



X ray Fluorescence in the IAEA and its Member States

Activities in the IAEA XRF Laboratory

A few selected examples of recent activities and results in the field of XRF are presented.

Participation in the 50th IAEA General Conference Exhibition – Protecting the Past for the Future

The 50th IAEA General Conference was held in Vienna Headquarters from 18-22 September 2006. During an accompanying exhibition the achievements of the Agency's Nuclear Sciences & Applications Department were presented, including the portable X ray fluorescence spectrometer manufactured in the IAEA Seibersdorf Laboratories (Fig. 1). The representatives of the Agency's Member States visited the exhibition frequently. They showed a great interest in the applications of nuclear analytical techniques, in particular X ray fluorescence spectrometry, to protection of cultural heritage resources and works of art. The exhibition called "Protecting the Past for the Future" has gained a public attention and it has been described by William J. Board in the New York Times article entitled "Rays and Neutrons, for Art's Sake" published on 24 October 2006.

In This Issue

- Activities in the IAEA XRF Laboratory, 1
 - Participation in the 50th IAEA General Conference Exhibition – Protecting the Past for the Future, 1
 - Support to Technical Cooperation Projects, 3
 - Conferences and workshops, 5
 - Announcement on IAEA Proficiency Test for XRF laboratories, 7
- X ray fluorescence in Member States, 7
 - Austria, 7
 - Belgium, 13
 - Philippines, 17
- Announcement of Workshop on Advanced X ray Spectrometry, WAXS 07, 19
- Publications of potential interest to the XRF community, 20



Fig. 1. Presentation of the portable XRF spectrometer during an exhibition accompanying the 50th IAEA General Conference, Vienna, Austria, 18-22 September 2006.

Recently the portable XRF spectrometer has been utilized by the Museum of Fine Arts in Vienna, Austria for investigation of various objects from the Museum's collections (Fig. 2). The spectrometer is capable of detecting chemical elements with the atomic number $Z > 11$ (sodium). The detection limits are in the range of single micrograms per gram and the adjustable beam spot diameter (0.1 mm and 1 mm) allows for both local and bulk analysis. In the work performed in the Museum the instrument was found very useful for chemical composition analysis of inorganic pigments, metal alloys, ceramics, and glasses. The cooperation with the Museum of Fine Arts in Vienna is continuing. Our present aim is further adaptation of the XRF spectrometer to meet specific requirements of measurements performed on works of art and development of algorithms for quantitative analysis of irregularly shaped objects.

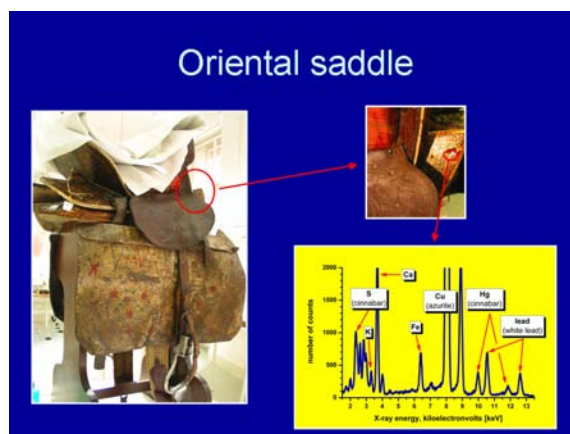


Fig. 2. Inorganic pigment identification by portable XRF spectrometry: oriental saddle, Arms and Armor Collection, Museum of Fine Arts, Vienna, Austria.

Further information on applications of the portable of XRF spectrometer in support of the study of cultural heritage objects is available from Dariusz Wegrzynek (D.Wegrzynek@iaea.org).

Development of a flexible multi-channel digital spectrometer

X ray and γ ray detection and measurement using high resolution detectors usually requires fast and low noise front-end electronics for pulse processing. Programmable digital filters are a superior alternative to the traditional analog electronics in terms of throughput and flexibility. For example, it is possible to implement optimal or near optimal filters which are difficult to achieve with analog techniques. Compact digital pulse processing is a good alternative to bulky analog electronics in the applications that need several detectors.

Today's state of the art hardware and software tools in the digital pulse processing can greatly improve and speed-up development of a high performance digital spectrometer. In a project carried out in co-operation with Mr. Mladen Bogovac, Croatia, Xilinx Xtreme DSP Development kit for Virtex-4 SX (Fig. 1.) was used as a hardware prototyping platform. The kit is based on the Xilinx's most advanced Virtex family of FPGAs equipped with two 14bits 105MSPS ADCs and two 14 bit 160 MSPS DACs. The Xilinx System Generator is used as a main software tool. It provides system modelling and automatic code generation from Simulink and MATLAB environment. The kit can operate as a

stand alone communicating with host via USB (optionally Ethernet) or plugged into the PCI slot.

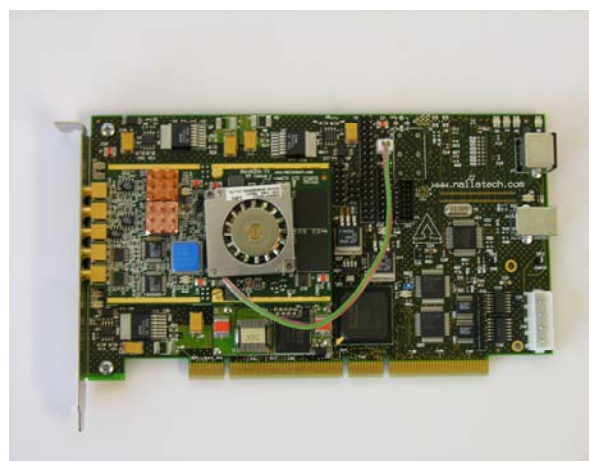


Fig. 1. The Xilinx's XtremeDSP Development kit for Virtex 4 used as a rapid prototyping platform for the multi-channel digital spectrometer.

The design targets measurements with high throughput. In order to utilize the ADC as effectively as possible, the input signal is passed to a pre-filter before being digitized. The pre-filter includes: differentiation, pole-zero cancellation, linear amplification and finally anti-aliasing filter. The converted data are processed by Virtex 4 in the full speed of 105 MSPS and 14bit resolution using continuously time domain filtering. As a

starting point a simple energy filter that gives triangular/trapezoidal output signal is used (Fig 2.). The output's signal SNR ratio is close to the optimal cusp shape for an exponential input signal. The filter is realized by the System Generator's blocks in the Xilinx's fixed point arithmetic. In order to remove slow changing DC component in the input signal, a Base Line Restorer (BLR) subsystem block is designed. The block continuously monitors filtered signal and averages it over a predefined time, and only when no pulse is present in the input signal. The averaged values are continuously subtracted from the filtered signal. The result of the subtraction feeds the Pulse Height Analysis subsystem block (PHA). The PHA is basically a peak detector engine gated by the Pile-up Rejector (PUR) subsystem block. The PUR is triggered by the fast filter that is identical to the energy filter except for a shorter peaking time. The calculated amplitude is stored into the System Generator's shared memory block in a three cycles, read-increment-write, that actually builds a spectrum. The BLR, PHA and PUR subsystem blocks are realized by the System Generator's MCode block. The MCode block enables compilation of the Matlab code into the FPGA. For the communication with the host computer, a dedicated VHDL module is created. This communication is using a separate 40MHz clock. The modules generated by the Multiple Subsystem Generator block are instantiated in the top-level VHDL project. The project is synthesized, placed and routed by the Xilinx Integrated Software Environment (ISE).

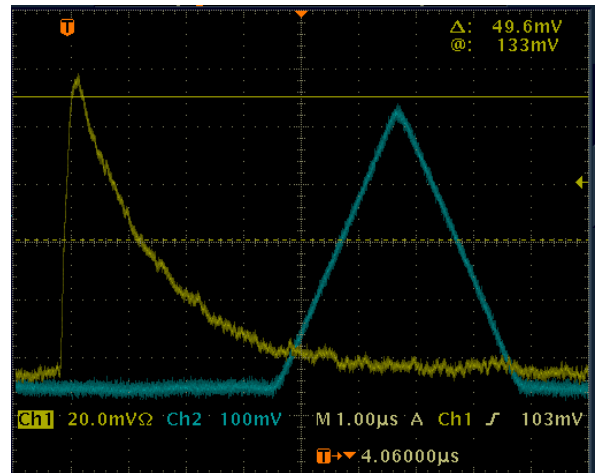


Fig. 2. Outputs of the analog prefilter (yellow) and of the triangular energy filter (blue) converted to the analog signal by one of the on-board DACs.

The XtremeDSP Development kit features an extension connector, so several modules can be changed. It allows extending the design from existing two channels to a desired number.

In order to test the design the pre-filter is directly connected to the Ketek GmbH Axas SDD 10 detector. The preliminary results show resolution comparable to the Canberra InSpector 2000. The fine tuning of the system is under the way.

