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XRF Newsletter

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X ray Fluorescence in the IAEA and its Member States

In This Issue

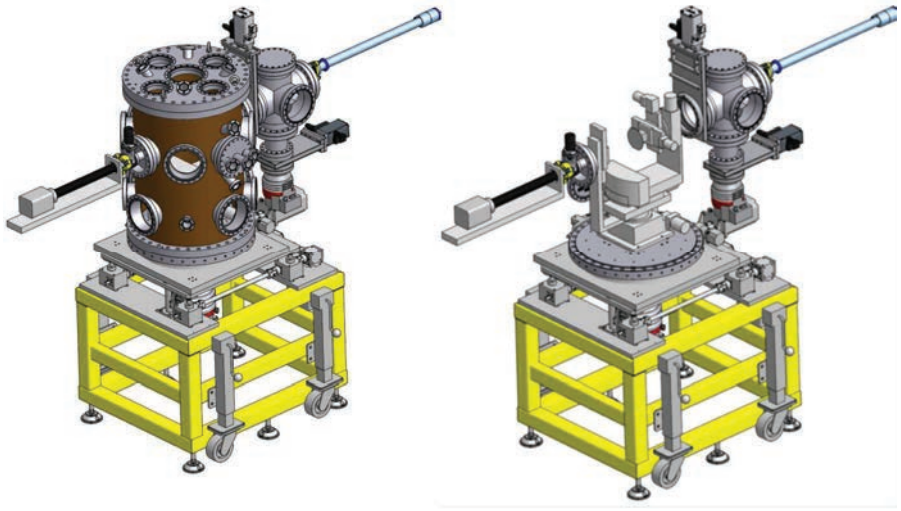
Activities in the IAEA XRF Laboratory

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

New Possibilities for the IAEA Developing Member States for Advanced X Ray Spectrometry Applications Using Synchrotron Light

Background

The Physics Section (PS) of the International Atomic Energy Agency (IAEA) supports through its dedicated programs and activities the development of interdisciplinary applications of laboratory and accelerator based X ray spectrometry techniques. In particular, the IAEA in recognition of the contribution of the Synchrotron Radiation (SR) and of its unique properties in the research and development has designated the Elettra Laboratory at Sincrotrone Trieste (EST) as an IAEA collaborative centre. The IAEA and EST have been in cooperation since 2005 in the organization of many training (schools) and promotion (workshop) activities for the SR analytical techniques with the continuous support of the International Center for Theoretical Physics (ICTP) in Trieste.

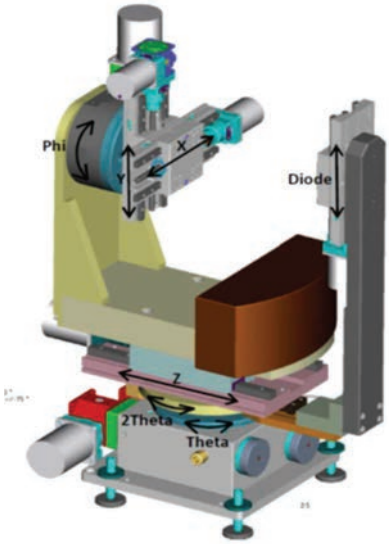


Schematic representation of the external and internal hardware of the UHV chamber, including the load lock chamber, the 7-axis motorized sample manipulator, the Silicon Drift Detector and the partially motorized transportable base.

Nowadays, the role of synchrotron radiation becomes more and more important in advanced analytical studies due to the growing interest for the development of novel and complex materials. For example, IAEA Member States (MS) have to establish efficient and environment-friendly energy production and energy storage technologies. The developing MS have also to effectively cope with the destructive impact of the growing industrialization on the environment and on human health, while maintaining their economic growth. These difficult goals can only be achieved by the introduction of novel technologies, which to a large extend depend on the development of advanced, structured materials. Environmental problems, as well as human health issues, can also be effectively diagnosed, monitored, and eventually remediated with modern technology based on structured materials. A significant contribution in these areas can be given by the application of synchrotron radiation based X ray spectrometry techniques and methodologies, such as the Total Reflection, Grazing Incidence/Exit X ray Fluorescence (TXRF, GIXRF/GEXRF) analysis, X ray Reflectometry (XRR) and Confocal micro-XRF analysis) which can provide with high sensitivity spatially resolved elemental information down to the nanometer depth scale. The elemental analysis is usually needed to be complemented with chemical speciation studies which can be accomplished by X ray absorption/emission spectroscopy techniques (XAS, XANES, EXAFS). Thus, the synergistic multi-technique application of X ray methods can provide an integrated analytical methodology for elemental, chemical, and structural characterization of materials. Apart from the usefulness of SR X ray spectrometry techniques it should be stressed that in the highly competitive research environment of SR facilities beam time can be obtained only on the basis of the scientific merit of proposals, selected by review panels, providing limited opportunities for hands on training. This situation creates a major gap for advanced training of scientists from IAEA developing countries to access and utilize the Synchrotron Radiation technology and associated techniques.

The IAEA Beamline End-station at the Elettra Sincrotrone Trieste

In response to the needs described above the IAEA in cooperation with the Physikalisch - Technische Bundesanstalt (PTB, Berlin) and the Technical University of Berlin (TUB), has initiated since mid 2011 a collaboration on the design, construction and operation of a novel experimental equipment (the so-called Ultra High Vacuum Chamber-UHVC) as beam-line end-station at the newly developed X ray Fluorescence XRF beamline at the Elettra Sincrotrone Trieste (EST) laboratory. The UHVC is based on a prototype design by PTB [1] and TUB and it is composed by an ultra-thin window Silicon Drift Detector (30 mm^2, <133 eV @ Mn-Kα, 75 eV @ C-Ka), photodiodes and a motorized 7-axis sample manipulator (with four linear stages, 'X', 'Y', 'Z', and 'Diode' and three (3) goniometers 'Theta', '2Theta' and 'Phi') so as to allow the application of the Grazing Incidence or Grazing Exit mode of X ray Fluorescence analysis (GI-XRF/GE-XRF), simultaneously with X ray Reflectometry (XRR) measurements. The 7-axis manipulator aims at moving the sample to be investigated in various directions/ orientations with respect to the exciting probe (GIXRF, GEXRF modes) or/and the detectors (XRR mode). The transverse range of 'Theta' axis is (-5° to 110°), for the '2Theta' axis (170°-270°), for the 'Phi' axis is ± 200° and for each linear stage about 110 mm. The technical specifications for the performance of the goniometers state an accuracy and reversal error better than 145 μrad and 34 μrad respectively, whereas for the linear stages the respective figures are 15 μm and 4 μm respectively. The UHV chamber is equipped with a load lock chamber and it is placed on a transportable partially motorized base stage that provides three degrees of freedom (two linear stages and one rotational) for aligning the whole UHV chamber.



Schematic representation of the 7-axis motorized sample manipulator with four linear stages ('X,' 'Y', 'Z', 'Diode') and three goniometers ('theta', '2theta', 'Phi').

The XRF beamline at the Elettra Sincrotrone Trieste based on a bending magnet source has been designed and developed to provide an X ray beam with tuneable energy in the range 2-14 keV with an approximate flux of 5 10^9 photons per second (at 5.5 keV, 2 GeV machine mode) by means of double crystal (Si (111), InSb) and Multilayer monochromator. An angular divergence (at exit slits) of 0.15 mrad, a resolving power of 1.15 10^{-4} (Si(111)) and a beam size (at exit slits) of 250 mm (hor) X 50 mm (vert) overview the specifications and expected performance of the synchrotron light to be delivered.

The UHV chamber is foreseen also to be used as standalone experimental facility by using a laboratory low-power air-cooled Mo anode X ray tube (with a maximum power consumption 50 Watt and maximum voltage 50 kV) as an exciting X ray source. An appropriate X ray optics module would be employed to deliver a monochromatic and parallel Mo K alpha radiation exciting beam with a squared beam profile of about 0.7mm x 0.7mm, energy resolution equal to about of 1% bandwidth, divergence of the parallel beam less than 0.02° in both directions and with an integral photon intensity after the optics equal to about 2 x 10^6 photons/s.

Analytical Applications

It is well known that the GIXRF analysis at very low incidence (at the regime of the critical angle for external total reflection) is benefited by the formation of the X ray Standing Wave (XSW) due to the interference of incident and reflected wave fronts. In this case, the intensity of the incident radiation features nodes and antinodes just above or mainly below the sample surface providing a powerful tool to probe elemental concentrations at the nanometer scale with high chemical sensitivity, typically from ppb to ppm. The GIXRF analysis in combination with XAS techniques allow the characterization of intermediate or buried interfaces, from their composition to their coordination spheres and short-range structure organization, properties which are crucial in the development and control of many advanced material compounds [1-3]. Thus, targeted analytical applications refer to the integrated characterization of energy storage and conversion micro- and nano- scaled materials, micro- and nano-electronics, advanced substrate materials (impurities/dopants), life sciences and investigation of environmental processes through the characterization of atmospheric pollutants. These activities would support the establishment in MS of efficient and environment-friendly energy production and energy storage technologies, and to effectively monitor, diagnose, remediate environmental and human health related problems.

Current status and Future perspectives

During 2012 important and critical phases for the development of the UVC chamber end station were completed: The majority of the hardware components, devices and equipment have been acquired, whereas a LabView based application has been developed and tested to control all UHVC devices/detectors using an Intuitive Graphical User Interface providing tools for real time data analysis and imaging. The LabView based application is interfaced with customized per equipment Tango Devise Servers to facilitate communication with the existed instrumentation at the Elettra Sincrotrone Trieste. The installation and commissioning of the UHVC end-station will take place in the third quarter of 2013, whereas from the mid of 2014 it is expected to be accessible to the end-users from the IAEA MS. To support the access to the UHVC end-station, the PS-IAEA is planned to launch in 2013 a Coordinated Research Project (CRP). The main objective of this CRP would be to increase the quality and the competitiveness of MS research in the field of synchrotron radiation-based X ray spectrometry methods by supporting and facilitating the experimental work and hands on training at the UHVC end-station of the Elettra XRF beamline.

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[1] LUBECK, J., et al., A Novel Instrument for Quantitative Nanoanalytics Involving Complementary X ray Methodologies, Rev. Scientif. Instrum. **84** (2013) 045106-7.

