IAEA
International Atomic Energy Agency

XRF Newsletter

A newsletter of the IAEA's Laboratories, Seibersdorf
Issue No. 17, July 2009

ISSN 1608–4632

X ray Fluorescence in the IAEA and its Member States

In This Issue

Activities in the IAEA XRF Laboratory

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

Automation of micro-beam scanning XRF spectrometer

With the assistance of an external consultant (Mr. Mladen Bogovac, Ruder Boskovic Institute, Zagreb, Croatia) further improvements have been made in the laboratory micro-beam scanning XRF spectrometer. The recent development and status of the instrument are presented.

1. Introduction

The micro-beam scanning XRF spectrometer (Fig. 1) at the XRF laboratory, IAEA Laboratories Seibersdorf, has been gradually developed to a fully computer controlled system for elemental mapping and 2D/3D X ray absorption and X ray fluorescence computed tomographic imaging in confocal and parallel beam geometry.

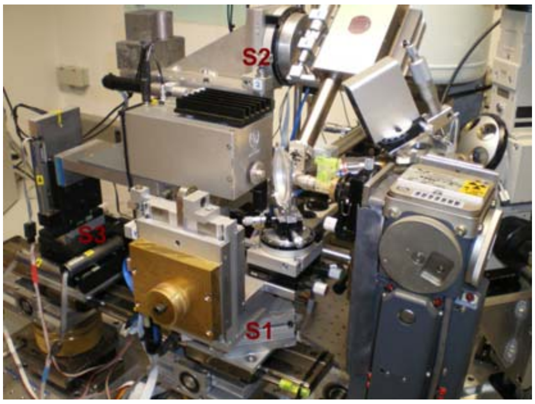

Fig. 1. The micro-beam scanning XRF spectrometer features three multiple axis stages: two for detector alignment (S2, S3) and one for sample manipulation (S1).

The system features either digital [1] or analog [2] multi channel analyzers that are synchronized with computer controlled sample motion [2]. Recently, the software for motion control has been improved in order to perform automatic identification of the individual particles and manipulation of multiple motorized stages for easy alignment of the system.

2. The control software for multiple motorized stages

The XRF system features several motion stages. In particular a measurement with a highly focused X ray beam, down to 10 μm with monocapillary or 30 μm with polycapillary-lens, requires a very precise movement of the sample. Therefore, a 4-axis xyzθ motorized micrometer stage (see Fig. 1, S1) is used for sample manipulation. In addition a low magnification (x15) camera for sample inspection is mounted. Further, the confocal tomography requires precise alignment of the system in such a way that the focal point of the X ray lens used for beam focusing and the focal point of the X ray half-lens attached to the X ray fluorescent (confocal) detector match perfectly. For this reason, the confocal detector is attached to the 3-axis motorized stage (see Fig. 1, S2). Finally, in order to reduce scattering radiation, the detector used for absorption measurements is fine collimated which also requires precise alignment of the collimator and focused beam (see Fig. 1, S3).

The computer control of all stages (sample, confocal and absorption detector) requires developing adequate software and synchronizing it with data collection. The software has been written in C/C++ using Microsoft Visual Studio and runs under Microsoft Windows. Each moment the software can control one predefined stage and camera for a live video streaming as well. The motorized stages are driven by different controllers (Physik Intrumente C812, Physik Instrumente C843 and Oriel Encoder Mike Controller 18001) featuring different commands and communication channels (R232, PCI, ISA bus). If needed, they may be upgraded and replaced in the feature. Therefore, all communication with controllers is encapsulated in separate DLL libraries (Dynamic Link Library), one for each controller. Each DLL is linked with one instance of the main program on run time and uses additional DLLs and drivers supported by vendors in order to communicate with hardware. The main program has a graphical user interface (see Fig. 2 right) enabling easy set-up and control of up-to 4 axes per each stage.

The motion of each stage can be monitored on the computer screen for inspection. The camera control is implemented with a camera specific DLL. As a majority of today's cameras and video controllers support Microsoft Direct Show, a DLL that implements a simple Direct Show graph as shown in Fig. 2 left has been developed. The graph comprises a sequence of fundamental processing steps known as filters. It was built using Direct Show's ICaptureGraphBuilder2 interface that may automatically add SmartTee and appropriate color space converter filters to the graph (see YUV filter in Fig. 2 left). The VMR9 filter is used for video rendering and overlaying of live video with a drawing surface (bitmap) using alpha blending. The drawing over a calibrated live video enables easy definition of the sample scanning area.

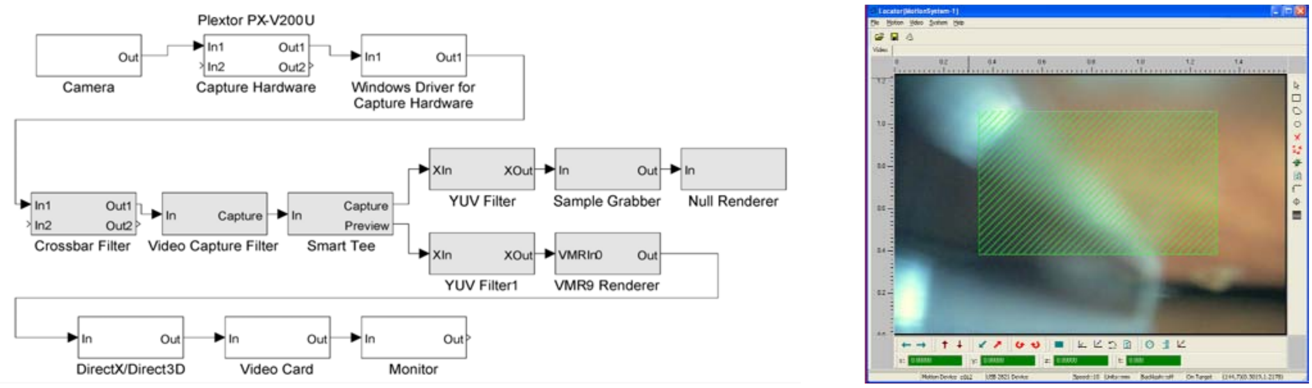

Fig. 2. Left: a simple DirectShow graph (greyed boxes) that was implemented in a DLL comprises a set of software filters and enables, together with other software and hardware components (white boxes), live video streaming and capturing. Right: a running instance of the motion control software showing user defined rectangular scan area over the live video image.

Calibration of the live video streams requires knowledge of the position of the beam spot on the video surface, actuator's pulse counts per unit traveling distance and the video format. The beam position can easily be found by using X ray intensifying screen or two tungsten micrometer thick wires that are parallel to the xy axes and form a 'cross'. Moving the cross in x and y axis directions, and monitoring number of counts in the X ray fluorescence (emission) or absorption detector, one can find the position of the X ray beam with micrometer precision and position the center of the cross in the front of the beam. The focal point can be found then by moving the cross along the beam direction and the cross can be positioned at the beam focal point.

The confocal detector has a half-lens attached and its focal point should match the focal point of the beam. This can be achieved in an automatic way by collecting the X ray image of the cross when the cross is positioned at the beam focal point and the confocal detector is moving.

3. Individual particle identification

A 'fast scan' (typically 100 ms per pixel) reduces the time of analysis and makes possible the scanning of larger regions of the sample with an increased probability of finding the particles of interest. The fast scan generates emission and possible absorption maps. The maps are then used for particle identification. After the particle is found, Si(Li) X ray detector can be used to better characterize (precise identification) of the individual particles by measuring X ray fluorescence spectra with a longer collection time.

