatter images were compared.

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SYNCHROTRON MICRO-TOMOGRAPHIC RECONSTRUCTION OF GUNSHOT RESIDUES AND 3-DIMENSIONAL LEAD DISTRIBUTIONS

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Microtomographic analysis enjoys several benefits in the utilisation of a synchrotron X-ray source. The X-rays are tunable allowing for optimisation of contrast, they are intense enabling rapid analysis (~10 minutes per sample) with high resolution (~1 micron) and the energy has a very narrow bandwidth ($\Delta E/E \sim 10^{-4}$). This technique has been utilised for recreating the morphological structure of primer derived residues from a variety of ammunition types. Resulting morphologies are reliant on the original ingredients. In addition, the narrow bandwidth achievable on a synchrotron source (at the sacrifice of flux) allows investigations into absorption changes across elemental absorption edges. Subtraction of tomograms either side of the Pb-L(III) edge enabled 3-dimensional reconstructions of the Pb distributions within individual GSR particles. Again, features are reliant on the primary ingredients used in the ammunition.

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**SCANNING TRANSMISSION X-RAY MICROSCOPY WITH
A FAST-READOUT CCD DETECTOR**Alessandra Gianoncelli¹, Graeme R Morrison¹, Burkhard Kaulich³¹*C2RMF - UMR CNRS 171, AGLAE, Palais du Louvre, Paris, France*²*King's College London, Dept of Physics, UK*³*Sincrotrone Trieste, Italy*

The use of a CCD as the transmitted x-ray detector in a scanning x-ray microscope allows a number of new imaging modes to be realised. In practice, a full CCD frame of data is collected for every pixel in the raster scan of the sample, and real-time processing of these data enables the particular form of image contrast to be chosen by the user. The effective detector response of the system is thus software-configurable, so that different forms of image contrast can be generated from the same dataset. For example, symmetric detector response functions will produce images with absorption contrast, while anti-symmetric responses will produce phase contrast images; both forms of image contrast can be generated simultaneously, in perfect registration, from the same set of data collected during the sample scan. In combination with through-focal series, and the acquisition of image data on either side of an x-ray absorption edge, a detector system with a configurable response can thus provide a wide range of information about the complex transmittance of the sample.

To be successful, such a system requires a fast-readout CCD detector, so that the frame-readout time does not limit the raster scan rate of the microscope. The system described in this paper is based around an electron-multiplying CCD system (iXon DV860 from Andor Technology) that combines fast frame-transfer readout with very high sensitivity. The detector consists of a Peltier-cooled CCD array of 128 by 128 sensors, and makes use of visible light coupling to a phosphor screen, to make it easy to operate over a wide range of photon energies, from the oxygen K edge upwards. It has been tested successfully on the Twinmic end-station at the Elettra synchrotron.

In principle, each image scan can generate a very large volume of data, but for routine operation the active area CCD can be re-binned to a smaller effective number of pixels, allowing both faster frame readout times, and reducing the overall data volume. Examples of the use of the system to study the complex refractive index of samples at sub-micron spatial resolution will be presented.

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THREE-DIMENSIONAL CHARACTERIZATION OF U AND Pu CONTAINING PARTICLES FROM TELKEM, KAZACHSTAN