[2] POLLAKOWSKI, B., et al., Nondestructive and Non-preparative Chemical Nanometrology of Internal Material Interfaces at Tunable High Information Depths, Anal. Chem. **85** (2013) 193-200.

[3] UNTERUMSBERGER, R., POLLAKOWSKI, B., MÜLLER, M., BECKHOFF, B., Complementary Characterization of Buried Nanolayers by Quantitative X ray Fluorescence Spectrometry under Conventional and Grazing Incidence Conditions, Anal. Chem. **83** (2011) 8623-8628.

Assessing attenuation effects in TXRF analysis

Quantification in Total reflection X ray fluorescence analysis is based on the assumption that the sample areal density (ρX) is so low that attenuation effects can be considered as non-matrix dependent and to be only proportional to the density of the sample. The intensity of measured characteristic radiation (s^{-1}) is commonly assumed to be proportional to elemental areal density of the element as if derived from Sherman equation for the case of infinitely 'thin' sample:

$$N_i\left(s^{-1}\right) = S_i(E_0) w_i \rho X \qquad (1)$$

where N_i is the count rate of characteristic emission selected for the analysis of the element i, w_i is the mass fraction and $S_i(E_0)$ is the instrumental response [$s^{-1}g^{-1}cm^2$] to the excitation with x-rays having energy E_0.

To overcome the uncertainties arising from differences in the droplet residue position and the unfeasibility of establishing the values of ρX, a known amount of an element not expected to be present in the sample is added during sample preparation (internal standardization) and calibration is based on relative (to that of the internal standard) sensitivity:

$$\frac{N_i}{N_{st}} = \frac{S_i(E_0) w_i}{S_{st}(E_0) w_{st}} \qquad (2)$$

This approach indeed provides a robust calibration basis. However, the assumed model is often applied to analytical problems without a proper assessment on whether the assumed conditions are fulfilled. Some particular cases requiring a careful assessment of attenuation effects include:

- Establishing the upper concentration levels where expression (1) is still valid during the calibration procedure.

- Analysis of samples with high concentration of dissolved matter that is not effectively detected.

- Analysis of elements using low energy characteristic emission.

- Uneven distribution of the internal standard and the element of interest in the droplet residue.

A study was started at the IAEA NSAL to assess the attenuation effects in TXRF.

For an ideal cylindrically shaped droplet residue the intensity of fluorescent radiation I_f for the element i can be more accurately described using cylindrical coordinates as:

$$I_f = 2K_i(E_0)\rho_i\varepsilon(E_i)I_0(E_0)\frac{1-e^{-\mu(E_i)\rho X}}{\mu(E_i)\rho}\int_0^R 2\int_0^\pi \exp\left[-\rho\left(\mu(E_0)\left[\sqrt{R^2-r^2\sin^2\theta}-r\cos\theta\right]\right)\right]d\theta r dr \qquad (3)$$

In expression (3) R and X are the radius and the thickness of the residue, r is the distance of the element from the centre of the residue and θ the azimuthal angle. $\mu(E)$ refers to the sample effective attenuation coefficient for energy E, $I_0(E_0)$ is the flux of the excitation radiation, $\varepsilon(E_i)$ the detector efficiency and $K_i(E_0)$ is the X ray production. Attenuation of the excitation radiation is dependent on $\mu(E_0)\rho R$, whereas the attenuation of the fluorescent radiation depends on $\mu(E_i)\rho X$.

If the sample preparation produces a reproducible cylindrically-shaped sample residue, then attenuation corrections are possible using expression (3). One integral in expression (3) cannot be solved analytically but can be cancelled out if internal normalization is performed. However, the latter is only possible if both internal standard and the element of interest are homogeneously distributed in the sample dry residue. Several sample preparation procedures have been tested to verify whether this assumption is valid. Figure 1 shows an example of the uneven distribution of elements resulting from sample preparation procedure based on using a 1:1 dilution with 0.2 % Polyvinyl Alcohol (PVA) solution.

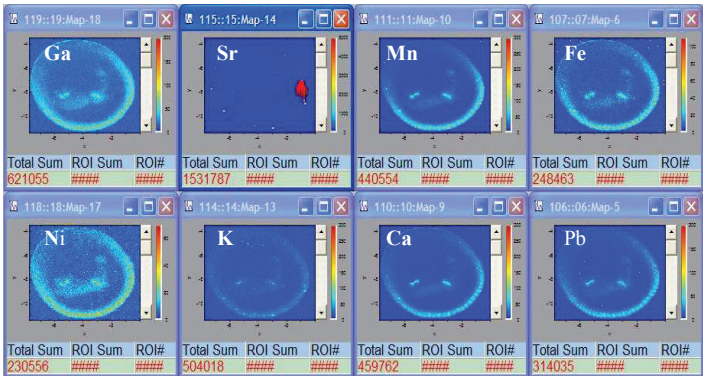
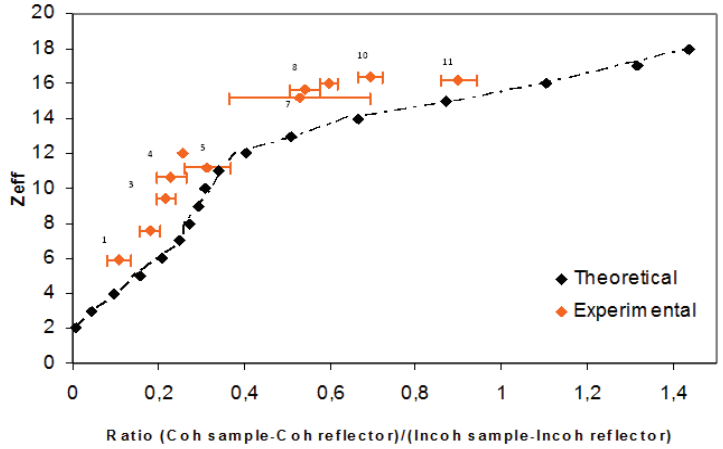


Fig. 1. Distribution of elements in the sample dry residue, as revealed by micro-XRF scanning.

Notes:
Scanning procedure: Focal spot 30 microns, step 50 microns, measurement time per spot 5 seconds.
Sample preparation 1:1 dilution with PVA (0.2 %), 5 µL sample dried under room temperature

Sample total attenuation coefficient for the excitation energy can be calculated from an effective atomic number found for the sample, which in turn can be established using the ratio of measured scatter peaks (see Fig. 2).



1) CH_2
2) $(NH_4)_2CO_3$
3) Na_2CO_3
4) $(NH_4)_2HPO_4$
5) $(NH_4)_2SO_4$
6) $MgSO_4$
7) $NaCl$
8) NH_4Cl
9) $MgCl_2$
10) K_2CO_3
11) K_2SO_4

Fig. 2. Assessing the effective atomic number of sample residue using scatter peaks.

The sample areal density can be assessed from experimental calibrations made for different amounts of dissolved matter in different effective atomic number solutions using the ratio of internal standard to incoherent scatter (see Figure 3). The suitability of using the proposed expression to correct the differences in attenuation for quantification is under evaluation.

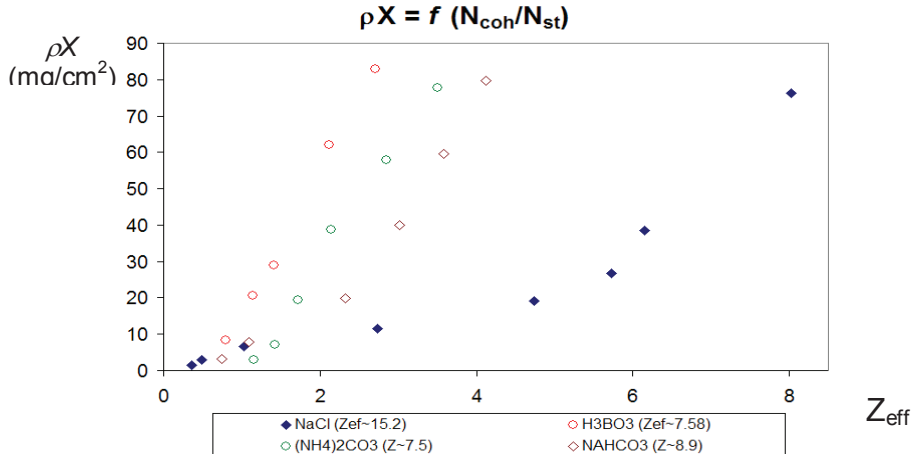


Fig. 3. Assessing sample areal density (mg/cm^2) from experimental calibrations.

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IAEA Technical Meeting on "The advanced analytical techniques for Laboratory and Industrial applications, TM-42593, 24-28 September 2012, IAEA Headquarters, Vienna, Austria

Advanced analytical techniques based on nuclear radiation and technology, play a key role in analytical applications with a major impact on the socio economic development of the IAEA Member States. A wide range of industrial applications are supported by different nuclear radiation probes and advanced analytical techniques; for example, applications in pharmaceuticals and biotechnology, mining, mineral exploration and mineral processing, semi-conductors, automotive, semi-conductors, metallurgy, cosmetics, bulk chemical synthesis utilizing synchrotron radiation, modification of light metals, high energy implantation for microelectronic applications, doping of semiconductors using ion-beams and finally using neutron beams in pharmaceuticals applications, chemical products and in high-end mechanical engineering for the nuclear and aerospace sectors.

The Technical Meeting had the following objectives:

- To review the current status and trends in the development of advanced analytical techniques using nuclear radiation probes (X rays, ion beams and neutrons),
- To review current and future needs and requirements of industrial sector for advanced characterization of materials,
- To define criteria and requirements for the analytical techniques that are beneficial for industrial applications, and
- To support exchange and sharing of cross-cutting information and know-how between scientists working in R&D of analytical techniques and industrial applications.