In order to find the particle automatically a simple ‘thresholding’ algorithm was developed and tested for a simple sample. The sample was prepared by deposition of soil particles on a Mylar foil. Both emission and absorption images were taken simultaneously by scanning an area of approximately 5 mm × 5 mm with 50 µm resolution and 100 µsec preset time per pixel. Typical image (map) is shown in Fig. 3a. It features high image contrast and uniform background. In the first step, the algorithm calculates average number $\overline{N}$ of counts in the map and its standard deviation $\sigma_{\overline{N}}$ according to formula 1 taking into account number of counts N_{ij} at each position (*i*,*j*) on the whole *m* x *n* pixels image. In the second step, all counts in the map that are α ($\alpha \approx 3$) standard deviations above average value in the emission map or below average value in the absorption map are discarded and the average value and the standard deviation are calculated again. The second step is repeated until the relative change in the standard deviation is less than a predefined value (0.1%). Finally, the thresholds $N_T^{(em)} = \overline{N} + \beta\sigma_{\overline{N}}$ and $N_T^{(ab)} = \overline{N} - \beta\sigma_{\overline{N}}$ for emission and absorption maps respectively are calculated, where β is predefined as a constant (usually $3 \le \beta \le 6$).

$$\overline{N} = \frac{\sum_{i=1}^{m}\sum_{j=1}^{n} N_{ij}}{mn} \qquad \sigma_{\overline{N}}^{2} = \frac{\sum_{i=1}^{m}\sum_{j=1}^{n} w_{ij}(N_{ij} - \overline{N})^{2}}{\sum_{i=1}^{m}\sum_{j=1}^{n} w_{ij}} \qquad w_{ij} = \frac{1}{\sigma_{N_{ij}}^{2}} = \frac{1}{N_{ij}} \tag{1}$$

The thresholds are used to find the particles in the following manner. First, all positions with counts above the threshold in the absorption map or below the threshold in the emission map are tagged with zero. The remaining positions contain particles and they are filled (see Fig. 3b) with a unique non-zero tag using well known boundary fill algorithm. Then, each particle can be probed with the emission detector using time preset selected before the fast scan started.

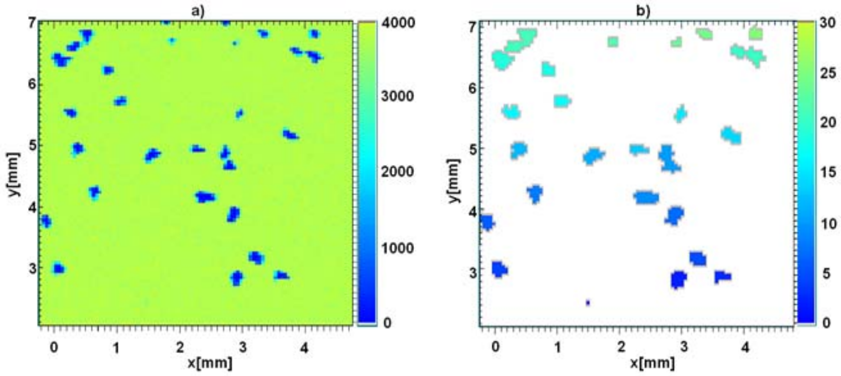

Fig. 1 X ray fluorescence map (a) obtained in a fast scan mode is used for automatic individual particle identification using simple 'thresholding' algorithm. The algorithm generates a map (b) with colour coded particles.

Conclusion

Software for manipulation with multiple stages has been developed and implemented. It allows easy positioning, alignment and video surveillance of the micro-beam scanning XRF spectrometer. The software is coupled with the existing data acquisition software and enables definition of the sample's scan area from its live video image.

A simple and efficient algorithm for identification of individual particles from X ray absorption or X ray fluorescence images has been developed and applied. The algorithm is convenient for images with uniform and noise background.

Further information on the micro-beam scanning XRF spectrometer is available from Ernesto Chinea Cano (E.Chinea-Cano@iaea.org.)

References

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Meetings and conferences

2nd Research Coordination Meeting under the IAEA Coordinated Research Project on Unification of Nuclear Spectrometries: Integrated Techniques as a New Tool for Material Research, Athens, Greece, 11 – 15 May 2009

Introduction

Over the last years the IAEA supported a substantial number of laboratories in Member States in establishing nuclear spectrometry facilities for various applications. These laboratories are being used in support of applied research, teaching and education as well as providing analytical services for industry, environmental studies, cultural heritage, food and agriculture and human health. In most cases the nuclear analytical techniques such as energy dispersive X ray fluorescence (EDXRF), particle induced X ray emission (PIXE), particle induced gamma emission (PIGE), Rutherford backscattering (RBS), etc. are used independently and provide information on a specific characteristic of the analyzed materials. In order to characterize the materials in a comprehensive way or to improve the quality of the analytical services provided by the laboratories, a combined use of a few techniques is often required. In recent years advanced laboratories, such as synchrotron sources, started to perform measurements using integrated instruments and simultaneous processing of data where outputs of the analytical techniques are used as inputs to a common data processing procedure. In this way the quality of characterization of various materials by using multiple analytical techniques improved considerably. In order to coordinate the research efforts of laboratories towards better integration and unification of nuclear spectrometries this CRP was proposed under the Project D.3.03 on Improvements in nuclear spectroscopy applications. The CRP is enhancing proper utilization of nuclear analytical methods in Member States and helping them to develop nuclear instruments for special applications.

One of the major areas of integration is the application of synchrotron radiation sources for X ray micro-fluorescence, micro-diffraction, X ray microscopy, micro-tomography, and absorption techniques used for elemental analysis, 2D and 3D imaging and chemical speciation. Portable XRF spectrometers were used with other techniques for integrated applications and better utilization of the equipment. Software simulation programs were also implemented to design integrated nuclear spectroscopy systems to optimize the measurement geometries, detection limits, and spatial resolution. A combination of XRF-PIXE and PIXE-PIGE setups and integration of data processing procedures were used to extend the applicability range of the X ray emission techniques for a better characterization of the materials. Integration and unification of nuclear spectrometries were achieved including hardware and software components, measurements and data collection, data processing and data interpretation.

The meeting held in Athens, Greece was attended by the following participants: Ms. C. Vazquez (Argentina), Mr. D. Cohen (Australia), Ms. Ch. Streli (Austria), Mr. P. Van Espen (Belgium), Mr. R. Van Grieken (Belgium), Mr. V. Desnica (Croatia), Mr. G. Mesa (Cuba), Mr. A-G. Karydas (Greece), Mr. S. Ridolfi (Italy), Mr. P. Kump (Slovenia), Mr. N. Hamdan

(United Arab Emirates) and Mr. G. Havrilla (United States of America) – see Fig.1.

Fig.1. Participants of the 2nd RCM (credit: A. Markowicz)

During the meeting a visit was organized to the Institute of Nuclear Physics at the National Center for Scientific Research "Demokritos" to introduce the participants to the experimental facilities such as the 5.5 MV TN Tandem accelerator and mobile micro- and milli-beam XRF spectrometers, as well as to the research work carried out at the Institute in the field of analytical applications of integrated nuclear spectrometry techniques (see Fig. 2).