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Radioactive particles containing refractory radionuclides such as uranium and plutonium have been more frequently released to the environment during severe nuclear events than previously anticipated. Following nuclear weapons tests (e.g., at Maralinga, Australia; Mururoa, French Polynesia; Nevada Test Site, USA; Semipalatinsk, Kazakhstan), reactor explosions and fires (e.g., Chernobyl, Ukraine; Windscale, UK), and aircraft accidents (Thule, Greenland; Palomares, Spain) a major fraction of refractory radionuclides released to the environment have been identified as radioactive particles. Particle characteristics such as the activity concentrations and activity or isotopic ratios are source dependent (depending on fuel burn-up), while properties such as size distribution, shape, crystalline structures and oxidation states of matrix elements also depend on specific release conditions. Information on particle characteristics that have a strong influence on weathering rates is essential to estimate the ecosystem transfer rate for particle-affected areas. Within the Semipalatinsk nuclear test site in Kazakhstan, two fresh water crater lakes (Tel'kem I and Tel'kem II) were created by nuclear explosions conducted in 1968 by the Soviet Union, in order to evaluate the feasibility of canal construction/river diversion by means of nuclear explosions. A single plutonium fission device with a yield equivalent to 240 T of TNT was used at Tel'kem I. During the Tel'kem II experiment three similar fission devices were used approximately 1.5 km to the west of the first test. Both tests were subsurface and produced craters and surrounding rings of spoil. Subsequently, both craters became filled with water to form freshwater lakes. An IAEA survey in 1994 indicated "significant levels of actinide contamination, in the form of large particles or fragments" and more recent investigations reported plutonium levels exceeding 50 kBq/kg. The vast majority of the Pu was associated with the >63 µm fraction. Particles in samples collected from Tel'kem I and Tel'kem II were identified by autoradiography revealing the presence of numerous heterogeneities. Furthermore, selected radioactive particles were subjected to gamma spectrometry to quantify gamma emitters and to scanning electron microscopy, interfaced with an X-ray micro-analyzer, in order to characterise the surface structures of particles prior to conventional and micro-X-ray fluorescence analysis (XRF) at HASYLAB BL L. Since this investigation revealed the particles to be strongly heterogeneous with respect to their overall major-element composition, while simultaneously a very high correlation between the U and Pu abundance was observed, additional investigations by means of absorption X-ray microtomography (using a Scyscan 2011 nanotomograph), confocal micro-XRF at the ANKA FLUO-TOPO beamline and scanning micro X-ray diffraction at HASYLAB BL L were performed. The resulting data give a much clearer picture of the internal structure of the particles, revealing a unmolten, crystalline U/Pu-poor core surrounded by an amorphous, foamy U/Pu-rich coating, which is likely to be the result of the flash-freezing of liquefied nuclear material upon contact with a mineral grain. The results allowed us to gain a significantly better understanding of the formation mechanism of these particles and to model better their leaching behaviour and therefore their environmental harm on the short and long term.

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DEPFET ACTIVE PIXEL SENSORS AND PNCCDS FOR ROOM TEMPERATURE IMAGING X-RAY AND ELECTRON SPECTROSCOPY

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Two - dimensional arrays of silicon X-ray detectors have been developed since many years. In order to reach Fano limited energy resolution they required cooling down to -100 C or less. They were either based on conventional CCD concepts, derived from the devices originally developed for optical applications. Or they were composed by Si(Li) or Ge detector elements with coarse position resolution. Under those conditions every pixel must be connected to a readout chain. Most recently, a big step forward towards (close to) room temperature operation of up to $500 \mu\text{m}$ thick depleted back illuminated active pixel sensors and frame store pnCCDs was made. Both device types are derived from the concept of sideward depletion – the underlying principle of silicon drift detectors. A dedicated fabrication process and the high speed operation of the new detectors, (e.g. up to 1200 frames per second at a format of 64×64 and 256×256 with a pixel size of $51 \times 51 \mu\text{m}^2$ and $75 \times 75 \mu\text{m}^2$) were yielding energy resolutions at the Mn $K\alpha$ line at 5.9 keV of 140 eV (FWHM) at an operation temperature of -10°C only. This operation allows for position resolved high count rate spectroscopy easily achievable with thermoelectric coolers. In the preliminary analysis of the data, the peak to background was 2000:1. This is mainly due to the not yet optimized pattern analysis of the photon events distributed over more than one pixel and the unification of other split events.

One of the detector types under study is an active pixel sensor based on the DEPFET principle for the European X-ray mission XEUS and the French SIMBOL_X mission. The electronic noise contribution of the DEPFET amplifier is 2.5 electrons (rms) at room temperature. The resulting spectroscopic performance is dominated by thermally generated leakage currents, typically 100 pA per cm^2 at full depletion of $450 \mu\text{m}$. Spectra at various operational conditions will be shown to define the bandwidth of specific applications.

A second detector type, the frame store pnCCD, will equally be briefly described. The reliability and robustness of this class of devices will be highlighted through applications in heaven and on earth. They have shown good energy resolution as well: $\Delta E = 150$ eV (FWHM) at -20°C with a 256×256 large 4 cm^2 large device with 200 frames per second readout speed. The device was developed for the German eROSITA mission. The same detector was recently used in a TEM at the MPI für Biochemie, Martinsried, Germany.

The system configuration of both detector types, including the ASIC front-end electronics will be introduced to demonstrate the compactness and the the low power operations of the systems.