Further information on the development of the multi-channel digital spectrometer is available from Dariusz Wegrzynek (D.Wegrzynek@iaea.org).

Support to Technical Cooperation projects

The XRF Group at Seibersdorf provides assistance to a number of IAEA Technical Cooperation (TC) projects where XRF is used as one of the analytical techniques. The following events related to TC projects were supported in 2006:

Progress Assessment Meeting for Regional TC Project on Improved Information about Urban Air Quality Management (RAS/7/013), Bandung, Indonesia, 7- February 2006

The purpose of the meeting attended by the National Project Counterparts from Australia, China, India, Indonesia, Mongolia, Myanmar, New Zealand, Pakistan, Philippines, Sri Lanka, Thailand, Vietnam, an expert from USA and IAEA staff was to review and assess progress against the objectives of the project, to discuss data evaluation and interpretation, to assess role and contribution of end-users, Regional Resource Units and Lead

Country Coordinator, to identify actions to ensure sustainability of the project as well as to review the work plan for the coming years. Recognizing the accomplishments of the current project and its positive impact on air quality management across the Asia-Pacific region the participants of the meeting confirmed their interest and intention to continue the activities under a new project on "Characterization and source identification of air

particulate pollution in the Asian Region and their impacts on trans-boundary pollution, visibility, climate change and human health". It was generally agreed that the new project will bring additional benefits and further enhance the utilization of the unique long-term database

generated by using nuclear analytical techniques (XRF, NAA and ion beam analysis) under the current project. A detailed work plan for the coming years was designed in order to focus on new issues in air pollution such as visibility, health and climate change.

Regional Training Course on Implementation of Portable X ray Fluorescence Analysis and Ion Beam Methods in Cultural Heritage Studies (RER/1/006), Athens, Greece, 27 – 31 March 2006

The training course held under the regional TC project RER/1/006 on "Nuclear Techniques for the Protection of Cultural Artefacts in the Mediterranean Region" was organised by the Institute of Nuclear Physics, National Centre for Scientific Research "Demokritos" in cooperation with the Directorate of Ancient and Modern Monuments, Hellenic Ministry of Culture, and IAEA. Twenty participants representing the nuclear research centres and end-user institutions from Albania, Bosnia and Herzegovina, Croatia, Cyprus, Greece, The Former Yugoslav Republic of

Macedonia, Malta, Serbia and Montenegro, Slovenia and Turkey attended the training. A major objective of the event was to present principles, methodology, advantages and limitations of portable XRF techniques and ion beam analytical methods for characterization of cultural heritage objects such as wall paintings, architectural objects, pigments and ancient alloys. Special emphasis was on practical applications of a portable XRF spectrometer developed in Greece for in-situ measurements in a museum.

Task Force Meeting to Design and Prepare ICT Materials in the Field of Nuclear Analytical Techniques Including Gamma-, Alpha- and X ray spectrometry (RAF/0/020), Algiers, Algeria, 17 – 21 June 2006

The purpose of the Task Force Meeting attended by the participants from Algeria, Egypt, Kenya, Morocco, South Africa, Tunisia and USA was to review, compile and select the available (conventional) teaching materials in the fields of gamma-, alpha- and X ray spectrometry to be included into the ICT (Information Communication Technology) – based modules, to identify target trainees and define modalities for

development of ICT-based materials as well as to discuss possible integration of the ICT-based materials into an overall training program in support of an AFRA Network for Education in Science & Technology. It was agreed that the ICT-based modules, currently under development by the experts, will be distributed for evaluation to the project coordinators and tele-centres established in Member States under the project RAF/0/020.

First Project Coordination Meeting for Regional (AFRA) TC Project on Developing Urban Zone Air Pollution Monitoring (RAF/4/019), Kenitra, Morocco, 11 – 15 September 2006

The purpose of the meeting attended by the National Project Coordinators from Algeria, Burkina Faso, Cameroon, Democratic Republic of Congo, Egypt, Ethiopia, Ghana, Madagascar, Mali, Mauritius, Morocco, Niger, Senegal, Sierra Leone, Sudan, United Republic of Tanzania and Tunisia was to review the current activities in the field of air pollution monitoring (including available facilities and partners) and to review the project document for 2007-2010 including regional priority needs, training courses, detailed work plan and performance indicators. In general, the

meeting demonstrated that countries involved in the project are diversified as far as technical infrastructure and institutional set-up are concerned. The project will be managed at the national level by both nuclear research centres and environmental protection agencies which make the implementation of the project very challenging and creates a unique opportunity for strong interactions with the end-users. It was agreed that in each country a National Coordination Team will be set up to involve all major stakeholders. Moreover, the participants decided to share nuclear analytical

techniques available in some countries for the benefit of the whole region. As a result of the meeting a standard package of sampling equipment is being provided to majority of the participating countries.

Further information on support to TC projects is available from Andrzej Markowicz (A.Markowicz@iaea.org)

Conferences and workshops

Staff of the XRF Group attended a number of conferences and workshops in 2006. Below there is a short summary of selected events attended:

55th Annual Conference on Applications of X ray Analysis, Denver, USA, 7 – 11 August 2006

The Conference was attended by more than 300 participants from all over the world. The programme of the Conference covered the following topics: (i) medical applications of X ray analysis, (ii) new developments in XRD and XRF instrumentation, (iii) quantitative XRF analysis, (iv) thin films analysis, (v) applications of high-energy X rays, (vi) X ray optics, (vii) industrial applications of XRD, (viii) detectors and sources, (ix) stress analysis, (x) fusion applications, and (xi) trace analysis. The first two days were dedicated to workshops on: (i) specimens preparation, (ii) high resolution XRD, (iii) basic crystallography, (iv) trace element analysis, (v) micro-beam X ray characterisation, (vi) new generation of XRD databases, (vii) basic XRF, (viii) quantitative XRF, and (ix) energy-dispersive XRF. During the Conference an exhibition of about 40 major companies in the field of XRF and XRD took place. An invited paper on “Recent developments in trace element- and micro-analysis at the IAEA XRF Laboratory” (A. Markowicz, D. Wegrzynek, S. Bamford, E. Chinea-Cano) was presented. A special emphasis was on trace element in-situ XRF analysis and integration of micro-analytical techniques such as micro-beam XRF, micro-tomography, and confocal geometry set-up for study of individual particles, biological materials etc. Development of new spectrometers, improvements in methodology of XRF analysis including sample preparation and quantification procedures as well as selected applications for analysis of environmental and biological materials, cultural heritage objects were also covered. During a Workshop on Trace Element Analysis a lecture on “In-situ trace element determination by using portable XRF spectrometers” was given. Principles

of in-situ measurements and portable XRF spectrometers together with associated interfering effects and relevant correction procedures were covered. Finally a poster on “X ray phase-contrast tomography of malaria transmitting mosquitoes for morphology studies” (D. Wegrzynek, E. Chinea-Cano, A. Markowicz, S. Bamford, B. Knols, M. Helinski, P. Wobrauschek, C. Strelu, N. Zoeger, R. Simon, T. Weitkamp, C. Frieh) was presented jointly with P. Wobrauschek and C. Strelu, Technical University, Vienna. The contribution described principles and corrections applied in X ray phase-contrast tomography as well as the first results obtained by the IAEA Laboratories at Seibersdorf in collaboration with Atominstut, Technical University, Vienna and Research Group of Synchrotron Radiation, Karlsruhe, Germany, for study of morphology of mosquitos (the poster was selected by the organizers the best XRF poster of the 2006 Denver Conference)

The 2006 Denver Conference confirmed that the major developments in the field of XRF are currently related to X ray optics and applications of synchrotron radiation sources for characterisation of materials by complementary use of various analytical techniques. Progress in thermoelectrically cooled semiconductor detectors resulted in availability of Si-PIN detectors of 1000 μm thickness with substantially improved detection efficiency for X rays in the region of 15 – 30 keV. Availability of low-power X ray tubes often combined with X ray optics provides micro-sized focused beams with extremely high flux density which allows new applications in microelectronics, biomedicine, archaeology and geology.