The TM participants demonstrated diversity geographically (Australasia, Africa and Europe), experimentally (synchrotron based analytics, ion beam facilities, lab-based and hand held analysis with quantification, standardization in gamma spectrometry and data processing) and in

applications (environment, pharma, bio- and nano-tech, material studies, cultural heritage and medical areas). The TM report concluded that advanced facilities such as synchrotron radiation techniques offer immense power for advanced materials characterization in a broad range of industrial applications, but scientific interactions and communication with industry needs intensification and the establishment of new channels of communication; particularly to assist less experienced scientific communities in applied and industrial oriented research, but also to provide scientists with the opportunity for gaining appreciation of industrial needs and priorities. Finally, the meeting participants suggested that Member states and the IAEA should enforce training activities in advanced analytical techniques as well as in project development, management and achieving accreditation. Various recommendations were formulated, directed to the IAEA and Member States with the objective to promote translation of science and R&D into industrial capability, to promote and enhance the impact of science and researchers in industry and to develop recognition of application of knowledge.

Participants and Contributors in the Technical Meeting Report

ABOH, Innocent K. (Ghana), CZYZYCKI, Mateusz (Poland), EICHERT, Diane (Italy), EUARUKSAKUL, Chanan (Tailand), FAZINIC, Stjepko (Croatia), KEMPSON, Ivan (Australia), MUSA, Muhammad Auwal (Nigeria), VOUTCHKOV, Mitko K (Jamaica)

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The participants of the TM-42593, 24-28 September 2012.

Regional Training Course (AFRA) on the Use of ICT Materials for Nuclear Analytical Techniques
Kinshasa, Democratic Republic of the Congo, 15-19 October 2012

The International Atomic Energy Agency within the Technical Cooperation Project RAF/0/026 'Sustaining the Regional Capability for the Utilization of Information and Communications Technologies for Human Resource Development (AFRA V-6)' and in cooperation with the Government of the Democratic Republic of the Congo through the Commissariat général à l'énergie atomique (CGEA), Centre régional d'études nucléaires de Kinshasa (CREN-K), organized a Regional (AFRA) Training Course for Trainers on The Use of ICT Materials for Nuclear Analytical Techniques in Kinshasa, Democratic Republic of the Congo, from 15 to 19 October 2012. Eight (8) scientists from African countries and seven (7) locals attended the training course.

The purpose of the training course was to introduce the ICT-based materials developed through the support of IAEA on nuclear related analytical techniques, including X ray, alpha and gamma spectrometry. The content of ICT modules was presented, and means of integrating the ICT-based materials into conventional teaching and training in nuclear-related analytical techniques was demonstrated and discussed. In particular, the role of nuclear analytical techniques in environmental monitoring was highlighted and relevant analytical methodologies were presented. The possibility to enhance the teaching into nuclear analytical techniques by means of available free-ware simulation software was explored and discussed with the participants who acquired hands on experience in the utilization of freeware software (PyMca, developed at ESRF, France, http://pymca.sourceforge.net). External lecturer's duties were undertaken by Mr Samuel Akoto Bamford, University of Ghana, School of Nuclear and Allied Sciences, Department of Nuclear Safety and Security and Mr Moussa Bounakhla, Centre national de l'énergie, des sciences et des techniques nucléaires (CNESTEN), whereas course director was Mr Tshiashala

Mutshipaie Dikolela Arthur, Commissariat général à l'énergie atomique (CGEA), Centre régional d'études nucléaires de Kinshasa (CREN-K)

The training room where the RTC was conducted in Kinshasa.

From left to the right: Mr A. Karydas (IAEA), Ms E. Octavie Rasoazanany, Ministère de l'éducation nationale et de la recherche scientifique (MENRS), Ms F. Boujelbane, Centre National des Sciences et Technologies Nucléaires, and the lecturers Mr M. Bounakhla and Mr S. A. Bamford.

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Consultants Meeting on 'Development of a Distance Learning Module on Environmental Monitoring using X ray Fluorescence and Ion Beam Analysis Techniques', Vienna, 12-14 November 2012

Introduction

Conventional educational materials and training programs have been developed and provided by the IAEA since a long time, following requests of Member States mainly through Technical Cooperation (TC) projects. However, such training tools suffer from a number of restrictions, including limited access, cost effectiveness, language and even cultural barriers.

In order to overcome these limitations, the IAEA has undertook the development of distance learning material by the use of Information and Communication Technology (ICT), introducing new learning methods, formats and resources. ICT materials provide the means by which many of the outputs of Agency programmes are produced and efficiently delivered to their intended recipients.

Various ICT materials have been already produced so far by the Agency in the field of nuclear instrumentation and analytical techniques. However, the continuous development of technology requires creating new material or properly updating the already existing modules.

One of the main interests of Member States is the characterization of suspended particulate matter (or atmospheric aerosol) and the study of its possible consequences on climate change, human health and material damages. Actually, problems associated with air particulate matter are of great concern in many developing countries, since in highly populated cities the amounts of total suspended air particulate (TSP) are far in excess of the World Health Organization (WHO) guideline ranges.

The characterisation of atmospheric aerosols in the environment requires the determination of the composition of the aerosol particles as a function of their dimension. An exhaustive time and spatial resolution, as well as particle size separation, calls for vast numbers of analyses, thus fast, high sensitivity, multi-elemental, quantitative techniques are required. Also the non-destructiveness aspect of the analysis is important in order to combine results with the ones obtained by complementary techniques applied to the same sample. All these requirements are met by nuclear-related analytical techniques like Ion Beam Analysis (IBA) and X ray Fluorescence Analysis (XRF). Sampling techniques (including typology of filters and methodology of collection) are fundamental for a satisfactory analysis, while statistical analysis tools are crucial for the identification of emission sources of pollutants.

Since most developing countries are installing facilities to utilize the above mentioned techniques, especially the XRF analysis, there is a strong demand of training on the analytical characterization for atmospheric aerosol.

Scope of the meeting

A Consultants' Meeting was organized from 12-14 November 2012 by the Nuclear Spectrometry and Applications Laboratory of the IAEA in order to review and update analytical methodologies and best sampling, measurement and data analysis practices applied for the characterization of atmospheric aerosols. The meeting aimed at outlining and producing a summary (syllabus) for a ICT-based distance learning module for atmospheric aerosol studies, covering sampling practices, characterization by nuclear-related analytical techniques and identification of emission sources.

Results

The meeting participants reviewed the best practices in several aspects of suspended particulate matter studies, including sampling of atmospheric aerosol, measurement using nuclear-related analytical techniques and data analysis for source apportionment. Web techniques for communication (forums, chat rooms, virtual boards, video conference or virtual classrooms, wikis) and specific tools in learning content managements systems (testing, access managements, open source modules or commercial solutions) were reviewed as well. The participants also discussed and indicated requirements and priorities for building learning capacities for the characterization of atmospheric aerosol in developing Member States with limited resources.
The meeting participants agreed on main topics to be faced and adopted when the planning and implementation of a campaign for atmospheric aerosol studies is scheduled. Having in mind that the end users of the ICT-based distance learning modules on environmental monitoring could come from widely different technological and scientific background, the participants agreed that also very basic recommendations and guidelines should be covered in order to avoid trivial pitfalls and mistakes.

In this respect, the provision of recommendations and guidance for sampling (where, how and when to sample, instrumentation needed and sampling strategies, selection of proper substrate material, sample handling) is a key topic. Several relevant details on best practices for sampling can be accessed from the database (http://db-airmontech.jrc.ec.europa.eu/) of the AirMonTech EU project, compiling information to harmonize current air pollution monitoring techniques and to advise on future monitoring technologies and strategies.

Concerning the nuclear-related analytical techniques, elemental analysis will be mostly performed using the non-destructive techniques ED-XRF and PIXE (amongst the IBA techniques). PIXE offers higher sensitivity (especially for low-Z elements as Na, Mg, Al, Si…) in shorter measuring times than ED-XRF (ED-XRF) requires long time measuring time in order to meet ppm detection levels without damaging the sample, as it happens in WD-XRF). Obviously, being PIXE an accelerator-based technique, it could not be easily accessible, especially in developing countries. PIXE and ED-XRF have very good performance for particulate matter characterization but, as most elemental techniques, they cannot resolve the chemical speciation, so complementary analysis either by the use of IBA techniques such as Elastic Scattering methods (EBS and/or PESA for C, N, O and/or H measurements) or by Ion Chromatography (for secondary inorganic ions), Thermo-Optical methods (for elemental and organic carbon) is recommended to get most of the aerosol mass. Indeed, the coupling of PIXE with EBS for mass closure exercises is very valuable.

The participants of the meeting also agreed that the Nuclepore and Teflon materials are the best suited filters for aerosol collection in view of elemental analysis with nuclear-related techniques, especially ED-XRF and PIXE, with Teflon being preferred in case that Elastic Scattering analyses are envisioned as well. Moreover, Teflon is much easier to manage in gravimetric measurements. The use of Quartz fibre filters is mandatory if carbonaceous compounds speciation with Thermo-Optical methods is an issue.

Finally, data evaluation and interpretation protocols for source apportionment studies, together with tools already available in the web for

supporting interpretation of experimental atmospheric aerosol data (i.e. air mass backward trajectories calculations), were discussed by the participants. A methodology based first on the use of Principal Components Analysis (PCA) to identify the number of sources and their nature, and then on the use of Positive Matrix Factorisation (PMF) to confirm the source profile was suggested.

The participants finally agreed on the structure of a syllabus to be used as a reference guideline for the development of one or more ICT-based distance learning modules for atmospheric aerosol studies, covering aerosol sampling, characterization by nuclear-related analytical techniques and identification of emission sources.

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The following experts have participated and contributed to the Consultants Meeting:

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The European X ray Spectrometry Conference (EXRS 2012) Vienna, IAEA Headquarters, 18-22 June 2012

The 15th European X ray Spectrometry Conference (EXRS-2012, http://www.ati.ac.at/ EXRS2012/) was held in Vienna, Austria from 18-22 June 2013, organized by the Atominstitut (ATI), Vienna University of Technology (VUT), hosted by the International Atomic Energy Agency (IAEA) under the patronage of the Austrian Federal Ministry of Science and Research, and the European X ray Spectrometry Association (EXSA. The conference was co-chaired by Prof. Ch. Streli (ATI) and the Head of the IAEA Nuclear Spectrometry and Applications Laboratory (NSAL), Dr. A. Markowicz, whereas two (2) other IAEA staff, Dr. A. G. Karydas and Dr. R. Padilla-Alvarez contributed in the local organizing committee.

The number of participants was 350 from 47 countries with significant participation from developing countries and from non-European countries including USA, Japan and the Russian Federation.