The sensitivity for X-rays and electrons of both device types is excellent: The high quantum efficiency for X-rays ranges from energies of 70 eV (90%) to 15 keV (90%). Electrons can be imaged directly up to energies of 1 MeV. The radiation hardness for the back illuminated devices is extremely high, only limited by the leakage current generated through the damage.

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**CHARACTERIZATION OF ENVIRONMENTAL RADIOACTIVE
MICROPARTICLES BY SCANNING ELECTRON MICROSCOPY (SEM)
COMBINED WITH ENERGY-DISPERSIVE X-RAY SPECTROMETRY
(EDXRS)**

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The aim of this paper is to show the information obtained, by applying the SEM and EDXRS techniques, about the physical and elemental characterisation of radioactive microparticles which are present nowadays in the terrestrial environment of Palomares, Spain. In 1966, and due to an aircraft accident, two nuclear weapons experienced their chemical explosion when impact on land, provoking the dispersion of their content in about 2.3 Km². Although several cleaning-up operations were carried out after the accident, a fraction of the radionuclides dispersed remains in the zone, mainly in the form of high activity concentration microparticles, also called hot particles.

To perform this study, in 2002, several superficial soil samples were collected in the affected zone. From the bulk matrixes, by using radiometric techniques, a total of three hot particles were isolated and mounted on carbon tapes before their analyses. Then, the three hot particles were identified and characterized with high resolution scanning electron microscopy (Philips XL 30-FEG) with EDXRS system attached (EDAX DX4 with Ge-detector).

Using the Backscattering Electron Imaging (BEI) mode, the hot particles were identified taking in consideration that they are chiefly formed by elements with high atomic number which produce an increase in the intensity of the output signal (bright areas in the image). In addition, by using the Secondary electron Imaging (SEI) mode, information about the morphology and size of the particles was obtained. Finally, semi-quantitative elemental concentrations data at the electron beam spot were provided by EDXRS, while through X-ray mapping was possible to analyse the distribution of individual elements in the particles.

From the SEI images it was possible to observe that all the hot particles present a high porosity and that their sizes ranged from 20 to 60 µm, while the BEI images indicate that they are partially coated by bulk soil material. Moreover, uranium and plutonium have been identified in the electron induced X-ray spectra as principal components of the hot particles while the coatings contained elements typical in soil samples as Si, Al and Fe. The U and Pu distributions obtained using X-ray mapping are quite similar (indicating its homogeneous mixture) and are coincident with the brightest areas in the BEI images.

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**SPACIAL XRF DISTRIBUTION CHARACTERISTICS ASSOCIATED WITH
POLARIZED EDXRF SPECTROMETRY**

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Polarized EDXRF spectrometry has found extensive use in elemental analysis of various materials. The main advantages of P-EDXRF over conventional EDXRF line in its very low scattered radiation background and remodeled excitation spectrum which lead to selective characteristic X-ray excitation. Thus, significant high signal to background ratio can be observed and much lower detection limits can be obtained than those by conventional EDXRF especially for such elements as Cd, Ag, Sn, In, Sb. On the other hand, to ensure the primary (excitation) X-rays being effectively polarized and sample irradiated by polarized X-rays, only narrow X-ray beams are allowed to reach the polarizer and the sample. That presents a critical question: what an area of the sample surface is contributing to the obtained XRF intensity. To this, an experiment was designed and carried out.

The sample was a small piece of disk-like sold with a diameter of about 3 mm. Three typical targets namely HOPG, Mo and Al₂O₃ were used to irradiate characteristic lines Pb Ma(Sn La), Pb La and Sn Ka respectively. The detector was a Si(Li) type with a resolution of 148 eV at 5.9 keV. By placing the sold piece in different positions on a 4 μm polyethylene film window fixed to a sample cup, a manual scan was made over about 3 cm² an area to which the excitation X-ray may reach. Altogether 33 spots were scanned with equal displacements. The obtained intensities and percentage intensities were mapped for Pb Ma(Sn La), Pb La and Sn Ka respectively. Results showed that the total areas contributing to XRF signal were over 2 cm² for the above three target. And Pb Ma and Sn Ka maps, irradiated by HOPG and Al₂O₃ respectively, showed very high intensities in the center parts while very low in the out skirts. The sum of intensities from 4 spots in center areas (corresponding to about 7 x 7 mm²) represents over 50% of overall integrated intensities of the 33 measured spots. And the sharpest areas of Pb Ma and Sn Ka were a little bit shifted. Pb La and Sn La maps showed much larger distribution areas with center the most intensive and changing weak gradually toward the outer parts. Though Sn La was measured by HOPG target, it was irradiated mainly by scattered primary x-rays because its energy is higher than the specific energy (~2.9 keV) of the target.