Fig.2. Visit to the Institute of Nuclear Physics at the National Center for Scientific Research "Demokritos" (credit (A. Markowicz)

Conclusions

The CRP has assisted Member States to improve characterization of materials by the utilization of nuclear spectrometry instruments and techniques. This has been achieved through the development of integrated/unified instruments and analytical methods which have been implemented by laboratory-scale and synchrotron facilities, thereby increasing the application of nuclear spectrometry techniques across a wide range of disciplines, including environmental pollution monitoring, industry, cultural heritage, human health, geology, biology, agriculture and food production.

Specifically, the CRP has developed/constructed/ evaluated integrated multifunctional instruments based on the nuclear spectrometry techniques as well as new software for handling and operation of instruments including data acquisition, processing and presentation of data. This has greatly assisted new end-users across a broad range of disciplines to take full advantage of these techniques.

Examples of multifunctional instruments that were successfully integrated include TXRF-EDXRF, SR-TXRF-XANES, PIXE-PIGE, PIXE-XRF, micro-XRF and micro-XRD, portable XRF and micro-Raman spectrometry. These techniques have been successfully applied, for instance, to the analysis of Pre-Colombian and contemporary gold artifacts, discovery of hidden underlying Van Gogh in "Patch of Grass", identification of airborne-pollutants in New York Metropolitan Museum of Art and Wawel Royal Castle in Cracow, Poland, and study of pigments in Manos and Susques caves in Argentina.

Furthermore, several areas have been identified which need to be addressed by future research, including:

- Knowledge of key fundamental atomic parameters, such as fluorescence yields, Coster-Kronig transition probabilities, ionization cross sections
- Well characterized micro-reference materials for 2D and 3D imaging.
- Development of protocols for handling and operating instruments with different analytical range, resolution and sample characteristics for a broad range of materials.
- Handling and maintaining sample integrity during preparation and analysis.
- Improvement and evaluation of the cost-effectiveness of analytical techniques to improve/optimize competitiveness of XRS.
- Development of new applications

The participants of the RCM concluded that further research in these areas is important and could be pursued in the future CRP efforts.

The full meeting report is in preparation and will be available from the author upon request. The results of the CRP will be published in an IAEA-TECDOC (to be available in 2010).

Further information about the 2nd RCM and the results of the CRP is available from Andrzej Markowicz (A.Markowicz@iaea.org).

Conference on Non-destructive and Microanalytical Techniques in Art and Cultural Heritage TECHNART 2009, Athens, Greece, 27 – 30 April 2009

The Conference was organized jointly by the Institute of Nuclear Physics, NCRS "Demokritos", Athens, and the Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (FORTH), Heraklion, Crete, Greece. It took place at the National Hellenic Research Foundation in Athens. The Conference was attended by about 160 participants from all over the world. Sixty two oral presentations (including 12 invited talks) and 100 posters were presented. The participants demonstrated and discussed the latest advances in analytical instrumentation, methodology and applications in archaeology, art history and conservation science including characterization of pigments, stones, metals, glass, ceramics, resins, fibres etc. Particle (neutrons, ions) and photon probes available at large research facilities, bench-top and mobile instruments are currently applied for advanced and non-destructive characterization, imaging and remote sensing of cultural heritage (CH) materials. Experts, practitioners and users of these techniques and analytical methodologies attended.

Upon the invitation of the Organizing Committee of TECHNART 2009 a talk on IAEA activities related to applications of nuclear analytical techniques for characterization and protection of cultural heritage objects was presented during a session on Mobile Spectroscopy. The contribution covered recent results obtained under the relevant IAEA Coordinated Research Projects (CRPs) and Technical Cooperation (TC) projects. A substantial part dealt with the contribution of the Instrumentation Unit, IAEA Laboratories to the development of portable X ray fluorescence (XRF) spectrometers, methodology of in situ measurements, and training in the field of nuclear analytical techniques (mostly X ray spectrometry) applied for characterization of cultural heritage objects. Special emphasis was on the advantages of in situ analysis and portable instruments as well as on methods to improve analytical performance and to extend the applicability range of X ray spectrometry. The current results of a new joint project between the Vienna Museum of Fine Arts (Kunsthistorisches Museum – KHM), Atomic Institute (ATI), Vienna University of Technology, and the IAEA Laboratories at Seiberdsdorf on the development of an upgraded (trans)portable XRF spectrometer were presented in a separate talk given by staff of the KHM.

Conclusion:

The Conference was an excellent opportunity to present and promote the role of nuclear analytical techniques (NATs) in support of characterization and protection of cultural heritage objects. Major advantages of NATs include multielemental capability, truly non-destructive character of analysis, portability, possibility to perform bulk and local analysis, imaging capability, low cost and speed of analysis. These techniques are often used in combination with other analytical techniques such as Raman microscopy, neutron diffraction, X ray diffraction, infra-red spectroscopy, neutron tomography, chromatography, nuclear magnetic resonance, mass spectrometry etc. in order to generate complementary results for better characterization of CH objects. It appeared that the contribution of the IAEA through CRPs and TC projects as well as applied (adaptive) research and development at the IAEA Laboratories at Seibersdorf are important and relevant to the needs of Member States in the field of CH. Nuclear research laboratories and cultural heritage institutions from more than 40 Member States are currently beneficiaries of IAEA efforts in this field.

The next Conference on this topic (TECHNART 2011) will be organized in Berlin, Germany in 2011.

Further information on TECHNART 2009 is available from Andrzej Markowicz (A.Markowicz@iaea.org).

X ray fluorescence in Member States

During the last months we have received contributions from Australia, Austria, Italy, Slovenia, Sri Lanka and United Arab Emirates on the current XRF activities including Ion Beam Analysis. Below there are communications based on the original submissions (with only minor editorial changes).

Australia

Ion Beam Analysis and X ray Methods at the Australian Nuclear Science and Technology Organisation (ANSTO), Menai, NSW, Australia

Contributor: David Cohen, Rainer Siegele (rns@anstov.gov.au), Mihail Ionescu and Ed Stelcer

The Australian Nuclear Science and Technology (ANSTO) is a research establishment of around 900 people located approximately 30 km south west of Sydney, Australia. ANSTO has several research institutes, including Bragg, Radiopharm, Materials and Environment. These institutes alone include about 300 research and technical support staff. ANSTO's major facilities include a light water reactor, a cyclotron and two linear ion beam accelerators.

The Open Pool Australian Light water reactor (OPAL) is a 20 MW pool reactor using low enriched uranium fuel, and cooled by water. OPAL is a multipurpose facility for radioisotope production, irradiation services and neutron beam research - it is a Neutron Factory. Its compact core is designed to achieve high performance for the production of thermal neutrons.

OPAL Reactor at ANSTO May 2006

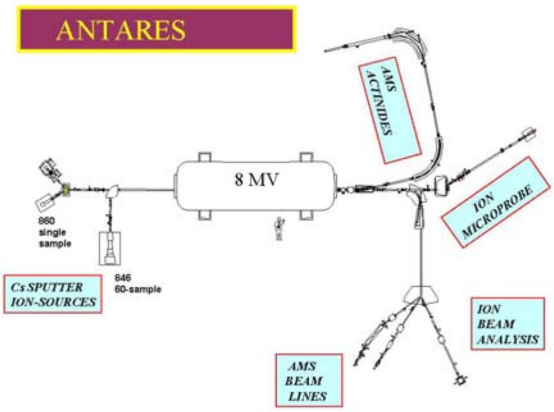
Since 1992 ANSTO has also operated the National Medical Cyclotron (NMC) at the Royal Prince Alfred Hospital in Camperdown, Sydney. The National Medical Cyclotron is a 30 MeV proton machine and cost about $20 million. It produces short lived isotopes for PET as well as radioisotopes such as gallium-67 and thallium 201 for medical diagnostic procedures.