The EXRS2012 attracted a significant number of industrial vendors (31) who exhibited the latest X-ray instrumentation available on the market. The exhibition was arranged in the most central point of the IAEA premises at the Vienna International Center (Rotunda), thus not only Conference participants, but also IAEA Staff and external visitors had the opportunity to obtain information on the instrumental advances in the field.

The whole conference took place in the new Conference Centre of the IAEA in the Vienna International Centre (VIC), offering outstanding facilities appreciated by the participants. The opening session was honoured by the presence of the Rector of the Vienna University of Technology (VUT), the Dean of the Faculty of Physics of the VUT, the Director of the Atominstitut, the Director of the Division of Physical and Chemical Sciences of the IAEA Department of Nuclear Sciences and Applications and the President of the EXSA.

The scientific program included 22 invited talks, 42 oral scientific presentations, 15 short presentations from companies (exhibitors) and 210 poster presentations distributed in two poster sessions. The contributions covered a wide range of basic and applied research topics in the field of X ray Spectrometry (XRS) with particular emphasis in X ray sources, optics and detectors, quantification methodology in XRF analysis, TXRF, GIXRF and related techniques, X ray imaging and tomography and in XRS analytical applications in nanoscience related materials, Art/Cultural Heritage and in Earth and

environment related sciences. During the EXRS2012 an update on the International Initiative on X ray Fundamental Parameters was presented by B. Beckhoff, M.-C. Lépy, and J. Hoszowska (more info can be found at the following link: http://www.exsa.hu/news/?page_id=380).

More information can be provided by A.G. Karydas (A.Karydas@iaea.org).

Reference:

STRELI, Ch. and MARKOWICZ, A., "Editorial of the EXRS2012 special issue", to be published in X ray Spectrometry, 2013.

A group photo of the EXRS2012 participants at the IAEA Headquarters.

The Director of the Division of Physical and Chemical Sciences of the IAEA Department of Nuclear Sciences and Applications Ms Meera Venkatesh, the Director of the Atominstitut Prof. Dr. Hannes-Jörg Schmiedmayer and the Dean of the Faculty of Physics of the VUT, Prof. Dr. G. Badurek (from left to right), during the official opening of the EXRS2012 conference.

The participants of the EXRS 2012 conference during a session held in the main auditorium room.

A poster session during the EXRS2012 conference.

X ray Fluorescence in Member States

Australia

Applications of Large Area XRF Mapping of Metals in Biology at the Australian Synchrotron

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Synchrotron light sources have provided highly versatile X ray sources for XRF mapping. The intensity, polarization and monochromatic nature provide several benefits for studying trace level elemental distributions in low Z materials such as biological samples. The greater intensity and collimation enable efficient focusing for small probing beam size. The polarization reduces detected scatter and the monochromatic incident beam reduces spectral background which improves signal to noise and detection limits. The ability to tune the incident energy also allows for easy distinction of elements with overlapping emission lines by selectively determining which elements are excited while omitting others. This can also be utilized to further optimize detection limits or conduct X ray absorption spectroscopy. Collectively, these properties provide an incident beam that is ideally suited to mapping metals down to trace levels. XRF mapping however has suffered from long acquisition times due to the need of a relatively long acquisition time (on the order of up to 1 second) and overheads (up to approximately 0.5 seconds) per pixel. This has meant that in order to produce a map with a large number of pixels, an extravagant amount of time has been required, despite the sophistication of the synchrotron beam.

Through development between CSIRO, Australia, and Brookhaven National Laboratory, USA, a detector (the Maia detector) has been commissioned at the Australian Synchrotron revolutionizing XRF mapping [1]. It enables acquisition up to approximately 1,000 times faster than previously available. Considering a map collected over a 3 hour period with the Maia detector consisting of 2.5 million pixels, could previously have required 1 month of uninterrupted beamtime. Obviously, this speed of analysis provides unprecedented mapping of large areas and of increased sample numbers, greatly improving statistics. In addition to this, large range motors and continual development of operating and processing software have facilitated large area maps with user friendly and fast quantitative data analysis.

Metals, down to trace levels, in biology play roles in homeostatic and morbid processes as well as being associated with diagnostic and therapeutic applications. Bulk analytical methods have provided immense information on the links of metal fate with many of these fields of research and development. However compartmentalization, heterogeneity and associations of metals play important roles in their effects, hence while the bulk concentration of a metal can be comparable between two scenarios, their impact on an organism can be distinctly different depending on how they ultimately interact (depending on variables such as ligands, speciation, biocompatibility, associations etc.). With this in mind there is a need to understand distributions and variability of metals at cellular levels. Rapid mapping now allows such analysis with improving statistics and understanding of the ‘greater picture’. In this article we have included several examples where larger area mapping is enabling basic science for new understanding in the distribution and fate of metals in biological samples with emphasis on gold nanoparticles and ingested lead.

Gold Nanoparticle Fate

In this section we highlight some aspects of mapping gold nanoparticles in biologic samples. The broad development and application of nanoparticle based technologies requires extensive study of their fate, interactions in biology, transport and effects.

Heterogeneity in Cellular uptake of Gold Nanoparticles and Impact on Therapies

At micro/cellular levels heterogeneity in biochemical processes, physical and chemical environments impact fate of nanoparticles. Understanding variability at the cellular level is likely to play an important role in the effectiveness of nanoparticle based therapies such as radiosensitization effects [2]. Figure 1 shows a map of gold in a cell culture acquired with the Maia detector at the Australian Synchrotron in 3 hours and comprises 2x2 micron pixels over an area of 3x1.5 mm. The localized concentrations of gold indicate internalization and compartmentalization of the nanoparticles. In comparison with optical microscopy, less than 50% of the cells have internalized gold.

Developing research is attempting to accurately represent the cells that constitute a tumour and their response to ionizing radiation. This is being achieved by modelling a single cell in the Monte Carlo particle tracking toolkit Geant4 [3]. By modifying the standard Geant4 toolkit we were able to duplicate and randomize (parameterize) the position, scale and rotation of the cells to construct an entire tumour composed of individual cells. Each cell is composed of the primary biological structures of a real cell such as the membrane, cytoplasm, endoplasmic reticulum, nucleus and nucleolus. Each region of the cell has been allocated a realistic elemental composition to ensure the particle interactions and deposited dose are simulated accurately [4].

This model is being used to investigate the dose enhancement effect of gold nanoparticles in radiotherapy. The dose enhancement effect was measured by comparing the absorbed dose in the cells in a control simulation (no gold present) with simulations in which gold was present within the cytoplasm of the cells.

In order to produce physically, chemically and biologically accurate results, the distribution of the gold nanoparticles and their concentrations within the cells must be known. The use of the X ray fluorescence microscopy beamline at the Australian Synchrotron Centre enables us to image and measure the position and concentration of the internalized gold nanoparticles in the cells. Using these data and extracting geometrical arrangement from higher resolution images on the nanoscale the simulation can be more precisely calibrated. Once the experimental data has been incorporated into the cell simulation, it will enable the radiosensitization effect and mechanisms to be quantified.

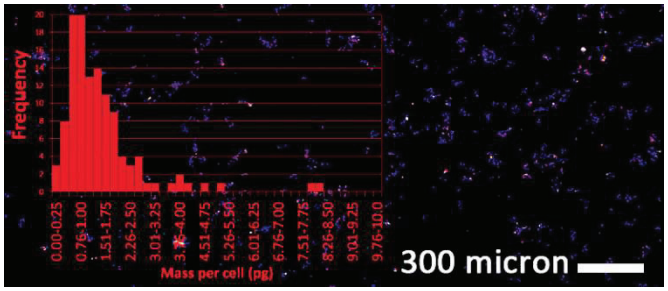

Fig. 1. Internalized gold nanoparticle distribution in a breast cancer cell culture.

Quantifying heterogeneity is assisting in understanding effects in therapeutic applications. In this model the median quantity of gold in cells with internalized nanoparticles was 1.2 pg.

Pharmacokinetics of gold nanoparticles represented in hair

In animal models the mobility, fate and pharmacokinetics of nanoparticles are of fundamental importance in any study [5]. We explored the potential of mouse whiskers to incorporate nanoparticles from systemic blood flow. The concept of hair analysis is that anything in the blood supply of the rapidly growing hair cells in the dermal papilla will become incorporated in the hair structure and grow outwards to form a pharmacokinetic profile along the hairs' longitudinal axis [6, 7]. Large area mapping facilitated imaging multiple hairs from multiple animals which would otherwise not make the study feasible (Fig. 2a). Figure 2b shows a pharmacokinetic profile extracted from the gold distribution in a mouse whisker. The decay correlates well with blood pharmacokinetics. In addition, this study demonstrated small amounts of gold randomly deposited in the hairs over the following 14 days between administration of the

nanoparticles and extracting the hair sample. This indicates long term mobility on nanoparticles and assists in understanding nanoparticle behaviour and fate while utilizing fewer animals. Further to this, such studies can indicate inter-animal variability.

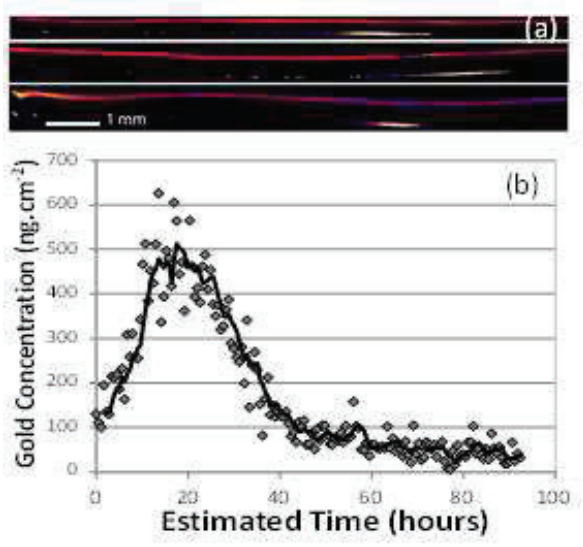

Fig. 2. XRF images of Zn with corresponding images of Au in three mouse whiskers (a). By measuring the rate of growth in each hair, the gold distribution in these samples was used to construct pharmacokinetic profiles (b) with a half-life determined to be approximately 7 hours.