The relatively small irradiation areas of the polarized targets may require better sample homogeneity and attention should be taken when small pieces of samples were to be analyze

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DETERMINATION OF SULFUR CONTENT IN OIL WITH BENCHTOP WDXRF

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Determination of the sulfur content of automotive fuels is important. High concentration sulfur causes degradation of performance of catalyst in automobiles and increases NO_x. Concentration of sulfur in oil are being tried to be kept lower than 10ppm recently. Small XRF instruments for this analysis have been requested in recent years. ISO20884 specifies the wavelength-dispersive X-ray fluorescence (WDXRF) test method for the determination of the sulfur content in oil. In this regulation, the apparatus is required to be WDXRF type and to be capable of measuring both S-K α fluorescence lines and the background.

We developed a bench-top WDXRF instrument which satisfies this requirement and has enough sensitivity for 10ppm sulfur. We specially designed a monochromator for WDXRF instrument so that it can reflect both S-K α lines and the background by using one fixed crystal. A large curved graphite crystal was so designed that it reflects S-K α lines by one part and also reflects background lines by the other part without rotation of the crystal. Monochromated S-K α X-rays and the background X-rays are both focused on different positions at a detector window. Design of the optics was optimized by referring X-ray ray-tracing simulation. This fixed monochromator optics contributes the stability of the X-ray intensities. We measured the diesel fuels and motor gasoline with the instrument. Lowest limit of detection was achieved to be 0.3 ppm and the standard deviation was 0.17ppm for the 10ppm sulfur samples. These values are satisfactory for the analysis of 10 ppm level sulfur in oil.

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DETERMINATION OF X-RAY RESONANT RAMAN SCATTERING CROSS SECTIONS OF NICKEL EMPLOYING BOTH SYNCHROTRON RADIATION AND PROTON INDUCED X-RAYS

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The Resonant Raman Scattering (RRS) effect on Nickel was studied by means of highly monochromatic polarized and unpolarized exciting radiation, respectively. Experiments involving polarized exciting radiation were carried out in the four-crystal monochromator (FCM) beamline for synchrotron radiation from 2 keV to 10 keV at the electron storage ring BESSY II of the Physikalisch-Technische Bundesanstalt (PTB). Resonant Raman spectra of thin Ni foils, having variable thickness, were accumulated at the Ni-K α and Cu-K α X-ray beam energies. In the Institute of Nuclear Physics of the NCSR "Demokritos", at the 5.5 MV Tandem accelerator, the Resonant Raman spectrum of a thick Nickel target was also recorded for an unpolarized Cu-K α exciting beam produced after the proton ionization of a thick Cu target by 1.7 MeV protons in a three-axial orthogonal geometry. In each case, the individual spectra characteristics are described and compared in terms of the excitation conditions. The experimentally determined RRS cross-sections are presented, while the contribution of the RRS effect in the mass attenuation coefficients below the Ni-K edge is also discussed.

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FAST DETERMINATION OF MINERAL NUTRIENTS IN MILK POWDERS USING WDXRF

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With simple preparation (pelletizing) allied to rapid measurements, X-ray fluorescence is a good candidate for the food industry to be implemented near the production lines. Today, EDXRF and WDXRF (low power = 50 W max) are successfully used for the quantification of several analytes in milk powders and processed cereals.

In this study, we present our latest results obtained (for Na, Mg, P, Cl, K, Ca, Fe and Zn) with high power WDXRF system (2.4 kW) with a total measuring time lower than 4 minutes, instead of 15 minutes with lower power WDXRF system.

Pellets of 10 grams (diameter of 40 mm) were prepared under 2 to 4 tonnes of pressure. For each sample, 3 pellets were prepared and analysed. Limits of quantification and repeatabilities were evaluated. Samples were split into calibration and validation sets. Using robust statistics, an evaluation of the XRF method was performed by comparison with data from the reference methods. Reference values were obtained by Inductively Coupled Plasma-Optical Emission Spectroscopy and by potentiometry for chloride.

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