ANSTO also operates two accelerators: the 10 MV ANTARES accellerator and the 2 MV STAR accelerator. Each of those has a number of beam lines and supporting facilities. These accelerators and their associated ion beam capabilities are the focus of the research for this particular project. In addition we also operate a high current 50 kV ion implantation Metal Vapour Vacuum Arc (MEVVA) Facility for surface modification studies.

10 MV Tandem Accelerator- ANTARES

The 10 MV Tandem Accelerator was commissioned in 1991. It provides ion beams with energies in the range from approximately 3 MeV to 100 MeV, depending on the ion species, with beam current intensities up to a few microamps. Virtually any naturally occurring isotope can be produced as a beam, free from contamination by other elements, isotopes or molecular ion species. A range of experimental facilities and analytical services are under continual enhancement on this new facility. This facilities has 3 ion sources for injection into the accelerator terminal, 3 high energy Accelerator mass spectrometry (AMS) beamlines and 2 high energy Ion Beam Analysis (IBA) beamlines including a state of the art world class high energy, heavy ion microprobe.

ANTARES high energy end



ANTARES beamline layout

Applications: AMS including high precision 14C dating (0.3%); IBA applications, studies of basic nuclear, atomic and solid state processes; high sensitivity elemental composition analysis; high resolution depth profiling of surface structures and thin films. The heavy ion nuclear microprobe is capable of focusing MeV heavy ion beams up to iodine to spot sizes with diameters of the order of 1 µm.

Applications include: surface and bulk analysis of solid state materials, environmental pollution monitoring, archaeological artefact elemental determinations, studies of pigment composition in paintings, biological studies using tracer elements and studies of geological material.

Heavy Ion Nuclear Microprobe

One of the beamlines on ANTARES includes a high energy, heavy ion microprobe with the capability to focus beams of protons of a few MeV to 100 MeV iodine beams into 1 µm spot sizes. The focusing elements are a triplet system (as shown in the picture below) and have the ability to scan over areas up to 2×2 mm if required. This produces elemental 2D maps of a range of materials.

Nuclear Microprobe end station showing the vacuum chamber, quadrupole triplet, scanning magnet and the collimating slits.

The Nuclear Microscope vacuum chamber.

A wide range of ion beam techniques such as Particle Induced X ray Emission (PIXE), Rutherford Backscattering (RBS) and Elastic Recoil Detection (ERD) can be used as a microanalysis tool for materials, environmental and geological analysis. The ANSTO microprobe has been applied in advanced studies in materials and environmental research, as well as in industry, biology and medicine.

2MV Tandetron Accelerator – STAR

The STAR Tandetron accelerator can produce a wide range of light and medium ions, with energies from a few hundreds of keV to 4 MeV, and are used for a diverse range of activities in the fields of materials analysis, biological and environmental studies, as well as basic nuclear physics. The STAR accelerator also has an AMS 14C beam line used for routine radio carbon measurements.

STAR accelerator

STAR beamlines

One beamline has a target chamber and data collection facility for simultaneous PIXE, PIGE (Proton-Induced Gamma-ray Emission) and RBS. Sample holder can take up to 60 samples in vacuum and measurement of samples is automated.

A second IBA beamline is a Multi-Angle Detector Positioning System - XYZ Target Manipulator - UHV target chamber with charged particle detectors for depth profile measurements of light elements such as hydrogen, carbon and oxygen, using forward recoil and nuclear reaction techniques. These are used for measurement of water turnover in desert lizards using 18O as a biological tracer, depth profiling of ion implanted species in semiconductors.

Scientific Scope

Characterization techniques such as Particle Induced X ray Emission (PIXE), Particle Induced Gamma Ray Emission (PIGE), Rutherford Backscattering (RBS) have been developed individually and applied quantitatively for many years at ANSTO for both thick and thin samples. All these techniques rely on MeV ions from low to medium positive ion accelerators. PIXE and PIGE are used for elemental analysis and RBS is used for depth profiling of elements in environmental, geological and functional materials samples. All these accelerator based ion beam analysis characterization techniques are non-destructive, afford a high sensitivity, are suitable for most elements in the periodic table and provide short measurement times.

It is well established that PIXE is mostly used for elements with atomic numbers above Al. In addition, when used in conjunction with appropriate X ray filters, the contributions of dominant elements can be diminished, and thus enhancing the sensitivity for trace elements.

For medium proton energies of a few MeV created by common ion beam accelerators, the PIGE technique is mostly suitable for light element analysis, like Li, Mg, Na and Al, where the cross sections for gamma ray production tend to be larger.

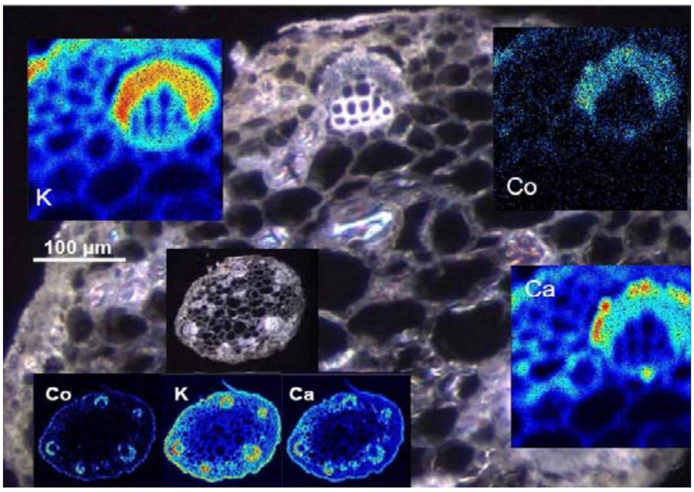
On the other hand, RBS is ideally suited for determining the depth distributions of trace elements heavier than the major constituents of the matrix or the substrate or for determining absolute matrix compositions for light elements such as carbon, nitrogen or oxygen.

It is possible to use a combination of PIXE, PIGE and RBS simultaneously, as a single stand-alone package for quantitative elemental analysis. This integrated capability takes advantage of the strength of each individual technique, providing a better tool for characterization of materials. Each technique provides unique sample matrix information which can be iteratively feed back into the quantitative concentration estimates to produce more reliable results. In addition, this tool is designed to handle the analysis of large numbers of samples and spectra in batch mode, increasing the efficiency of the total analysis process.

Elemental mapping using a focussed Ion Beam

With a focused ion beam the distribution of elemental concentrations can be mapped across the sample, which is useful in a number of different applications, where the samples have a microscopic structure. One example is the analysis of plant tissue to map the distribution of trace elements.

A plant is said to be a metal hyper-accumulator, if it can internally concentrate various metals with elemental concentrations of more than 1,000 mg/kg of dry weight for nickel, copper, cobalt, chromium or lead; or more than 10,000 mg/kg for zinc or manganese. The metal hyper-accumulators discovered so far are believed to be the result of adaptive evolution of the plants to hostile environments over many generations.