International Workshop on Science for Cultural Heritage, Miramare-Trieste, Italy,
23 – 28 October 2006

The Workshop attended by about 90 participants covered the following topics: (i) materials science for cultural heritage, (ii) archaeological prospection, (iii) techniques in paleoanthropology, (iv) environmental and climatic impact on cultural heritage as well as practical sessions to demonstrate both portable and laboratory instruments and methodologies. A paper on “Applications of nuclear analytical techniques for study of cultural heritage” (D. Wegrzynek, E. Chinea-Cano, A. Markowicz, S. Bamford, M. Rossbach, M. Ferrari, G. Mank, N. Dytlewski, A. Mendoza-Cuevas, G. Buzanich, P. Wobrauschek, Ch. Strel, M. Griesser) was presented. It was emphasized that elemental analysis of archaeological artefacts and cultural heritage objects can help to reveal ancient material usage, technology of preparation, identification of provenance and in some cases, can also provide an indirect dating tool. A highly valuable result of

elemental fingerprinting can be the identification of forgery by the detection of anachronistic materials. Nuclear analytical and related techniques are of particular interest for archaeologists because of their multi-elemental capability, generally high level of reliability and most important, non-destructive nature of analysis. Recently XRF, INAA, PIXE, RBS are widely accepted and routinely applied by researchers, art historians, restorers and curators in cultural heritage studies and restoration. In order to support study of cultural heritage objects, a dedicated (trans)portable X ray fluorescence spectrometer has been designed and manufactured at the IAEA Seibersdorf Laboratories. The spectrometer was applied for chemical composition analysis of bronze samples and pigments as well as for study of provenancing of works of art in the Museum of Fine Arts in Vienna.

European Conference on X ray Spectrometry - EXRS 2006, Paris, France, 19-23 June 2006

The Conference was attended by about 300 participants from 40 countries and included 16 oral sessions and more than 180 poster contributions. During a commercial exhibition more than 20 suppliers presented their equipment related to X ray analytical methods. The sessions covered the following areas: (i) interactions of X ray with matter, (ii) micro-beam techniques, (iii) applications in art and archaeometry, (iv) applications in earth and environmental science, (v) synchrotron radiation instrumentation, (vi) X ray absorption spectroscopy, (vii) data processing, (viii) applications in materials and nanotechnology, (ix) total reflection X ray fluorescence, (x) new instruments, (xi) quantification, (xii) new detectors, (xiii) X ray optics, and (xiv) X ray imaging techniques. A paper on “Phase-contrast enhanced X ray tomography of malaria transmitting mosquitoes” (D. Wegrzynek, E. Chinea-Cano, A. Markowicz, S. Bamford, B. Knols, M. Helinski, P. Wobrauschek, C. Strel, N. Zoeger, R. Simon, T. Weitkamp, C. Frieh) was presented during the session on X ray Imaging Techniques. In the contribution the results of the experiments carried

out at the ANKA Synchrotron Facility, Karlsruhe, Germany were discussed. The relevant project was coordinated by the Instrumentation Unit and carried out jointly with the Entomology Unit, IAEA Seibersdorf Laboratories, the Atominstitut, Vienna, and the ANKA Synchrotron Facility, Karlsruhe, Germany. The results of experiments performed at ANKA demonstrated the usefulness of X ray phase-contrast tomography for investigation of morphological changes in the irradiated mosquito specimens.

In general, papers presented at the Conference confirmed a rapid development of advanced X ray analytical techniques. The most noticeable advances are observed in detector technology, e.g. large area, high throughput, low-noise liquid nitrogen-free detectors are becoming available. Also a new concept for X ray focusing optics based on nano-polycapillary structures and shaped polycapillary lenses was presented. Substantial increase in number of applications has been observed in the fields of life sciences, material research and archaeometry.

Next European Conference on X ray Spectrometry (EXRS 2008) will be held in Croatia in 2008.

Further information on the IAEA contributions presented at the Conferences/Workshops is

available from Andrzej Markowicz (A.Markowicz@iaea.org)

Announcement of IAEA Proficiency Test for XRF laboratories

The IAEA Laboratories at Seibersdorf will organize the third worldwide proficiency test for XRF laboratories. This time, the test involves distributing to participating laboratories a sample of environmental origin (clay) with established homogeneity and known target values of the analytes. About 100 grams of the material will be distributed to each participant which is sufficient for making analysis under the proficiency test and future use of the remaining part as a Reference Material.

The laboratories are requested to analyze the sample using established techniques following their analytical procedures. Based on the results of the proficiency test each participating laboratory will be able to assess their analytical results by using the specified standard performance criteria

and, if appropriate, to identify discrepancies and to correct their analytical procedures.

The official announcement will be distributed to the XRF laboratories in December 2006. The sample and the required documentation will be distributed in the first quarter of 2007. Completion of the exercise is planned for the third quarter 2007. The final report of the proficiency test will be distributed to the participants not later than 3 months after submission of the results.

In case you are interested in taking part in the proficiency test please inform A. Markowicz (A.Markowicz@iaea.org) immediately. Those laboratories which confirm their willingness to join the exercise will receive further details including reporting instructions.

X ray fluorescence in Member States

During the last months we have received contributions from Austria, Belgium and the Philippines on the current XRF activities. Below there are communications based on the original submissions (with only minor editorial changes).

Austria

Recent results of the ATI X ray group with SR-XRF

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Introduction

Total Reflection X ray Fluorescence (TXRF) technique is a special method of energy dispersive X ray fluorescence analysis extending the analytical performance of XRF in the trace and ultra trace element range. It is an internationally accepted and worldwide-applied analytical method with detection limits in the pg range using X ray tubes as excitation source. The obtained detection limits depend strongly on the excitation source and photon flux on the sample. To improve the detection limits, the use of new excitation sources offering more photon flux is required. Using rotating anode tubes, the detection limits obtained are in the some 100 fg range.

Synchrotron radiation turned out to be excellent suitable for being used as excitation source in TXRF and our working group was one of the pilot teams to reach detection limits in the fg range [1]. The applicability of TXRF ranges from any kind of liquid samples to all kind of samples where only small amounts are available. It is a microanalytical technique for environmental samples as well as for clinical, biological, art, forensic, industrial samples used for research and development purposes [2 - 5]. TXRF offers the advantage of an efficient excitation, a low background and the possibility of surface analysis, if the sample surface meets the

requirements for total reflection, like flatness and low roughness.

Installation of a new sample changer for SR-TXRF

Recently, a new sample changer for the Synchrotron Radiation induced Total reflection X ray Fluorescence (SR-TXRF) analysis vacuum chamber [6,7] at Beamline L at HASYLAB, Hamburg has been developed by the X ray Group of the Atomic Institute of the Vienna University of Technology. The performance of the instrumentation was increased by an automated reflector carrier capable of containing 8 quartz or silicon reflectors at the same time. After preliminary beam adjustments, the sample changing and parts of the sample adjustment are automated. This establishes the opportunity to measure 8 samples consecutively without the necessity to close the beam shutter and open the vacuum chamber - resulting in significant time saving during the beam time. The spectrometer is equipped with a Silicon-Drift-Detector (SDD) with an active area of 50mm².

The higher sample throughput which is now possible is especially desirable for the analysis of aerosols where a large number of samples has to be analyzed.

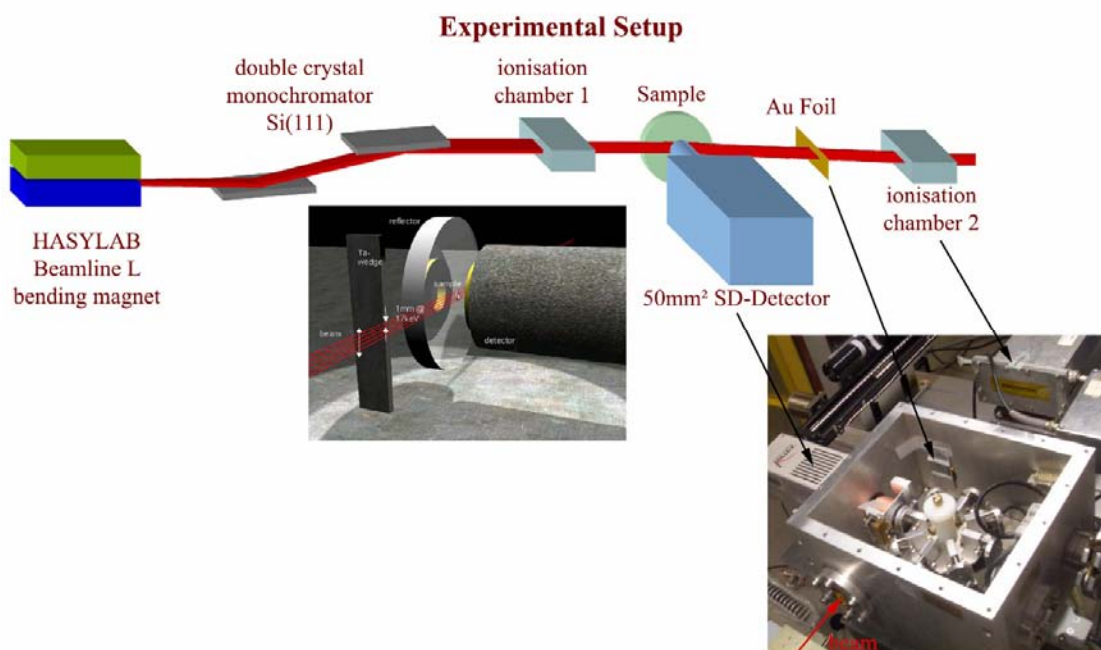


Fig. 1: Experimental setup at Beamline L, HASYLAB with TXRF vacuum chamber and sample changer. (Gold foil and ionization chambers are used for TXRF-XANES, see below.)