Gold Nanoparticle use in Tracking Lymph Flow

In tumour growth and metastasis (spread) the lymph drainage carries loose metastatic cancer cells through the lymph system where they can lodge and result in secondary tumours. Following the sentinel lymph node concept, these cells will primarily drain to a proximal node which will be the primary candidate in monitoring the stage and spread of a cancer. Gold nanoparticles have been used to track this flow and with proper functionalization act to label the down-stream lymph nodes (Figure 3a) [8]. This is with aim to assist in diagnostic and surgical procedures. Anti-CD45 antibody functionalized gold nanoparticles were injected into the foot pads of a mouse model.

The antibody was specifically chosen to target the CD45 antigen expressed in lyphmoid cells. Without functionalization the nanoparticles drained rapidly. However, the targeted nanoparticles were retained in the lymph nodes for many hours, labelling the relevant drainage route from an administration site. Figure 3b shows a gold map in a mouse lymph node. The ability to image the whole node for gold distribution is useful for characterizing the fate of these functionalized nanoparticles before conducting standard histology.

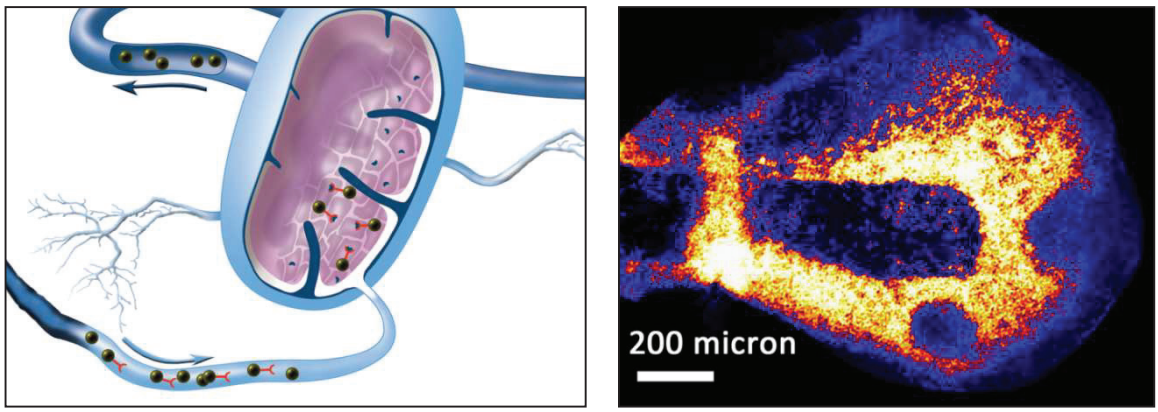

Fig. 3. Functionalized nanoparticles are retained in the lymph node and act to label lymphatic drainage pathways downstream from tumour.

Lead Ingestion, Metabolism and Fate

Understanding the mechanisms and effect of pollutant exposure from a range of environmental sources is important to maintain both the environment and human health. Unfortunately, exposure to pollutants is an inescapable part of living in today's society. Lead is a very good example of society's exposure to pollutants across periods of millennia. The Romans mined and smelted lead extensively for nearly a thousand years and utilized lead in cookware and storing and transport of water. The use of lead for a range of items continued until the 20th century when lead was increasingly used in paints and petrol, resulting in increased blood lead levels, particularly in children. Fortunately through the phasing out of lead in petrol and paints, blood lead levels have decreased worldwide. However, lead mining and use has left a legacy of lead

contamination in soils and dusts. The persistence of lead in the soil and dust is of major interest to many researchers as it is commonly believed that there is no known safe threshold for lead exposure. To understand the environmental hazard of pollutants such as lead at subclinical exposure levels, we have utilized the rapid developments in X ray Absorption Spectroscopy to investigate behaviour of pollutants in both in-vitro and in-vivo systems [9]. Identifying the mechanisms by which organisms regulate the uptake and excretion of pollutants in soils and dusts is critical to understanding the development of potential diseases or environmental impacts through long-term exposure. One part of the many layered levels of characterization is the use of X ray fluorescence Microscopy at the Australian Synchrotron to investigate the accumulation of pollutants in-vivo. Previously this would not be possible due to the time required to scan complete animal cross sections. The great advantage associated with the rapid rate of XFM sampling is the increased level of detail and multi-element analyse that may be obtained. In this small study, embedded cross sections of the mouse were analysed to assess lead distribution after the mice were exposed to lead contaminated soil (Figure 4). The lead levels in the mouse were relatively low which is in part due to the relatively low concentrations of lead in the contaminated soil. Lead soil concentrations were approximately 1000 mg kg-1. This level of lead contamination is markedly lower than observed in many mine site contaminated soils or in soils contaminated through smelter activities. The actual lead concentration in the mouse body was approximately 1.5 mg kg-1, relatively low for analysis by traditional electron probe methods. Utilizing the multi-element capability of the XFM, it is possible to identify a range of tissues in the mouse cross section. In this case, zinc has been utilized to identify the major tissues (Fig. 4a) and the accumulation of lead was identified in the renal cortex of the kidneys (Fig. 4b).

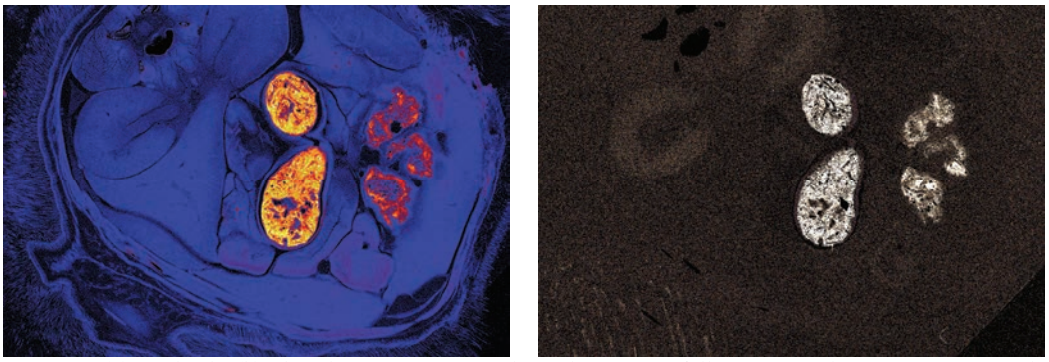

Fig. 4. XFM showing Zn (a) and Pb (b) distribution in mouse lateral sections following 18 days exposure to Pb-contaminated soil. (Fig. 1a: 1=spine, 2=kidneys, 3=liver, 4=stomach, 5=intestines).

Summary

Large area, rapid, XRF mapping is giving rise to new visualization of metals in biology. These examples demonstrate the ability to image large samples and/or many more samples at high resolution than previously feasible. Along with improved sensitivity and data processing this is providing statistics and insight into biological transport and fate relevant to numerous aspects of environmental, health and medical research. Rapid scanning provides images with less damage incurred by the sample and facilitates analysis with other modalities. For smaller samples it also enables XRF tomography in acceptable time frames (i.e. on the order of 10-15 hours for 100 rotations). Another technique to further evolve with this technology is the power to conduct X ray absorption near edge spectroscopic mapping by which large areas of chemical speciation can be imaged. It is expected that XRF imaging will contribute significantly more to biological sciences and research than what has typically been practical.

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Croatia

Activities on High-Resolution X ray spectroscopy at the Laboratory for Ion Beam Interactions (LIBI) of the Rudjer Boskovic Institute, Croatia

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Through the Laboratory for Ion Beam Interactions (LIBI), the Division of Experimental Physics of the Rudjer Boskovic Institute (RBI) operates and maintains the Tandem Accelerators facility that physically consists of the 6MV Tandem Van de Graaff and 1MV Tandetron accelerators, associated beam lines and measurement end-stations. The facility is used for research and applications in a range of fields, including nuclear and atomic physics, applications in materials science and development of advanced materials, radiation detector testing, air pollution monitoring, archaeometry, etc.

The accelerators are capable to deliver a wide range of ions, with energies from about 200 keV to tens of MeVs, to eight beam lines. The beam lines in use are equipped with specialized end stations: (i) nuclear microbeam in quintuplet configuration with MeV SIMS instrumentation recently installed; (ii) ERDA (Elastic Recoil Detection Analysis) for thin film analysis, (iii) two general purpose IBA (Ion Beam Analysis) stations equipped with two X ray detectors for PIXE (Particle Induced X ray Emission), Gamma-Ray detector for PIGE (Particle Induced Gamma-Ray Emission) and particle detectors for RBS (Rutherford Backscattering) spectroscopies; (iii) one beam line for analysis of objects in air; (iv) dual beam end station with unique capability to simultaneously deliver two ion beams to a target for ion beam modifications and/or analysis, equipped with high precision goniometer for ion beam channelling experiments; (v) plane crystal spectrometer high resolution PIXE; (vi) dedicated end station for detector testing; (vii) nuclear physics experiments end station.

LIBI is member of the SPIRIT consortium (www.spirit-ion.eu), funded through the FP7 Infrastructure project. The SPIRIT consortium integrates eleven leading European ion beam facilities from six EU member states and two associated states. Through SPIRIT, ion beams are made available for the modification and analysis of solid surfaces, interfaces, thin films and nanostructured systems. SPIRIT activities include sharing research infrastructure through trans-national access (TNA), networking and Joint Research Activities (JRA). LIBI is active in all three fields.

Here we will briefly review on the recent LIBI activities related to one of the key tasks within the SPIRIT Joint Research Activities, the one on chemical and molecular imaging, which among other techniques, investigate possible utilization of PIXE to provide bonding state information using

high resolution X ray wavelength dispersive spectrometers.

In this respect during the last decade we have performed high resolution PIXE investigations on a number of transition metal compounds in order to establish and apply the PIXE-based wavelength dispersive spectroscopy to determine chemical states of various transition metal compounds. In case of 3d transition metals (elements from Sc to Cu) the outermost 3d level becomes a broad band and in chemical compounds it forms the valence shells. Kα spectra of 3d transition elements are not so sensitive to chemical effects since they are emitted through transitions between inner shells. At the other hand, Kβ band components like Kβ', Kβ" and $K\beta_{2,5}$, are related to valence electron transitions. With the recent advances in WDX spectrometers, solid state and chemical effects on K X ray emission spectra have been investigated quantitatively providing experimental data on positions, relative intensities and shapes of individual K X ray features at the resolutions close to their natural line widths.