Stem section of sub-clover plant, which has been exposed to high levels of Co

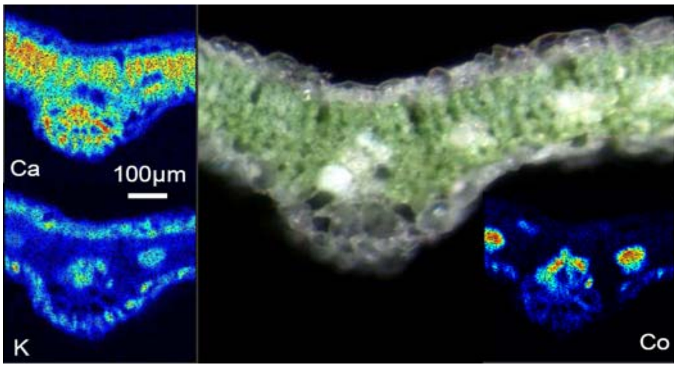
The use of metal hyper-accumulating plants has been proposed both for remediation of contaminated soils and for phyto-mining of low yield ore deposits. Hence the significant scientific interest in having a better understanding of the processes that allow these plants to grow in contaminated soils and accumulate high elemental concentrations of normally toxic metals.

It is important to know on a cellular and even sub-cellular level, in what specific parts of the plant the metal is accumulating. This can be achieved with high resolution X ray imaging using the heavy ion microprobe on the ANTARES accelerator at ANSTO.

The ANSTO microprobe can produce beam spot sizes of a few microns which are then scanned across hundreds of microns to produce X rays of elemental concentrations maps of different parts of the plant tissues. Elemental maps, obtained on the ANSTO microprobe, of both stem and leaf tissue of a cobalt accumulating plant are shown in the figures below. The first figure shows the stem cross section of Sub-clover a Co accumulating plant. The X ray elemental maps for K, Ca and Co are shown for the whole stem cross section as overlayed on top of the larger optical image.

The Co map shows that the metal accumulates in the epidermal region of the stem and also around the vascular bundles. Five vascular bundles are clearly identified in the maps. One of these bundles has been mapped with higher resolution, showing that the Co predominantly accumulates in tissue surrounding the bundles. The images clearly demonstrate the resolution that can be achieved. In both the K and Ca maps the cell wall are clearly visible.

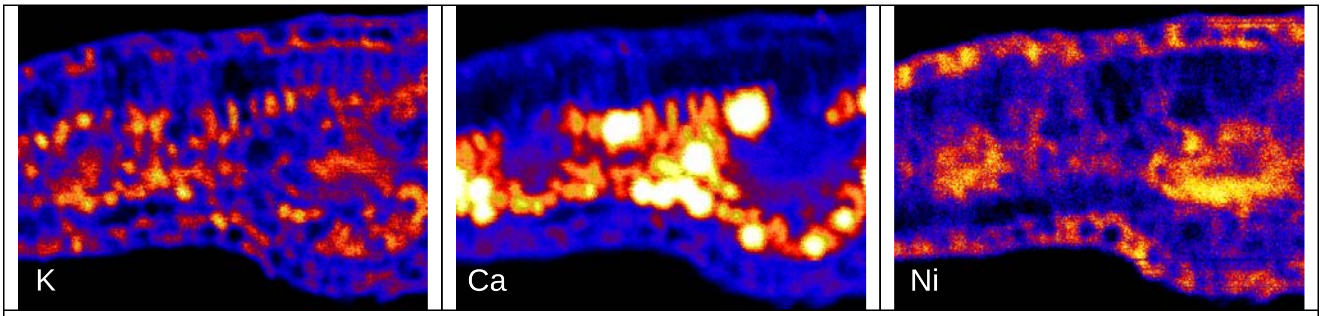
The figure below shows the leaf section of Haumaniastrum robertii. This plant is also a Co accumulator. The adaxial and abaxial epidermis of the leaf can clearly be seen in the elemental maps. The elemental map for K shows a high concentration in the epidermis while the concentration of Ca is lower compared the adjacent mesophyll. The Co maps also show an increased Co concentration in the abaxial epidermis, with the Co mainly concentrated in the cell walls.



Leaf section of the Co hyper-accumulating Haumaniastrum robertii

The highest Co concentration, however, are found in the vascular bundles the same as in the sub-clover stem. This means the Co stays in the vascular tissue through which it is transported into the plant and only a limited amount of Co is transported to the epidermis where it is stored.

This is in stark contrast to Hybanthus floribundus subsp. Floribundus, which is a Ni hyper-accumulating plant. K, Ca and Ni elemental maps of a leaf section if this plant are show in the images below. The Ni image shows Ni accumulation in the epidermis layer. Moreover, the image shows that the Ni is concentrated in the cell walls of the epidermis cells. This is a strategy commonly used by hyper-accumulating plants to store these metals, which is known as compartmentation.

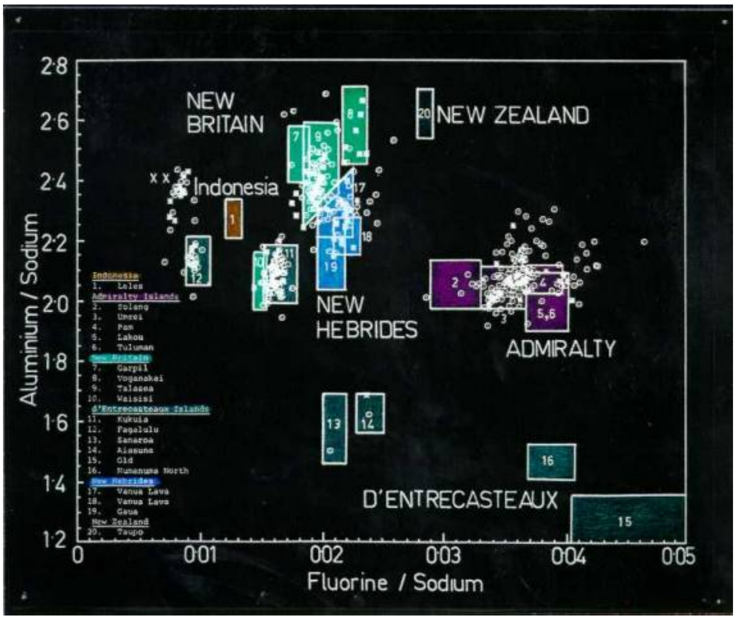


Elemental maps taken on a leaf section of Hypanthia floribundus subsp. Floribundus.

PIXE in Archaeology.

PIXE can be used to measure trace element concentrations with a high sensitivity in a non destructive way. This allows PIXE to be used in archaeology, to trace the origin of the obsidian rocks used in stone tool.

Obsidian stone tool



The graph shows the clustering of elemental ratios of obsidian stone tools and how this can be used to identify the origin of the obsidian rocks.

The image above shows such an obsidian tool. It is not uncommon for these obsidians to originate from thousands of kilometres away from where the tools are found. Hence they can be used to establish trade trading patterns. The right figure shows the Al/Na ratio as a function of the F/Na ratio for a large number of obsidian stone tools. The plot shows a number of clusters for the ratios. These clusters correlate with the areas form where the obsidian originates. Over the past 20 years a number of sources and their fingerprints have been established in the Papua New Guinea, South Pacific region using PIXE.