Trace element analysis of fine aerosol particles with high time resolution using SR-TXRF

This project is accomplished in cooperation with S. Török, J. Osán and V. Groma and deals with the analysis of impactor-collected aerosols to monitor local air pollution [8].

SR-TXRF is especially suitable for the analysis of aerosols because of the inherent properties of synchrotron radiation like natural collimation, broad spectral range and high intensity. These qualities in combination with the advantages of the TXRF geometry producing a low background enable the detection of trace and ultra trace amounts (ng/g, fg/g) of most elements.

An important point for the investigation of these aerosols was the possibility to perform a multielement analysis with a high temporal resolution (<10 min) to identify potential particle sources. To investigate a time and temporal variation of elemental concentrations short time collections are necessary. It could be shown that even masses collected in these short times are sufficient for SR-TXRF analysis.

Particles have been collected on silicon wafers at different locations in Hungary and Austria using a seven-stage May cascade impactor. The collection was performed only at stages 5, 6 and 7 (with

aerodynamic cut-off diameters of 1, 0.5 and 0.25 μm respectively) because the investigation was focused on the fine aerosol fraction exclusively. Each stage of the May impactor has an impacting slit therefore the collected particles are applied on the silicon reflectors as a thin strip with approximate dimensions of 20 mm \times 0.3 mm.

The energy of the synchrotron radiation was tuned to 17.5keV using the NiC multilayer monochromator and the vertical dimension of the beam set to 1 mm. The Vortex Radiant SDD was provided with a 1.5 mm wide Mo slit collimator to shield the fluorescence of possible contaminants lying beside the strip of collected aerosols.

The sample holders were mounted with the strip in vertical position and were scanned in 6 steps over a length of 6 mm. To calculate the mass of the present elements from the TXRF measurements a Cr standard with known mass and dimensions identically to those of the deposited aerosol particles was analyzed. With the known count rate (cps/mA) for the known mass, a calculation of the mass of the other elements using fundamental parameters is possible.

Exploiting the extremely high sensitivities offered by SR-TXRF for aerosol samples, analysis leads to detection limits in the pg/m^3 range for 20-min sampling time in the 0.5–1 μm aerosol fraction.

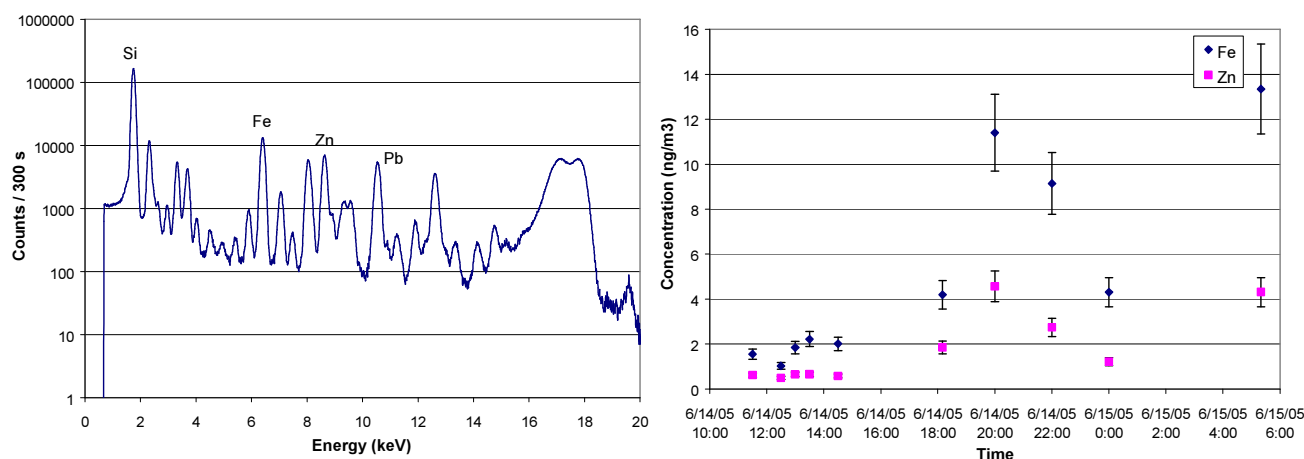


Figure 2: Left: typical SR-TXRF spectrum of an aerosol sample collected at stage 6 (0.5–1 μm). Right: temporal variation of Fe and Zn in the 0.5–1 μm aerosol fraction at Mátra (400 L air per sample).

Calibration with micro droplets generated by inkjet printers in element determination of aerosol samples with SR-TXRF

The main motivation accomplishing this project is the need for a calibration procedure that enables the determination of elements in a sample spot of

aerosols with SR-TXRF in short time and satisfying accuracy and precision. This work was done in cooperation with J. Broekaert and U. Fittschen [9, 10].

In atmospheric aerosols and biological samples, amounts are limited and the determination of very

low absolute amounts of elements is required. However, an accurate and reliable calibration of SR-TXRF analysis of particulate samples until now is often problematic.

As calibration with nano-droplets (10-50 nL) was found to give excellent results in the determination of trace impurities with TXRF in semiconductor material [11, 12] a calibration suitable for atmospheric aerosol analysis with SR-TXRF was developed by decreasing in volume to the pico-droplet (pL) range.

Within the framework of this project, the generation of micro droplets with commercial available and slightly modified inkjet printers, which are used to generate 5 to 130 pL droplets, was studied. The size of the droplets was

determined for five different printer types and eleven different cartridge types on surfaces of different polarity mainly from silicone coated and untreated quartz reflectors. The reliability of the printing of a certain amount of a single element standard solution was studied and related to common calibration in TXRF. The performance to print one and more droplets on a certain place was tested (Figure 3, right). The results showed that droplets generated by inkjet printers are smaller in diameter than the width of the Synchrotron beam used in the experiments between 50 and 200 μm depending on the cartridge type. The reliability of the dosing of single element standard solution is comparable to common calibration in TXRF and the printing of patterns in the μm range is satisfying.

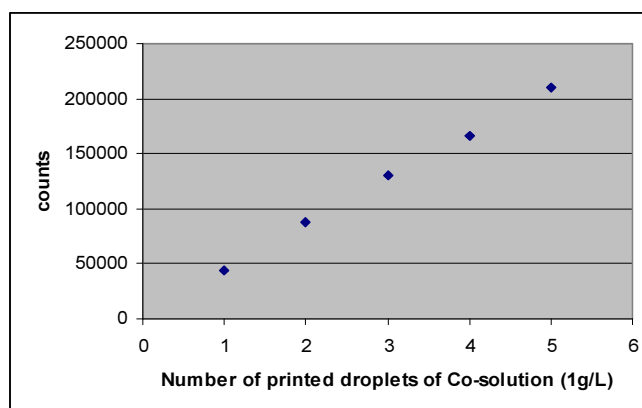


Fig. 3: Left: pico-droplet (Co 1g/L) printed by a modified HP500C on a silicon wafer investigated with a light microscope. Right: Five times 1 droplet of a 1g/L Co standard solution was printed successively with HP 500C on a quartz reflector

In atmospheric aerosol research, element speciation is important to assess their origin, toxicity and potential to influence climate processes. A major challenge in element speciation is to avoid chemical transformation during analyses. This easily occurs during sample preparation as used e. g. in fractionated solvent extraction or in applying chromatographic techniques.

X ray absorption near edge structure (XANES) measurements permit element speciation without dissolving the samples. As Si-wafers can be used as aerosol collection plates in an impaction device and as sample carrier for TXRF-XANES measurements, no additional step is necessary for sample preparation. Still there could be changes in element speciation during storage. Therefore the

stability of iron species in atmospheric aerosol samples stored under different conditions was studied. More measurements on this topic will be carried out in the near future.

XANES in TXRF geometry combines the advantages of detection of trace and ultra trace absolute amounts (pg, fg) of most medium Z elements and elemental speciation. This technique is therefore especially suitable to perform XANES on samples containing low concentrations of the element of interest. Within the scope of the next project XANES in combination with TXRF acquisition was utilized for speciation of arsenic in cucumber (*Cucumis sativus* L.) xylem sap. This work was done in cooperation with V.G. Mihucz, G. Zaray and V. Czech.

Arsenic speciation in cucumber (Cucumis sativus L.) xylem sap by K-edge TXRF-XANES

Comparing TXRF-XANES to chemical analysis with SR-TXRF, one has a lower sensitivity, as the flux transmitted by the crystal monochromator (Si-111) is about 100 times lower than that transmitted one by the multilayer monochromator. The XANES measurements were performed for As in xylem sap samples collected from cucumber plants grown in $2 \cdot 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$ arsenite [As(III)] and arsenate [As(V)], respectively, containing 4 time-diluted Hoagland nutrient solutions. Xylem sap was chosen for the investigations, because of playing an important role in the transpiration stream of the plants. Moreover, if plants can easily exudate xylem sap, no further sample preparation is required and, thus, cross-contamination can be avoided.