Our first Kβ X ray spectra were measured by MeV proton excitation using the RBI WDX system installed at the RBI Tandem Accelerator Facility. Later through SPIRIT collaboration we decided to collect two sets of independent measurements, one obtained by the RBI flat crystal type and another with the Josef Stefan Institute (JSI, Ljubljana, Slovenia) Johansson type crystal. Our colleague Luka Mandić from University of Rijeka (Department of Physics) participated in all experiments. First we measured Kβ spectra of selected V [1] and Ti [2] compounds by the RBI flat crystal spectrometer. Then we performed measurements on Cr [3] compounds with both spectrometers. Finally, in order to extend the set of high resolution spectra, we measured the spectra of selected Ti, V and Mn compounds employing the JSI Johansson type crystal spectrometer. All the measurements at JSI were performed owing to the SPIRIT TNA support. Detailed description of the methods used in the analysis and on the results obtained can be found in the recently published papers listed in the reference list, and here only a brief report is given, summarising the main results.

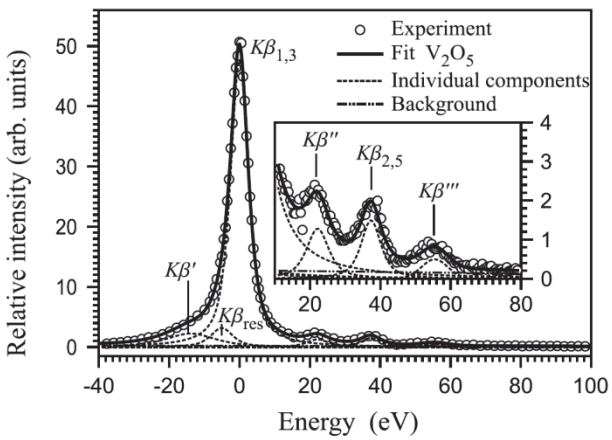

Fig. 1. Kβ spectrum of V_2O_5.

High-resolution Kβ X ray spectra induced by proton beams in thick Ti, TiO, Ti_2O_3, TiO_2, $MgTiO_3$, $FeTiO_3$, TiC, TiN, TiB_2, V, V_2O_3, VO_2, V_2O_5, VC, VN, VCl_2, NH_4VO_3, $VOSO_4$ x $5H_2O$, Cr, Cr_2O_3, CrO_2, CrO_3, K_2CrO_4, $K_2Cr_2O_7$, Mn, MnO_2 and $KMnO_4$ targets were measured independently with two PIXE WDX systems. The intensities and energies of the $K\beta_{2,5}$ and Kβ" lines relative to the $K\beta_{1,3}$ line were extracted. As illustration, Figures 1 and 2 show measured Kβ spectra of selected compounds obtained by the RBI WDX system.

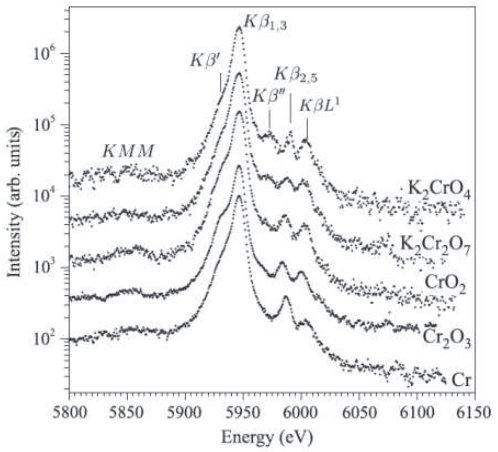

Fig. 2. Kβ spectra of chromium oxides.

The obtained database of collected Kβ X ray spectra was used finally for simple parametrization of experimentally determined Kβ" and $K\beta_{2,5}$ X ray relative positions and intensities over the range of 3d metals and their compounds with wide range of metal ligand bond lengths and various oxidation states for possible future practical use in X ray emission spectroscopy based on both solid state and WDS detection systems. As already explained, two independent experiments employing wavelength dispersive spectrometers with different experimental resolutions were performed in order

to exclude any possible effect of the experimental resolution on the extracted values. Results of our parameterization were compared critically with other experimental and theoretical values available in the literature. We believe that the parameterization obtained could be useful for chemical and structural speciation of 3d metal compounds and for improved interpretation of K X ray spectra of 3d transition metal compounds measured by solid state detectors. Brief results are illustrated below, while detailed results are given in [4].

Figure 3 shows energy separation between $K\beta_{1,3}$ and $K\beta_{2,5}$ as a function of the metal formal oxidation number for various 3d metal oxides. Our measurements and data from the available literature are given. Filled symbols represent our experimental data. All the other data, found or extracted from the literature, are shown as hollow symbols, irrespective of the used excitation modes. Our data are in general agreement with the extracted data from the literature. Therefore, each trendline represents total data set collected for individual 3d elements. The largest sets of data are for Mn and Cr compounds. Although individual data are scattered, the general tendency of the linear $\Delta E(K\beta_{2,5} - K\beta_{1,3})$ increase with the formal metal oxidation number is clearly seen for elements from titanium to iron. The figure indicates the $K\beta_{2,5}$ X ray line shifts to higher energies from about 2 eV per oxidation state for titanium oxides to about 0.7 eV per oxidation state for iron oxides.

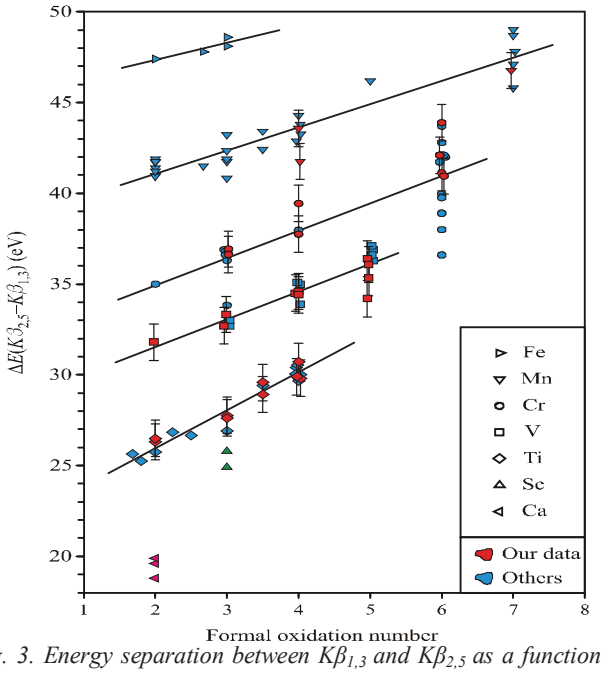

Fig. 3. Energy separation between $K\beta_{1,3}$ and $K\beta_{2,5}$ as a function of the metal formal oxidation number for various 3d metal oxides.

For parameterization of Kβ" and $K\beta_{2,5}$ X ray intensities relative to the sum of Kβ' and $K\beta_{1,3}$ intensities we assumed that these relative intensities I_{Ri} may be parameterized by the following functions:

$$I_{Ri} = nf_i(Z)e^{-a_i d}$$

i = 1,2,3 and stands for Kβ", $K\beta_{2,5}$ and sum (Kβ"+ $K\beta_{2,5}$), respectively
n - number of ligands (oxygen) per central metal ion
d - average bond length between the central metal ion and ligand
a_i - parameters associated with the exponential dependence of relative intensities
f_i - parameters associated with the Z dependence of relative intensities
Z - atomic number of the central metal atom in question

We defined scaled normalized intensities I_{Si} as

$$I_{Si}(d) = \frac{I_{Ri}}{nf_i(Z)} = e^{-a_i d}.$$

We then varied $f_i(Z)$ and a_i parameters (separately for each i in order to simultaneously: (i) convert all our experimental data from I_{Ri} to scaled values I_{Si} and (ii) obtain the best exponential fit of scaled normalized intensities I_{Si}.

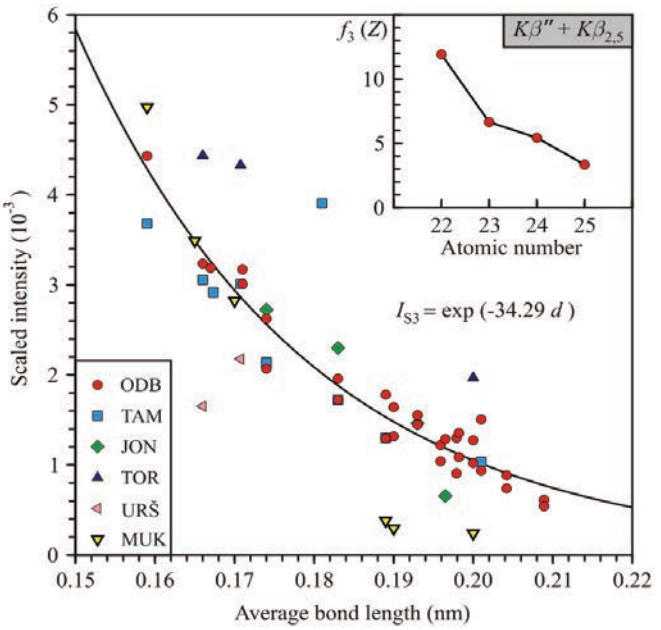

Fig. 4. Scaled intensities of the sum of Kβ" and $K\beta_{2,5}$ lines versus average metal - oxygen bond length. Scaled experimental values from our database (ODB) are fitted with exponential trendline. Related $f_3(Z)$ fit parameters are shown in inserted sub-graph. Experimental and theoretical data of related relative intensities published by other authors are converted by using the same parameterization and shown for comparison.

Figure 4 shows fitted scaled intensities of the sum of Kβ" and $K\beta_{2,5}$ lines versus average metal - oxygen bond length. In general, the figure shows that the experimental data of other authors

(obtained by various excitation mechanisms) are more or less scattered around the fitted curve through our data. The agreement between calculated and our average experimental values are better than 10% for most measured compounds.