Further information on ANSTO IBA techniques together with recent publications and Newsletters can be found on our WEB page at http://www.ansto.gov.au/environment/iba.html

Austria

Synchrotron radiation induced TXRF- XANES

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Abstract

X ray Absorption Near Edge Structure (XANES) analysis was used in combination with Total reflection X ray Fluorescence (TXRF) at different Synchrotron Radiation (SR) facilities to perform elemental analysis and speciation at trace levels. TXRF-XANES was used to perform analysis of contaminations on Silicon wafer surfaces and determine the oxidation state of Fe. Urban aerosols were sampled size fractioned and the oxidation state of Fe was determined for each impactor stage again using TXRF-XANES. The feasibility of XANES analysis at trace element levels using different SR-XRF setups was demonstrated.

Speciation of Fe on Si wafer surfaces with SR-TXRF XANES

This investigation was done in cooperation with MaryAnn Zaitz from IBM lab, Fishcamp, NY, USA.

SR-TXRF-XANES was used to determine the chemical state of Fe contaminations on a silicon wafer surface. The ability to characterise chemically the contamination on silicon wafers is of critical importance to the semiconductor industry. It provides information on possible unwanted chemical processes taking place on the wafer surface and helps in determining the true source of the contamination problem. This type of information is not readily accessible with standard laboratory equipment. Main purpose of the study was to test the method for a contamination issue as it could appear in a microelectronic VLSI (Very-Large-Scale Integration) production factory. This project was done in cooperation with M.A. Zaitz, IBM Microelectronics, Hopewell Junction, NY, USA.

SR-TXRF XANES measurements were performed at the bending magnet beamline L at HASYLAB using the Si(111) double crystal monochromator and a modified micro-XRF setup. The vacuum chamber was removed and the wafer mounted on an x,y,z,θ-stage. This modified setup allowed TXRF measurements with scanning capability. A laminar flow hood was used to prevent contamination during the measurement (Fig.1). Prior to the SR-TXRF-XANES analysis the wafer has been mapped using a laboratory TXRF analyzer (Rigaku TXRF 300) to determine regions of interest showing the highest Fe contaminations (Fig. 2).

It was shown that SR-TXRF in combination with XAS enables a XANES analysis of wafer surface contaminations even in the pg region within a reasonable time frame. The setup allowed a spatially resolved multi-element analysis of the wafers surface. Additionally the type of the contamination (residual, surface layer, bulk) and the chemical state of a specific element could be determined. All these investigations can be done non-destructively using the same experimental setup. The major problem of this setup is the measurement time and the need for an intense and energy tuneable X ray source. The wafer mapping and XANES scans are time consuming particularly for such low sample masses. The XANES evaluation showed, that a peak to background ratio below 10 for the element of interest in the fluorescence spectra will cause serious problems for the interpretation of the data. Within the time frame of 48 hours 3 points of interest could be investigated. A determination of the oxidation state of iron in the samples was possible (see Table 1). However, for the determination of the iron compound satisfactory results could be achieved for only one point (P5). The evaluation of the other points (P7, P21) using a linear combination fit procedure was not satisfactory due to the low Fe concentrations and the limited measurement time resulting in a poor signal to noise ratio of the XANES spectra. The evaluation of the XAS data revealed that the iron contamination in point P5 was a mixture of iron compounds dominated by iron-nitrate. Although the evaluation for P5 showed a low statistical uncertainty it could not be concluded that the contamination is a mixture of iron-nitrate and iron-sulfate exclusively. Within the frame of this feasibility study it was not possible to compare the Fe contaminations with every possible Fe compound. However, the presence of iron-nitrate and iron-sulfate on a contaminated wafer shows that several chemical reactions are taking place. The iron-sulfate is particularly surprising and we are trying to better determine why or how it was formed. This will be a topic of further investigations.

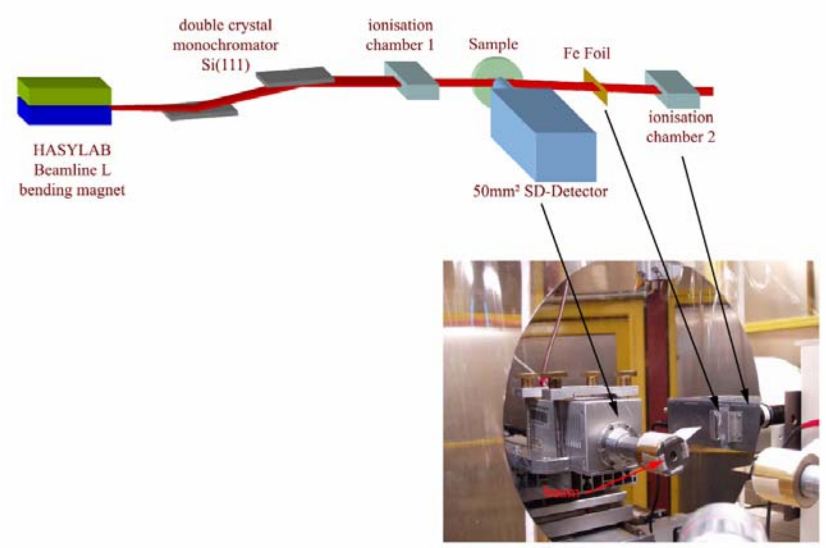


Fig. 1. Experimental setup at Hasylab, Beamline L (adapted from ref 1)

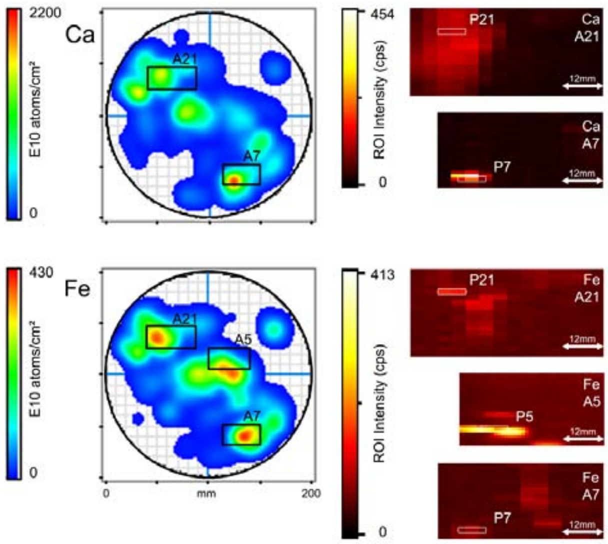
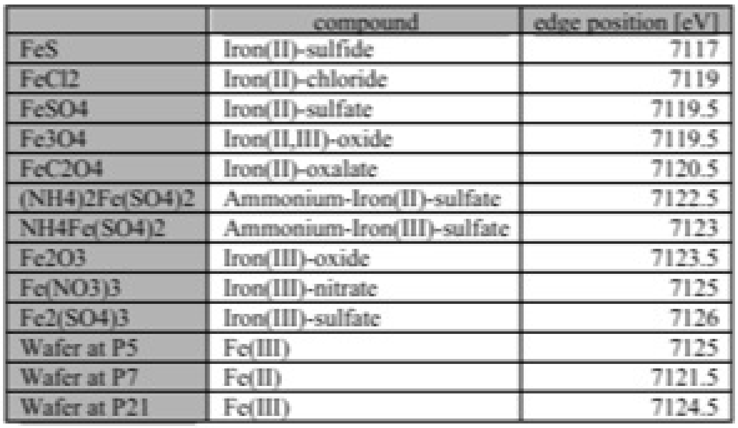