The toxicity of arsenic differs considerably in function of the oxidation state and chemical form. Inorganic As species, like arsenite and arsenate, are more toxic than the organic ones, e.g. monomethyl arsonic (MMA) and dimethyl arsinic (DMA) acids. Among the inorganic arsenic species, arsenate is less toxic than arsenite. Plants

may have the capability to change the oxidation state of arsenic therefore, this issue should be investigated. Experiments were performed by growing cucumber plants in hydroponics containing As(III) or As(V) in order to identify the arsenic species of the collected xylem saps by SR-TXRF. Moreover, the As concentrations of the samples were also determined. The big advantage of SR-TXRF is that the xylem sap can be directly measured after collecting it with micropipettes in Ar atmosphere, the latter to avoid oxidation state alterations, and drying on the carrier plates some μl from the samples.

Standard solutions of As(III) and As(V) were measured, the difference in the oxidation states of As could be proved with the performed XANES measurements.

Nutrient solutions containing $2 \cdot 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$ As(III) and As(V), respectively, used for plant growth were also measured. The differences in the XANES spectra have been documented, thus, the As(III) and As(V) peaks could be differentiated. Finally, the xylem sap of plants contaminated with As(III) and As(V), respectively, have been compared (Figs. 4 and 5).

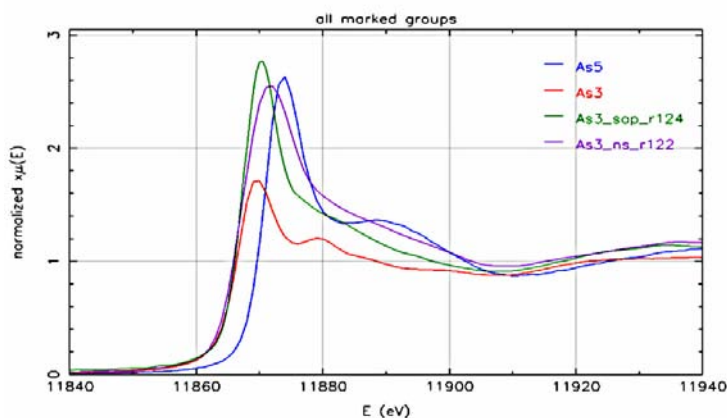


Fig. 4: XANES spectra of As(III) and As(V) standards, nutrient solutions containing As(V) in concentration of $2 \cdot 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$ and xylem sap of plants grown in this nutrient solutions.

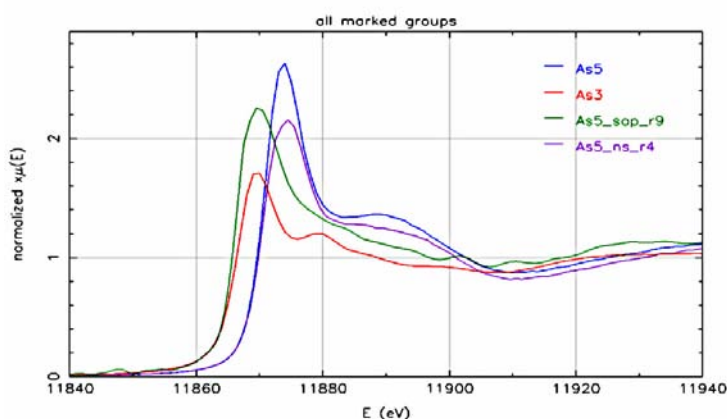


Fig. 5: XANES spectra of As(III) and As(V) standard solutions, nutrient solutions containing As(III) in concentration of $2 \cdot 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$ As and xylem sap of plants grown in this nutrient solution.

The XANES spectra of the xylem saps revealed the occurrence of As(III) in the saps independently of the oxidation state of As in the nutrient solution. This is in accordance with the reducing capacity of the higher plants. These results correspond to the outcomes obtained by HPLC-HR-ICP-MS [13]. It is postulated that the reduction of As(V) to As(III) is an essential process for arsenic detoxification (e.g., by depositing As(III) in the senescent leaves, fronds [14], although As(III) is generally more toxic than As(V). However, the reduction of As(V) to As(III) seems to be crucial, arsenate being a phosphate analogue, and thus, it can alter the energy metabolism of the plants.

Elemental Mapping of Human Bone by Confocal SR micro-XRF

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 systems. Once incorporated through ingestion or inhalation, Pb accumulates in the skeleton. However, little is known about how Pb is

distributed in calcified tissue on the microscopic level. Therefore our group studied the distribution of Pb in human bones slices using synchrotron radiation induced micro X ray fluorescence analysis (SR μ -XRF) in scanning and tomographic mode [15]. The project is performed in cooperation with the IAEA Seibersdorf Laboratories, XRF Group, Instrumentation Unit, Seibersdorf, Austria, the Ludwig Boltzmann-Institute of Osteology, Vienna, Austria as well as with the two German Synchrotron radiation facilities HASYLAB at DESY, Hamburg and ANKA, Karlsruhe.

The latest results were obtained by using the confocal microbeam setup at HASYLAB beamline L. With this setup a quasi-cubic detection volume, defined by the overlap of the focal cones of the two X ray optics (one in the primary beam, the second one in front of the energy-dispersive X ray detector) was used for analyses. Since this variant of SR μ -XRF offers the possibility to perform depth sensitive analysis it was used to determine the three-dimensional distributions of Pb and other (trace) elements in human bone (Figure 6) with an resolution of about 10 μ m (lateral and in depth).

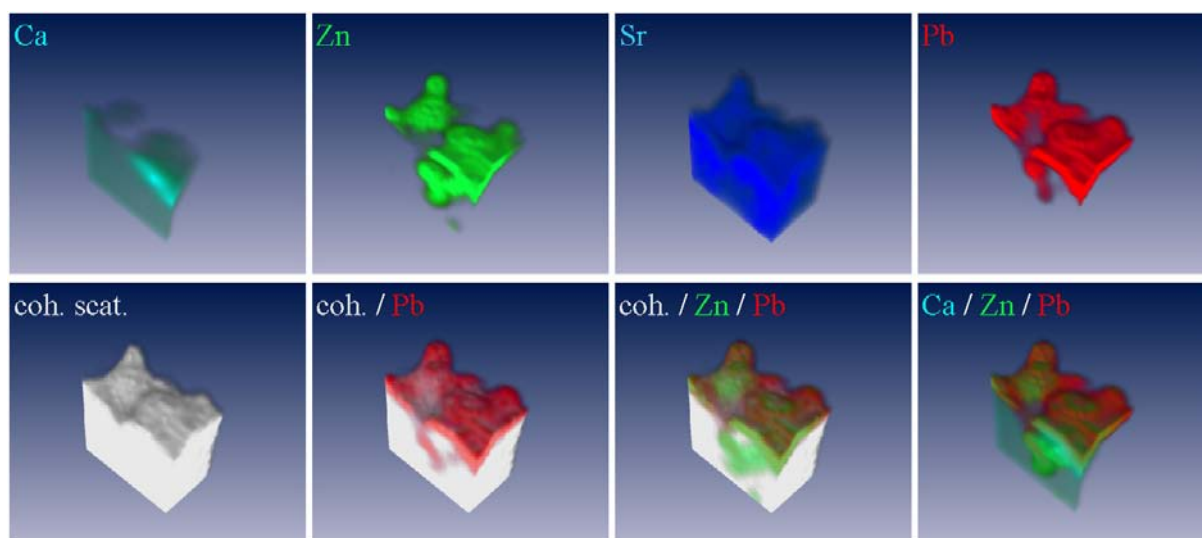


Fig. 6. Three-dimensional elemental distribution in a human patella sample. Distance of measurement pixel: 10 μ m (lateral and in depth); measurement time per pixel: 5s; scanned volume: 200 x 200 x 160 μ m³; total number of spectra: 7497.

The region for the scan in human patella was chosen to contain non-mineralized articular cartilage, mineralized articular cartilage and subchondral bone. From this measurement a very local distribution of Zn and Pb at the tidemark (the border between non-mineralized and mineralized

cartilage) could be detected [16]. These novel results of the specific accumulation of Pb in the tidemark of human bone may lead to further understanding and research on the effects of Pb on cartilage, bone biology and biomineralization.