Since all of our measurements have been obtained on thick targets, the influence of thick target self-absorption has been investigated using related X ray absorption near-edge-structure (XANES) spectra that are available in the literature to estimate mass absorption coefficients close to the K absorption edge. Although Kβ components are close to the K absorption edge, we found that among the samples measured only $K\beta_{2,5}$ lines are partly affected by thick target self-absorption for thick metalic targets (Ti, V, Cr, Mn). In case of oxides, thick target self-absorption is small even for $K\beta_{2,5}$ lines. On the contrary, intensities of $K\beta L^m$ (m = 1, 2, . . .) satellites are heavily influenced by the K-edge absorption. These lines correspond to the $K\beta_{1,3}$ line emitted with additional L spectator vacancies. Such satellites are emitted with the energy shifts above the parent $K\beta_{1,3}$ line. In case of 3d metals (up to Cu) such energy shifts are greater than the K binding energy of the ground-state atom even for $K\beta L^1$, and therefore related X rays suffer critical absorption in thick targets or passing through the filter containing atoms of the same element as the target. It is well known that contributions to K X ray spectra related to multiple ionization satellites are more pronounced in case of ionization by MeV protons (when compared to photoionization), and especially by heavier ions. This results in changes of Kβ/Kα X ray intensity ratios and in enlarged energy separation of Kα–Kβ X rays (as seen by low resolution solid state detectors) with the increase of the (heavy) projectiles energy.

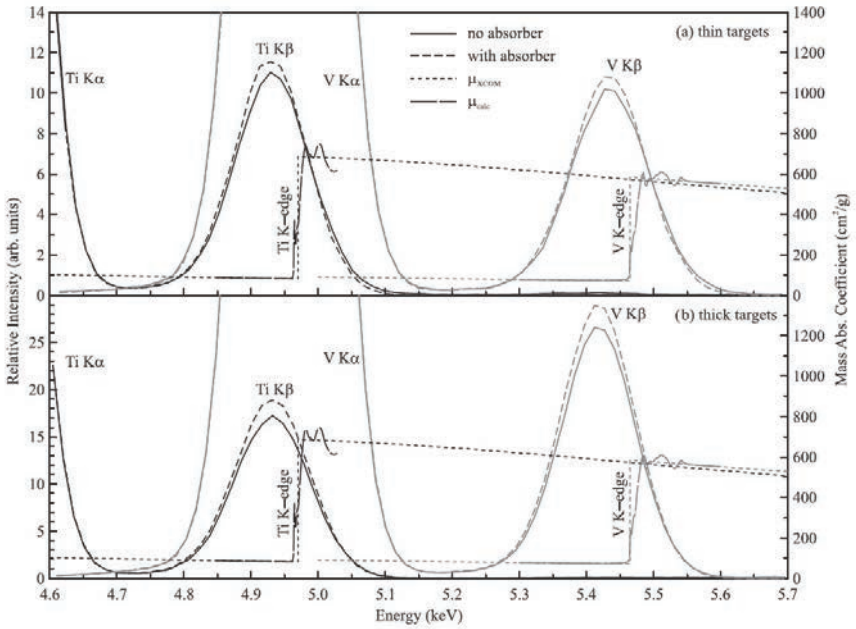

Fig. 5. K X ray spectra obtained from thin and thick Ti and V targets with and without absorber foils in front of the SDD detector. Kα peak intensities obtained with the absorber foils are scaled to the respective spectra obtained without absorber. Therefore the related Kβ peaks obtained with the absorber foils have higher intensities in the channels close to Kβ peak centroids.

In order to investigate the influence of the K-edge on self-absorption in 3d metals more precisely, we measured K X rays from Ti and V targets with and without Ti and V absorber foils of appropriate and well known thickness. Corresponding K X ray spectra were measured with standard Si(Li) and SDD detectors and by high resolution WDX setup, all with and without selected absorber foils.

Figure 5 shows that Kβ peaks from thin targets obtained with the absorber are distorted at the channels above the centroid position, where channel intensities obtained with the absorber have lower intensities. The reason is large absorption of the $K\beta L^m$ satellites through the absorber foil at the K-edge and above. This distortion is much smaller on spectra obtained from thick targets. This is since $K\beta L^m$ satellites are heavily self-absorbed within the thick target itself and their yield observed by the detector is much smaller than in the case of thin targets. The position and shape of the K absorption edge is also shown at the figures (as mass absorption coefficients on right hand-side scale).

High resolution measurements showed that while for Ti and V thick metal targets intensities of the KβL satellites are heavily influenced by the K-edge self-absorption, $K\beta_{2,5}$ line intensities from thick targets are only partly affected due to the overlap with the pre-peak in the absorption edge. The analysis shows that in case of thick Ti target ionization by 2 MeV protons, $K\beta_{2,5}$ intensity (relative to $K\beta_{1,3}$ + Kβ') will be reduced for 20% and relative intensity of KβL satellites will be reduced for a factor 3 compared to the respective relative intensities from thin targets. Details about the experiment and results are given in [5].

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Thailand

Introducing the micro X ray fluorescence beamline at the Siam Photon Laboratory and applications on archaeology

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The Siam Photon Laboratory

The Siam Photon Laboratory (SPL) is a synchrotron radiation facility in Thailand operated by the Synchrotron Light Research Institute (Public Organization) under the Ministry of Science and Technology, The Royal Thai Government. The SPL project has been established since 1996 to serve as an advanced national laboratory using synchrotron radiation as a source. The machine was donated by the SORTEC Corporation, Japan. However, some parts including the control system and the storage ring have been modified from FODO to Double Bend Achromat (DBA) magnetic lattices in order to have straight sections for insertion devices. The synchrotron radiation source at the SPL is a 1.2 GeV storage ring, consisting of four DBA sections with eight bending magnets and four straight sections (Fig. 1). Therefore, at least eight beamlines can be accommodated. The straight sections allow four insertion devices to be inserted. So far, one undulator with 60 periods (U60) of magnetic poles has been installed in one of the available straight section to produce higher flux in soft X ray region. One superconducting wavelength shifter will be installed in the beginning of 2013 for hard X ray beamline.

Fig. 1. The experimental area and a schematic diagram of the SPL storage ring

Since 2001, two beamlines including X ray Absorption Spectroscopy (XAS) and Deep X ray Lithography (DXL) have been opened for public. Today, seven beamlines including micro beam X ray Fluorescence beamline (μ-XRF) are now in full operation providing full range (from infrared to X rays) and high intensity of synchrotron radiation. So far, great numbers of experiments in vast varieties of research fields especially in agricultural, medical, environmental and material sciences have been carried out, and many results have been reported.

The micro-XRF beamline & End-station

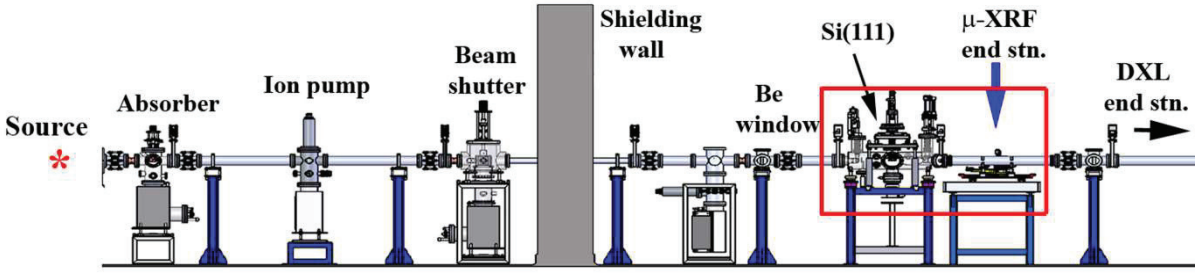

Fig. 2. Optical components of the upgraded beamline for DXL and μ-XRF at the SPL.

The beamline utilizes a bending magnet X ray source. A beryllium window with thickness of 100 μm is installed outside the radiation shielding wall mainly used to separate ultrahigh-vacuum and low-vacuum regions in the beamline. It also acts as a low-energy filter, leaving continuous X rays of energy 2 - 12 keV to reach the end-stations. The fixed aperture reduces the beam size to 5 mm x 2 mm (H x V) at the entrance of the focusing X ray lens. A Si(111) crystal is used to extract a monochromatic X ray beam of 8 keV for X ray diffraction experiments. However, when this technique is not in operation, the crystal can be lifted up to allow continuous X ray beam to reach other end-stations, i.e. μ-XRF or DXL. The μ-XRF end-station sits upstream of the DXL end-station, but is designed to be replaced by a 1 m-long vacuum pipe when the DXL end-station is in operation. Three gate valves are employed to maintain vacuum environments during the vacuum duct replacement.

As mentioned above, one of the in-operation beamlines is a micro-beam X ray Fluorescence spectroscopy & imaging (μ-XRF) beamline. Details of the μ-XRF beamline can be found in [1]. This beamline was originally designed for DXL technique. However, due to the simplicity of the beamline and the requirement of users, it has been modified to accommodate more end-stations in a time-sharing arrangement. In this new design, a new chamber made in-house equipped with a fixed aperture and a Si(111) crystal has been installed as shown in Fig. 2.

The μ-XRF end-station consists of four main components including an X ray optical system, a visible-light microscope, a motorized sample holder with three degrees of freedom, and an energy-dispersive detection system, as shown in Fig. 3(a). In order to achieve a micrometer-sized beam, a focusing system for X rays is essentially needed. Here, a polycapillary half-lens manufactured by UNISANTIS EUROPE GmbH is employed to focus an X ray beam to the order of 100 μm in diameter. This polycapillary lens is installed on a motorized stage with four degrees of freedom. It is aligned using two linear motors with

6 µm precision and two rotational motors with 0.006º precision from MISUMI, Japan. A CCD camera coupled to a 5x ZEISS objective lens is also used to specify and capture the measured area of a sample. Motor precision for the sample stage is 1.5 µm with the sample surface sitting at the focal point of the polycapillary lens. All motor motions are remotely controlled. Detection of the X ray fluorescence signal is via an energy-dispersive Si-PIN detector from AMPTEK, USA, with an active area of 13 mm^2 and energy resolution of 160 eV at the Mn Kα emission line. Energy-out signals from the detector are then registered at an MCA8000A multichannel analyzer (AMPTEK, USA) corresponding to the energy of X rays. Focused beam of the synchrotron radiation at the sample position was measured using wire scan technique. In this technique, a copper wire with diameter of 10 µm is placed at the sample position where the distance between the polycapillary lens and sample is 22 mm (focal length of the polycapillary lens). The beam size measurement is carried out by measuring the intensity of Cu Kα X ray fluorescence from the copper wire as a function of its horizontal position. The intensity of Kα X rays from copper can be plotted as a function of position as shown in Fig. 3(b), and the beamsize can be calculated. Moreover, the beamsize at different positions along the beam was also measured (see inset in Fig. 3(b)).