Fig. 2. Laboratory TXRF maps (left) with marked regions of the areas scanned by means of SR-TXRF (right). The marked regions on the left correspond to the areas on the right. The white boxes on the right localize the points of maximum Fe contamination which were selected for further investigations (P21, P5 and P7).adapted from ref 1



	compound	edge position [eV]
FeS	Iron(II)-sulfide	7117
FeCl2	Iron(II)-chloride	7119
FeSO4	Iron(II)-sulfate	7119.5
Fe3O4	Iron(II,III)-oxide	7119.5
FeC2O4	Iron(II)-oxalate	7120.5
(NH4)2Fe(SO4)2	Ammonium-Iron(II)-sulfate	7122.5
NH4Fe(SO4)2	Ammonium-Iron(III)-sulfate	7123
Fe2O3	Iron(III)-oxide	7123.5
Fe(NO3)3	Iron(III)-nitrate	7125
Fe2(SO4)3	Iron(III)-sulfate	7126
Wafer at P5	Fe(III)	7125
Wafer at P7	Fe(II)	7121.5
Wafer at P21	Fe(III)	7124.5

Table 1: Oxidations states and edge positions of standards and samples, adapted from ref 1.

Fe K-edge TXRF-XANES of atmospheric aerosols collected in the city of Hamburg

This investigation was done in cooperation with Prof. J. Broekaert and Dr. Ursula Fittschen, Department of Chemistry, University of Hamburg, Germany. To understand the effects of aerosols on human health and global climate a detailed understanding of sources, transport, and fate as well as of the physical and chemical properties of atmospheric particles is necessary. An analysis of aerosols should therefore provide information about size and elemental composition of the particles and - if desired - deliver information about the chemical state of a specific element of interest in the particles. Using the combination of SR-TXRF and XANES analysis it was possible to investigate the elemental composition of size fractioned atmospheric aerosols and the oxidation state of Fe in the aerosols even for small sample amounts due to short aerosol collection times. As mentioned before the project was accomplished in cooperation with the University of Hamburg, Hamburg, Germany.

The aerosols were collected in the city of Hamburg with a low pressure Berner impactor (see Fig. 3, left) on Si carriers covered with silicone (to prevent “bounce off” effects) over time periods of 60 and 20 min each. The particles were collected in four and ten size fractions of 10.0–8.0 µm, 8.0–2.0 µm, 2.0–0.13 µm 0.13–0.015 µm (aerodynamic particle size) and 15–30 nm, 30–60 nm, 60–130 nm, 130–250 nm, 250–500 nm, 0.5–1 µm,1–2 µm, 2–4 µm, 4–8 µm, 8–16 µm. SR-TXRF measurements were performed using the setup for TXRF comprising a vacuum chamber at HASYLAB bending magnet beamline L equipped with a sample changer capable of carrying eight samples at a time.

The results from the SR-TXRF analysis of the aerosols showed that 20 min of sampling time gave still enough sample material for elemental determination of most elements. Fe K-edge SR-TXRF-XANES analysis of the samples revealed that Fe was present in the oxidation state of three (predominately in the form of Iron(III) oxide) in all collected aerosols (see Fig. 3, right). This corresponds to other studies on the oxidation state of Fe in aerosols although in rain and cloud samples high amounts of Fe(II) were reported. Possible reasons why Fe(III) was exclusively found in the analyzed aerosols may be the place or the height where the aerosols were collected, or some oxidation which might occur during the condensation process. Finally, it can not be excluded that oxidation took place during storage or sampling, even though the sampling time was kept short and the samples were stored under argon atmosphere. Further studies will have to focus on these problems.

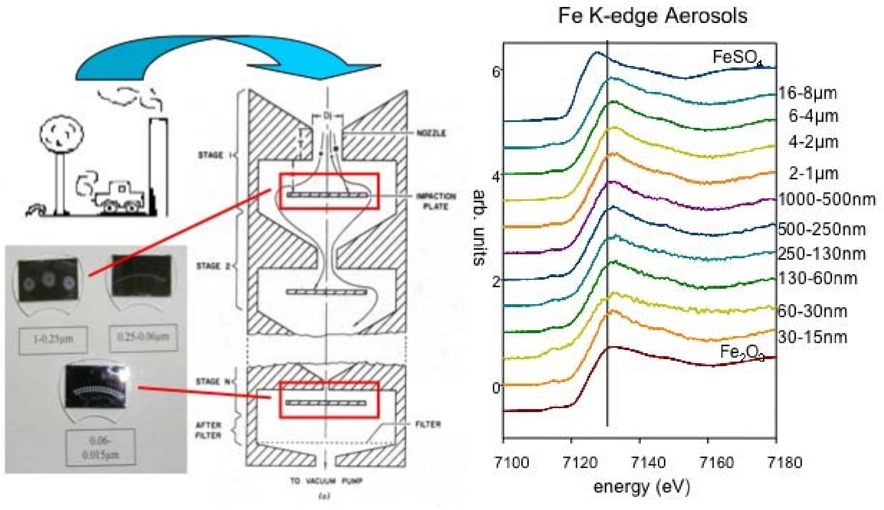


Fig 3. Principle of size fractioned direct sampling on Si wafers with a Berner impactor. (left). XANES Spectra for materials collected on various impactor stages (right), adapted from ref 2

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Austria and Sri Lanka

A new attachment module for secondary target excitation with sample changer and vacuum chamber

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A new secondary target attachment vacuum chamber was developed, designed and constructed at the Atomic Institute of Vienna Technical University X ray Laboratory and installed at the Atomic Energy Authorities, Colombo, Sri Lanka. The prerequisites were that the new system had to fit physically next to the Wobistrax TXRF spectrometer and to use the same existing X ray tube and an existing uplooking LN2 cooled Si(Li) detector. This new spectrometer replaces a simple secondary target system previously installed. The new system offers a 10 position sample changer integrated in a vacuum chamber. The secondary targets are exchangeable, and Mo, Zr, Ti, Al, KBr and Teflon as Barkla polarizer are available. The system is designed for the emission-transmission method for quantification but can also be used for air filter samples where the thin film model for the quantification is applicable.