References

- [1] R. Rieder, P. Wobrauschek, W. Ladisich, C. Strelí, H. Aiginger, S. Garbe, G. Gaul, A. Knöchel, F. Lechtenberg, Nucl. Instr. Meth. 355(2,3): 648 (1995)
- [2] A. Prange, Schwenke, Adv. X ray Anal. 35: 899 (1992)
- [3] A. Prange, H. Böddeker and K. Kramer, Spectrochim. Acta 48B: 207 (1993).
- [4] R. Klockenkämper, A. von Bohlen, L. Moens and W. Devos, Spectrochim. Acta 48B: 239 (1993).
- [5] R. Klockenkämper, A. Von Bohlen J. Anal. Atom. Spectrom. 7: 273 (1992)
- [6] C. Strelí, G. Pepponi, P. Wobrauschek, C. Jokubonis, G. Falkenberg, G. Zaray, X ray Spectrometry, 2005. 34(5): p. 451-455.
- [7] C. Strelí, G. Pepponi, P. Wobrauschek, C. Jokubonis, G. Falkenberg, G. Zaray, J. Broekaert, U. Fittschen, and B. Peschel, Spectrochimica Acta Part B: Atomic Spectroscopy. In Press, Corrected Proof.
- [8] J. Osán, S. Török, V. Groma, C. Strelí, P. Wobrauschek, F. Meirer, G. Falkenberg, HASYLAB Annual Report, 2005.
- [9] U. Fittschen, C. Strelí, S. Hauschild, G. Lammel, D. Rehder, G. Pepponi, P. Wobrauschek, F. Meirer, C. Jokubonis, S. Förster, J. Broekaert, G. Falkenberg, HASYLAB Annual Report, 2005.
- [10] U. E. A. Fittschen, S. Hauschild, M. A. Amberger, G. Lammel, C. Strelí, S. Förster, P. Wobrauschek, C. Jokubonis, G. Pepponi, G. Falkenberg, J. A. C. Broekaert, Spectrochimica Acta Part B, 2005. accepted.
- [11] T. C. Miller, C. M. Sparks, G. J. Havrilla, and M. R. Beebe, Spectrochimica Acta Part B: Atomic Spectroscopy, 2004. 59(8): p. 1117-1124.
- [12] G. J. H. Thomasin C. Miller, X ray Spectrometry, 2004. 33(2): p. 101-106.
- [13] V. Mihucz, E. Tatár, I. Virág, E. Cseh, F. Fodor, and G. Záray, Analytical and Bioanalytical Chemistry, 2005. 383(3): p. 461-466.
- [14] W. Zhang, Y. Cai, C. Tu, and L. Q. Ma, The Science of The Total Environment, 2002. 300(1-3): p. 167-177.
- [15] N. Zoeger, P. Wobrauschek, C. Strelí, G. Pepponi, P. Roschger, G. Falkenberg, and W. Osterode, X ray Spectrom, 2005. 34(2): p. 140-143.
- [16] N. Zoeger, P. Roschger, J. G. Hofstaetter, C. Jokubonis, G. Pepponi, G. Falkenberg, P. Fratzl, A. Berzlanovich, W. Osterode, C. Strelí, and P. Wobrauschek, Osteoarthritis and Cartilage, 2006. 14(9): p. 906-91

Belgium

Micro & Trace Analysis Centre (MiTAC), University of Antwerp (UA), Belgium

Contributors: *Roman Padilla, from CEADEN, Havana, Cuba, frequent long-term visiting researcher in MiTAC, and Koen Janssens, Pierre Van Espen and Rene Van Grieken, MiTAC*

There are several XRF spectrometers currently in use in MiTAC for the determination of elemental mass fractions in samples of diverse nature: a transportable energy-dispersive XRF unit employing $^{55}\text{Fe}/^{109}\text{Cd}$ radioisotope sources; a bench top spectrometer based on an X ray tube and additional filtering for excitation (MiniPAL-1, PANalytical) and a spectrometer using a polycapillary lens for micro-focus ($\sim 60 \mu\text{m}$) excitation. A novel XRF spectrometer was installed in 2005 (Epsilon-5, PANalytical), which has the advantages of selective secondary target excitation and of being capable to determine high atomic number elements by their K-lines. The latter is achieved by using a 100 kV, 6 mA Gd anode tube as a primary source and a Ge detector with ultra-light entrance window. The Epsilon-5 unit achieves lower detection limits by applying a

3-D polarized beam excitation, which effectively avoids scattered tube radiation to reach the detector. Besides that, MiTAC has two additional scanning electron microscopes with X ray microprobes (electron probe X ray microanalysis, EPXMA) allowing performing elemental analysis with high spatial resolution.

Three research groups are involved in studies employing X ray fluorescence or X ray related techniques. The main research fields and projects carried during the last five years are summarized below:

The group headed by Prof. Rene Van Grieken (see also the homepage: <http://webhost.ua.ac.be/mitac1>), called Environmental Analysis Group, carries out fundamental and methodological research of micro and trace analysis and the

application in material science and especially environmental issues. The latter include studies of atmospheric aerosols (deposition of pollutants to sea and land, effects on climate) and on the interaction of pollutants and cultural heritage items (buildings, paintings). The main relevant projects that are being carried out or have been carried out very recently are the following:

- *Identification and prognosis of atmospheric pollution in selected health resorts of Lower Silesia after the modernization of the two largest industrial plants in this region (Bilateral Flemish-Polish research project).* X ray techniques are applied to the analysis of samples with a complex matrix, both individual particles (aerosols, sands, sediments) and large-size solids.
- *Quantitative procedures for in situ XRF analysis of soils (Bilateral Flemish-Argentinean research project).* The adequate screening of soil plays a significant role, since soil pollution could have enormous impact on the contamination processes of ground water, in agriculture, etc. Especially in the case of toxic and heavy metals, the identification and monitoring of the contaminants is of great importance.
- *Investigation of the possibilities of a new XRF instrument equipped with high-energetic polarized excitation for applications on precious metals.* The purpose of the project is to investigate the possibilities of the use of high-energetic polarized XRF (using Epsilon 5, PANalytical, Almelo, Netherlands) for these analyses. The intention is to replace e.g. the present common ICP-OES analytical method for precious metals in spent car catalysts (which takes 5 days of sample preparation) in order to get a shorter time of analysis or a reduction of the preparation time. It appears that EDXRF with this instrument allows achieving the same precision and accuracy as ICP-OES, namely better than 1%, within one hour of total analysis time.
- *Preventive conservation in the Metropolitan Museum of Art, New York.* The project aims at assessing the gaseous and particulate air pollutants within (indoor) and around (outdoor) the very important Metropolitan Museum of Art in New York. Detailed mapping of, and studying the anthropogenic and natural atmospheric constituents (including XRF and EPXMA) within the museum, and proposing remedies to reduce the contamination, will eventually help in the conservation of the precious artworks in the museum.
- *Atmospheric nitrogen input into the North Sea: Inorganic and organic nutrient fluxes.* This project aims at the first comprehensive identification and quantification of the individual inorganic and organic compounds that contribute to the nitrogen loading of the air above the Southern North Sea. Elemental analyses by XRF and individual particle analyses by EPXMA are done to support the nitrogen research data (e.g. by identifying the source region based on the elemental fingerprints).
- *Properties of welding aerosol particles and optimization of their trapping.* In the processes of arc welding, a high concentration of toxic aerosols appears which pollutes the environment and damages people's health. The problem of cleaning the air from harmful products of the arc welding is thus actual and imperative. Fibrous filters that are usually used for such purposes are not always applicable; besides, in conditions of high concentration of solid particles, the life time of the common filters is too low. The latter can be substantially extended if, before filtering, the air is preliminarily processed by other methods (magnetic separation, electric filtering, etc.). The efficiency of these cleaning methods directly depends on the properties of aerosol particles, which can be very different for different welding technologies. In this project, the properties of such aerosol particles in typical conditions of ventilation systems before their entrance into filtering devices are studied by XRF and EPXMA.
- *Study of the influence of fine particles in indoor and outdoor air on chronic obstructive respiratory diseases in the Antwerp region on the basis of an improved chemical analytical methodology.* In order to determine the relation between the

respiratory symptoms and the composition of particulate matter, a full chemical characterization of the fine and ultra fine fractions is needed. These fractions consist, apart from inorganic components, mainly of soot and organic compounds. Organic and inorganic constituents are characterized (both qualitatively and (semi-) quantitatively) using state-of-the-art instrumental techniques, including XRF, EPXMA and micro-Raman spectrometry.