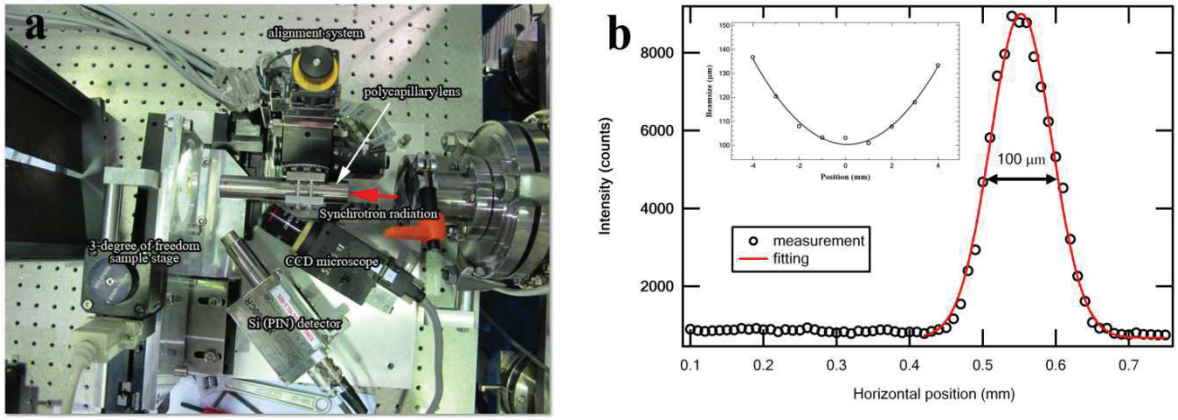

Fig. 3. (a) micro-XRF end-station and (b) intensity of Cu Kα X rays as a function of horizontal position. Inset:beam size as a function of position along the beam axis.

The applications

XRF is a well-known technique for non-destructive analysis; it is therefore a perfect tool for archaeological study. In Thailand, great numbers of valuable ancient objects have been found all over the country. Many of them have not yet been studied scientifically. We have thus been trying to investigate and study some of objects excavated in different regions of Thailand as shown in Fig. 4. Details can be found in references [2-5].

From the top left, pieces of historical decorative glasses found in the North of Thailand were examined qualitatively using the µ-XRF at this beamline. Results are corresponding to the results from other techniques including SEM-EDS and PIXE. A shard of Ban Chiang pottery shown in the top right was also studied. Ban Chiang is a UNESCO heritage site which spans three periods of pottery; pre-metal, bronze and iron ages. This sample used here belongs to the iron age pottery which has been found to have distinctive red pigment on painted surfaces and exquisite designs. XRF analysis of this red shard was of interest in studying the element distribution to provide insight into what materials were used for slip painting. Shown here are the distributions of three different elements (Fe, Mn and Ti).

A piece of enameled glass from Laem Pho historic site on the Eastern shore of the Gulf of Thailand shown in the bottom left was also studied. Laem Pho is one of the most important historic sites in the South of Thailand. Laem Pho was used as a commercial connection port between China and Middle East during the 7th – 13th Century A.D. Many of archaeological objects have been found including enameled glass. In this study, SEM-EDS, PIXE and µ-XRF have been used to obtain the chemical composition. The presence of transition metals such as copper, iron and manganese affected the glass colorations. Typological

classifications, technological observations and comparative studies serve to clarify the development and cultural inter-relationships of various glass objects along the trade and exchange networks in ancient maritime. Another example as shown in the bottom right is ancient burnt rice. Burnt paddy rice (or black rice) was found in religious buildings of the Buddhist and Hindu temples at the various archaeological sites in Thailand such as Ban Dong Lakon (Nakorn Nayok Province), Sri Mahosot (Prachin Buri Province), Puk Ri (Lop Buri Province), Yawuek (Buri Ram Province), Ban Krabueang Nok (Nakon Ratchasima Province), U-Thong (Suphan Buri Province) and Ban Dong Muang (Sara Buri Province). In this work, micro-XRF, SEM-EDS and FTIR spectroscopy were used to study chemical composition and elemental distribution. In the bottom right XRF maps of Cd, Ti and Cu of a rice grain from Ban Dong Lakon are shown.

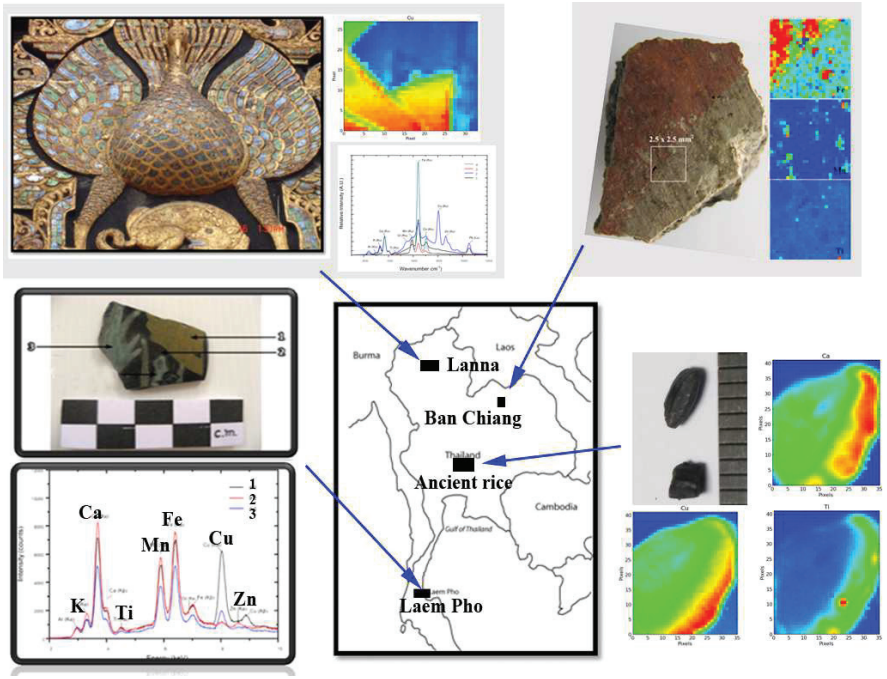

Fig. 4. Ancient objects from different area of Thailand; (top left) Lanna style glass form the North, (top right) Bang Chiang shard from the North-East, (bottom left) enameled glass from the South and (bottom right) ancient burnt rice from Central area.

Conclusion & future plan

The μ-XRF beamline end-station at the SPL has been in operation since the end of 2011 in time-sharing mode with DXL end-station. The beamsize of the synchrotron radiation at the sample position is 100 μm x 100 μm. Different archaeological samples from different ages and sites were selected to test the performance of the end-station. However, due to the low energy of synchrotron radiation from a bending magnet, a new beamline for μ-XRF technique at SPL has been designed using a multipole wiggler as a new source. The multipole wiggler has a magnetic field of 2.4 T with 5 periods compared to 1.44 T of the magnetic field of bending magnet. The new beamline will accommodate other two techniques including X ray Imaging and X ray Tomography. It is expected to be operational in 2014.

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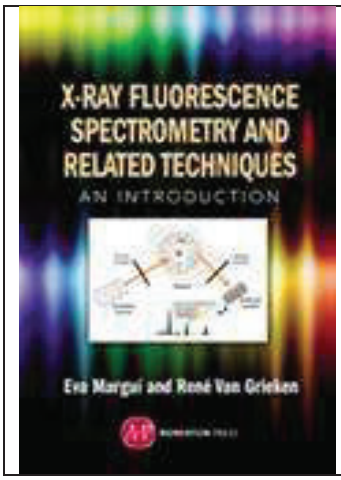
New books in the field of XRF analysis

X-Ray Fluorescence Spectrometry and Related Techniques: An Introduction, by Eva Margui, Rene Van Grieken, 142 pages, Print ISBN: 9781606503911



The book provides a comprehensive and up-to-date account of basic principles, recent developments, instrumentation, sample preparation procedures, and applications of XRF analysis. The book presents recent technological advances, including the design of low-power micro-focus tubes and novel X-ray optics and detectors, which have made possible to extend XRF to the analysis of low-Z elements and to obtain 2D or 3D information on a micrometer-scale.
Eva Marguí is an Associate Professor in the Department of Chemistry of the University of Girona. She is a researcher in the Analytical and Environmental Chemistry Unit of the same University. She is the author of more than thirty publications on XRF in high-level journals and has participated in different conferences in the field as an invited lecturer. She is the secretary of the European X-ray Spectrometry Association (EXSA) (2012).
René Van Grieken is a Professor in the Department of Chemistry of the University of Antwerp (UA) in Belgium, where he teaches instrumental analysis and environmental chemistry and is the Director of the environmental analysis group within Micro- and Trace Analysis Center (MiTAC). He is active with major European scientific organizations and has authored or co-authored over 800 publications.

Handheld XRF for Art and Archaeology (Studies in Archaeological Sciences) by Aaron N. Shugar and Jennifer L. Mass (Editors), Leuven University Press, 2012, 600 pages, ISBN-10: 90-5867-907-1

Following the dissemination of handheld XRF technology in cultural heritage analytical studies (according to the Editors perhaps more than 1500 units are in use worldwide for this purpose), this book focuses on methodological aspects of handheld XRF analysis demonstrating the wide range of analytical applications in the field of art conservation and archaeology. As the Editors note in the introduction chapter the main intention of the book is to provide standards of best practice for the XRF examination of the materials encountered in cultural heritage research. The fourteen (14) chapters of the book focus on experimental methodologies, protocols and limitations of handheld XRF analysis in dealing with glasses, porcelains, ceramics, Renaissance bronzes, historical silver alloys, paintings, manuscripts, photographs, paper, obsidians, soils and on-site application for archaeological materials.
Aaron N. Shugar is an Associate Professor of Art Conservation Science at Buffalo State College, Buffalo, New York
Jennifer L. Mass is a Senior Scientist in the Scientific Research and Analysis Laboratory Conservation Department at Winterthur Museum, Winterthur Delaware

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