- *"VIDRIO" (Determination of conditions to prevent weathering due to condensation, particle deposition and micro-organism growth on ancient stained glass windows with protective glazing).* This project involves the analysis of gaseous and particulate air pollution (by diffusion tubes, XRF, EPXMA) inside churches with historic stained glass windows with and without protective glazing. The aim of this project is to propose a general directive on the most appropriate operative methodology for preserving historic stained glass in respect to chemical, microclimate and micro-biological deterioration. The three major aims of the project are achieved with a global approach, in 3 important cathedrals and churches: the Sainte Chapelle (Paris), Basilique St. Urbain (Troyes) and the Cathedral of Cologne.
- *Development of electron probe X ray micro analysis (EPXMA) towards lighter elements and lower detection limits; application to environmental particles.* The fundamental goal of this project can be summarized in two objectives: Optimization of the measuring conditions, quantification procedures and data-evaluation techniques of 'ultra-thin window' EPXMA for computer aided analysis of a large number of particles (determination of the exact concentration of light elements and the speciation analysis of microscopic particles in environmental), and optimization of the experimental conditions in Grazing Exit (GE) -EPXMA, developing an improved instrumental configuration equipped with a wavelength dispersive X ray detector (WDX-version) and improved control and resolution of the tilt angle of the sample carrier.

- *Novel quantitative procedures for in-situ XRF analysis:* This IAEA CRP dealt with the development of a quantitative method based on partial least squares (PLS) calibration and Monte Carlo simulations which are used for in-field XRF measurements such as analysis of soils and artifacts from cultural heritage.

The group headed by Prof. Koen Janssens (see also homepage: <http://webhost.ua.ac.be/mitac4>), called X ray Microbeam Analysis Research Group, uses (synchrotron) X ray microbeams for non-destructive (trace) analysis and materials characterization. The following methods of analysis are employed: microscopic XRF analysis (elemental trace analysis), microscopic X ray absorption spectroscopy (oxidation state mapping) and X ray micro tomography (three-dimensional characterization of small samples). Applications are situated in the archaeometry and environmental fields. The projects in due course now are:

- *COPRA - A Compact Röntgen Analyzer:* to develop and introduce on the market a compact, light-weight and inexpensive micro-beam XRF instrument that allows local analysis of sub-mm samples with minor/trace level sensitivity.
- *Quantitative three-dimensional XRF and absorption spectroscopy at the micrometer scale:* experimental validation of Monte Carlo simulation codes for synchrotron XRF spectra obtained with high energetic incident X ray beams for heterogeneous samples, evaluation of poly-capillary optical elements for micro-focusing of X ray beams obtained with high-energetic primary X rays. In addition, attention is given to the development of data reduction algorithms for the evaluation of micro-XRF diffraction patterns. Experimental studies are conducted at HASYLAB (Hamburg, Germany) and ESRF (Grenoble, France).
- *Development and application of X ray absorption spectroscopy on the micro-scale.* The aim of the project is to assess the method of micro-XANES that permits the experimental determination of the local oxidation state of trace constituents in solid materials quantitatively. This means that at the end of the project, it should be possible to reliably estimate the composition of

mixtures of the same chemical element in different oxidation states or molecular forms (e.g., mixtures of Cu in metallic form, Cu₂O, CuCl, CuCl₂, CuSO₄ as found in cross-sections of corroded bronze artifacts, mixtures of Fe²⁺ and Fe³⁺ in glass, of U⁴⁺ and U⁶⁺ in hot particles, etc.)

- *Optimization of synchrotron instrumentation for micro-XANES (X ray absorption near-edge spectroscopy):* to improve and expand the experimental facilities at HASYLAB BL L in two ways: (a) by introducing of highly-performant polycapillary focusing optics and (b) by upgrading the counting electronics of the fluorescence detector from analog to digital form, to allow processing of higher count rates during fluorescent XANES measurements.
- *Development and application of a method for speciation of transition metals in pollution aerosols, based on synchrotron micro-XRD (X ray diffraction).* The project aims to develop a method for the quantitative determination of the different molecular/crystalline forms in which transition metals (such as Ni) are present in microscopically small particles. By means of irradiation with an X ray microbeam, a combination of three analysis methods in the same equipment can be used to reach this goal: μ -XRF (elemental composition), μ -XANES (oxidation states) en μ -XRD (crystal phases). The principal aim of the project is to develop μ -XRD into a reliable phase-identification and quantitative analysis technique and apply the method in a number of specific areas.

The group headed by Prof. Pierre Van Espen (see also homepage <http://chemometrix.ua.ac.be>), called Chemometrix Group, deals with the development of instrumental micro and trace analysis techniques. Main interests are computer applications and chemometrics: data processing, multivariate methods and software development. The more recent projects are:

- *Development of quantitative analysis procedures based on the combined use of Monte Carlo simulation and multivariate calibration.* Monte Carlo simulation is used to produce (simulated) spectra of

hypothetical standards. These spectra are then used to calibrate a multivariate model with the aid of partial least squares regression (PLS-R). Once the model is built, hundreds of spectra from real samples can be converted to elemental concentration values using simple matrix multiplication. The methods has been developed for XRF as well as for EPXMA and applied to various problems.

- *Development of new robust multivariate techniques.* Multivariate techniques like principal component analysis (PCA) en partial least squares regression (PLS) have proven to be very useful for the direct quantification of spectral data as well as for the interpretation of large datasets generated by instrumental analytical techniques. However these methods are very sensitive to outlying data, i.e. data that contain gross measurement errors or data from samples that are vastly different from the rest. The group has developed robust variants of these techniques that do not suffer from these problems and can deal with outliers without disturbing the multivariate model.
- *Improvements in spectrum analysis.* Recently some considerable improvements have been made to evaluation of X ray spectra using the non-linear least squares fitting code AXIL. A model to describe accurately the Compton scatter peaks was developed and an improved model for the fluorescence lines was introduced using step and tail functions. Also the possibility to fit Voigt profiles instead of simple Gaussian was implemented. Much attention was paid to keeping the number of fitting parameters with these new models to a reasonable number, so that a stable spectrum fitting procedure could be developed.
- *Applications of XRF and SEM-EDX in diverse fields.* SEM-EDX and XRF are applied to various scientific and industrial problems. An example is the compositional classification of archaeological ceramics based on non-destructive XRF analysis.

Philippines

XRF applications at the Analytical Measurements Research Section, Philippine Nuclear Research Institute

Contributor: *Flora L. Santos, Head, Analytical Measurements Research Section*
Staff: *Preciosa Corazon B. Pabroa, Joseph Michael Racho, Ryan P. Morco*

The Analytical Measurements Research (AMR) Section of the Philippine Nuclear Research Institute (PNRI) provides routine analytical services by using nuclear and related analytical services to local clients coming from industry, the universities and other government institutions. The AMR uses a KEVEX 771 secondary target XRF

spectrometer (see Figure 1) to analyze different types of samples. The KEVEX 771 allows analysis by direct, filtered or unfiltered modes, or by secondary target excitation. Excitation using secondary targets allows optimization of analytical parameters for different elements.



Fig. 1. The PNRI Kevex 771 secondary target XRF spectrometer. On right are air filters mounted on EPA-type filter holders.

Most of the samples analyzed in the laboratory so far are air filters. Samples are mounted in EPA-type sample holders and placed directly on the sample wheel. Each filter is analyzed using three conditions: Ti and Ge secondary targets in vacuum and Zr in air. 15-20 elements can be analyzed on air filters.

Recently, there has been demand for analysis of other types of samples: various metal artifacts suspected to contain precious metals; lichen for use as biomonitors; paint; construction materials; food samples and others. In order to produce an appropriate target for analysis, bulk samples are ground and homogenized using a SPEX 8000 Mixer Mill. For biological samples, a SPEX 6700 Freezer Mill, cooled with liquid nitrogen is utilized. Analysis is done using an Ag secondary target, at 30 kV, 0.5 mA and quantitation by the

Emission-Transmission Technique with Mo as absorber. Spectrum processing is by AXIL and quantitation by the QAES software by Dr. P. Kump of the Josef Stefan Institute, Slovenia. Some of the recent applications in the laboratory are described below.

1. Determination of Pb in paint

There is current concern in the country on indoor Pb pollution. Samples taken from old buildings have been submitted for Pb analysis. Paint is scraped off, ground and homogenized and pressed to form 13 mm pellets. Figure 2 gives a sample spectrum for paint obtained with a Ag secondary target showing characteristic peaks of elements used in paint pigment: Pb, Ti, Ca and Zn. Validation was done against soil reference material.

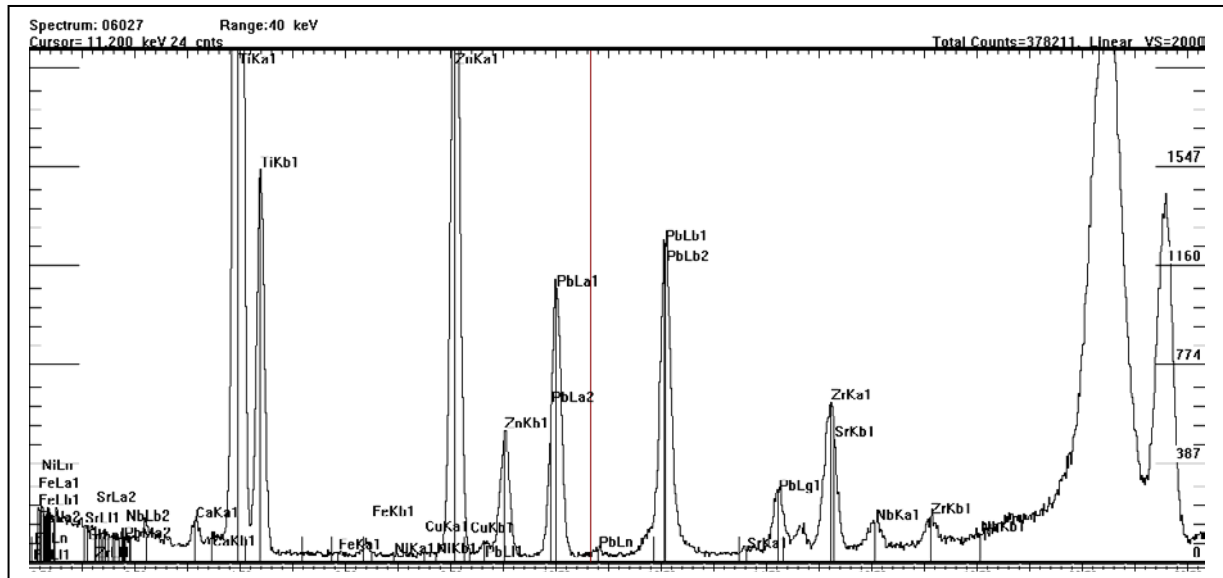


Fig. 2. Spectrum for paint obtained with an Ag secondary target.

2. Analysis of soil

Soil samples are ground and homogenized in the usual manner and then pressed to form a 31 mm pellet. Analysis is by the Emission Transmission Technique with the Ag secondary target and Mo

absorber as described above. The elements measured are Ca, Ti, Mn, Fe, Ni, Cu, Zn, Pb, Rb, Sr and Zr. Additional elements can be quantitated when analysis with the Gd secondary target is done. Figure 3 shows the peaks for additional elements: Sn, I and Ba.

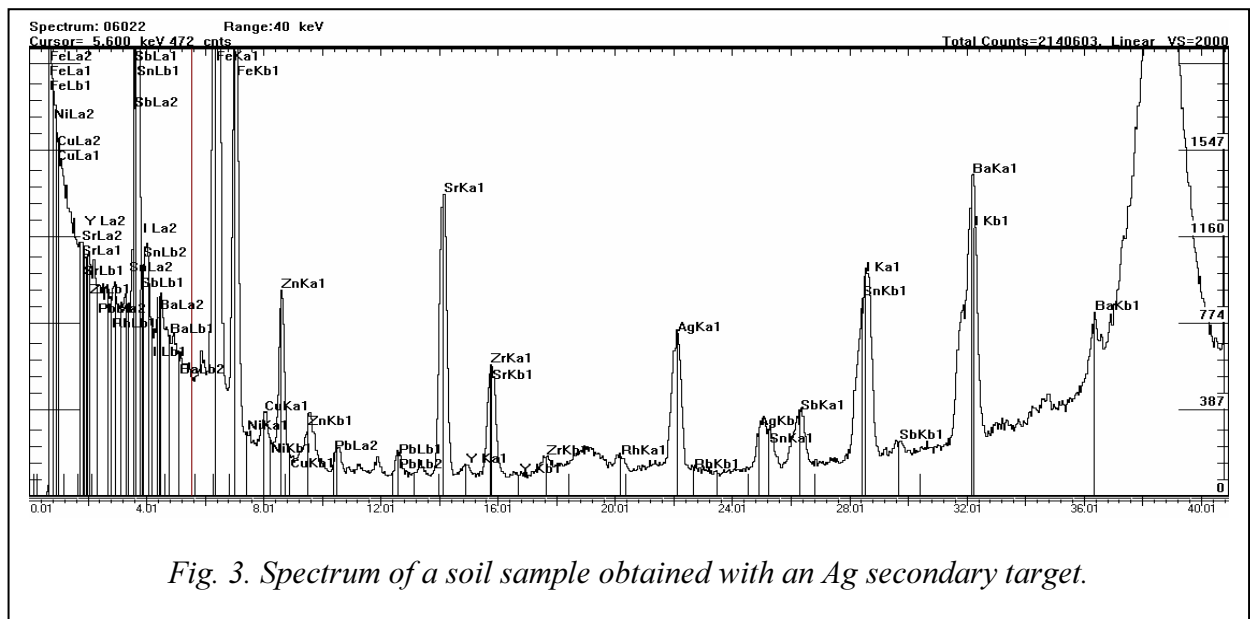


Fig. 3. Spectrum of a soil sample obtained with an Ag secondary target.

3. Determination of Iodine in fish

In connection with the food fortification program of the Food and Nutrition Research Institute, determination of iodine in fish is undertaken. The sample is again ground and homogenized and pressed to form a 31 mm pellet. Analysis is done using a Gd secondary target at 60 kV and 3 mA.

Conclusions:

The PNRI is one of the few local XRF laboratories accepting samples for analytical services. A secondary target XRF spectrometer has proven to be a useful tool to determine a wide range of elements in different types of samples.

Announcement of Workshop on Advanced X ray Spectrometry – WAXS 07



The number of participants is restricted to 20 and the acceptance will be done based on first come first serve principle. Nevertheless the organizing committee reserves the right to select suitable participants who meet the qualification criteria. For the participants from developing countries a financial support through appropriate on-going TC projects (as scientific visitors) can be considered.

Vienna University of Technology-Atominstitut (ATI)
&
IAEA Laboratories Seibersdorf

Workshop on Advanced X-ray Spectrometry WAXS 07

Vienna, September 10-14, 2007

Contact:
Christina Strelli, strelli@ati.ac.at

Homepage:
www.ati.ac.at/WAXS07

Scope:

Experienced scientists will have the opportunity to get familiar with the recent advances in x-ray spectrometry (XRS) including energy- dispersive x-ray spectrometry (EDXRS), total reflection x-ray fluorescence analysis (TXRF), synchrotron radiation induced XRF, portable XRF instrumentation, microanalysis based on photons and charged particles (PIXE).

General:

This workshop will be divided into a theoretical part with lectures and a practical part with applications and experiments to develop hands-on skills and experience. It will be held at two locations: the Atominstitut and the Instrumentation Unit, IAEA Labs in Seibersdorf.

Target participants:

Analytical chemists and nuclear physicists working with EDXRS in various fields like environmental pollution monitoring including analysis of air particulate matter and water samples, forensic applications, industrial applications, analysis of fine arts - and cultural heritage objects and biomedical applications.

Qualification:

Basic knowledge of methodology of XRS combined with a few years of practical experience.

Organizing Committee:

Gabriele Voigt (IAEA)
Andrzej Markowicz (IAEA)
Dariusz Wegrzynek (IAEA)
Christina Strelli (ATI)
Peter Wobrauschek (ATI)
Claudio Tunis (Abdus Salam International Centre for Theoretical Physics, Trieste)

Program:

The workshop will be held during 5 days, the morning sessions with lectures and in the afternoon practical exercises carried out in the laboratories. There will be 3 days in ATI and 2 days in the IAEA Laboratories at Seibersdorf.

The lectures will cover the following topics:

Modern x-ray detectors
New x-ray sources
X-ray optics
Sample preparation
Methodology and application of TXRF
Microanalysis
PIXE
Synchrotron radiation induced XRF as well as applications in environmental and material science
Characterization of cultural heritage and biomedical samples
Data evaluation, data interpretation, statistical analysis and special sample preparation will also be included.

The practical sessions will deal with:

Microanalysis
Portable XRF instrumentation
Sample preparation
TXRF
Demonstration of some commercial equipment

Fees:

EURO 200,-
cover handouts, CD of presentations, coffee, public transportation in Vienna and to Seibersdorf

Accommodation:

Direct booking by participants

Publications of potential interest to the XRF community

T. Venelinov and A. Sahuquillo, Optimizing the uses and the costs of reference materials in analytical laboratories, *Trends in Analytical Chemistry*, 25 (5), 528-533, 2006.

M. Bielewski, D. Wegrzynek, M. Lankosz, A. Markowicz, E. Chinea-Cano, S.A. Bamford, Micro-beam X ray analysis of individual particles with correction for absorption effects; *X ray Spectrom.*, 35, 238-242, 2006.

N. Dytlewski, G. Mank, U. Rosengard, S. Bamford, A. Markowicz, D. Wegrzynek, The International atomic Energy Agency's programme on utilization of accelerators, *Nucl. Instrum. Meth. Phys. Res. A* 562, 650-655, 2006.

Markowicz, D. Wegrzynek, S. Bamford, E. Chinea-Cano, Activities in the IAEA X ray fluorescence laboratory at Seibersdorf, *X ray Spectrom.* 35, 207-214, 2006



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