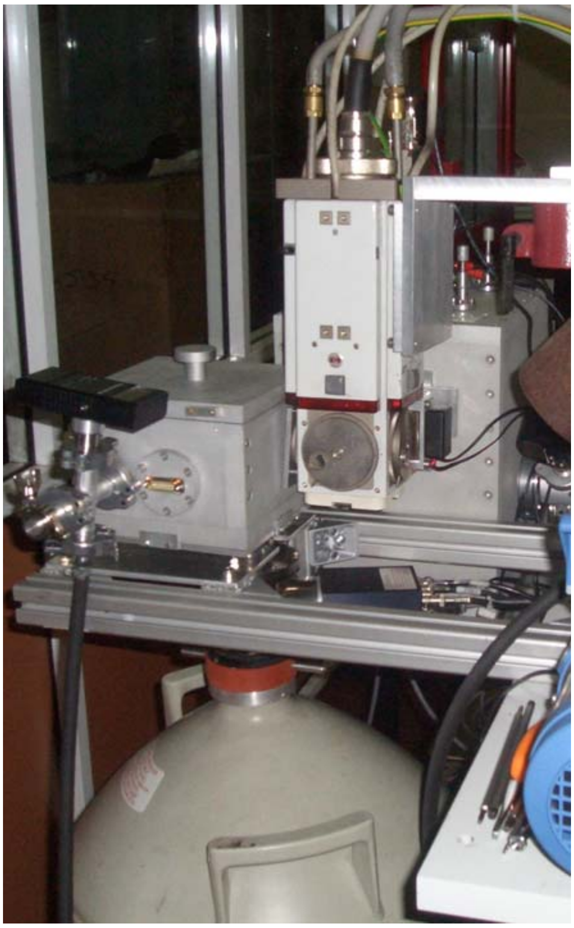

Fig.1. General view of the set-up

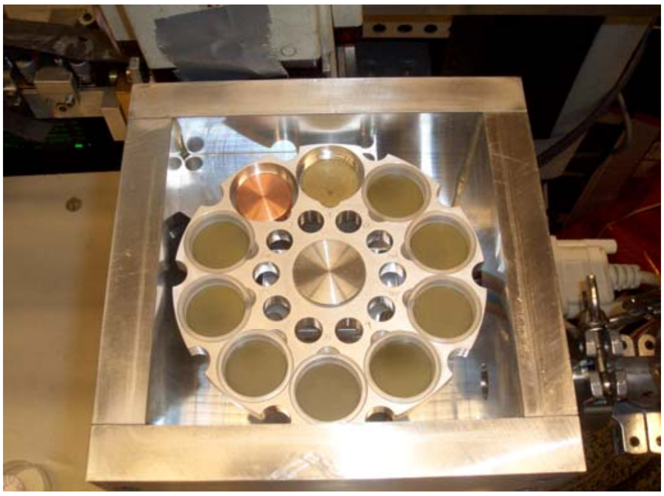

Fig. 2. Vacuum chamber with sample changer

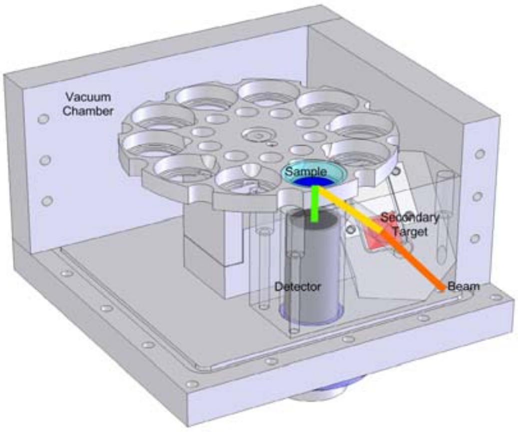

Fig. 3. The schematic view of beam path in triaxial setup for primary radiation, secondary radiation from the target and direction to the detector from the sample.

The vacuum chamber with the 10 sample tray is attached to a SEIFERT 4 window tube housing. The HV and window control is connected to the Seifert ID 3003 X ray generator. The WOBISTRAX - TXRF requires the line focus of the X ray tube in such a way that a horizontal parallel beam enters into the WOBISTRAX spectrometer. For that reason the tube housing is mounted at a tilt angle of 6°. The beam for the secondary target is taken from the point focus of the tube emitted through the window perpendicular to the line focus and therefore the radiation exit angle is not horizontal but about 6°upwards from the horizontal plane. However, the angle between primary beam and secondary beam is very close to 90° for optimum performance of the polarization effect due to this scattering angle. There are 6 secondary targets available allowing optimum excitation of the sample elements, including Mo, Zr, KBr, Co, Ti, Al and Teflon as polarizer of the full spectrum from the X ray tube.

The uplooking Si(Li) detector has an angle of 45° to the secondary beam. For optimum performance in the emission-transmission geometry the detector crystal is parallel to the sample surface.

Ten multielement pellets for all available positions of the tray, containing V, Co, Cu, Se, Sr can be used to determine the absorption coefficient of the sample for various energies in the emission-transmission mode following the QXAS software package for the quantification procedure.

The rotation of the sample changer is computer controlled. Vacuum of about 1 mbar is produced by a membrane pump and monitored by a digital vacuum meter.

A spectrum from Soil 7 IAEA reference material is shown on Fig 4. A 3 kW Mo X ray tube and Mo secondary target was used at 40 kV and 10 mA; measurement time was 1000 s.

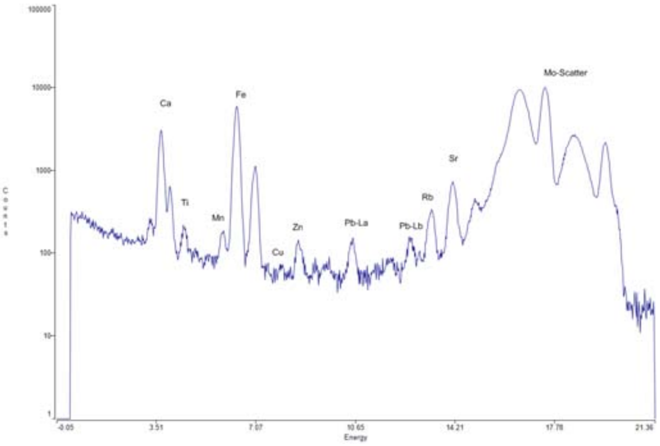

Fig.4. Spectrum of IAEA SOIL7 (Mo X ray tube, Mo secondary target, 40 kV, 10 mA, 1000s).

The detection limits of 2.5 ppm for Sr and 10 ppm for Zn were obtained for the above mentioned excitation conditions.

Italy

Analyses on stone monuments availing of EDXRF systems

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An important part of the world's cultural heritage is represented by stone monuments. A very dangerous weathering process which deteriorates stone monuments is caused by air pollution resulting from human activity. One of the worst pollutants for stone monuments is associated with sulphur compounds and, when all is said and done, with gypsum. Gypsum is a rather soluble compound that may be washed away by rain. It leaves the surface of the stone clean but eroded and open to new corrosive processes.

The element effectively measured for these analyses is sulphur connected with the transformation process of the calcium carbonate in gypsum. With the aim of calibration standards it is possible to quantify the presence of sulphur and therefore of gypsum on the surface of the statues.

In recent years in Italy different campaigns with transportable EDXRF instruments have been conducted in situ for investigation, mapping, registration and evaluation of stone-degradation phenomena related to sulphate formation on stone and stone-like materials by quantifying sulphur concentrations directly associated with the presence of gypsum.

The aim of the campaigns is to carry out in situ non-destructive analyses in order to create spatial and temporal maps of the evolution of the sulphurisation of marble surfaces.

The last campaign that just started involves study of 5 ancient marble statues located in different parts of the city of Rome. The statues are undergoing restoration and the measurements started immediately after the end of the cleaning work on a blank surface and conducted regularly in time to build eventually a map in time and space of the degradation of marble surfaces in Rome. The next marble artefact that will be analysed is "La bocca della verità" located in Santa Maria in Cosmedin in Rome which is well known to the tourists who put their hands in the mouth of the marble with the danger of being cut off if the tourist is a liar.

In literature there are several examples of the use of transportable X ray fluorescence systems, which use calcium and palladium anode X ray tubes for sulphur excitation. In both cases, instead of using the Bremsstrahlung radiation of the tube, the fluorescent lines of the anode material are used; the K-series calcium lines in the first case and the L-series palladium lines in the second one, with the purpose to neutralise the intrinsic calcium K-alpha line present in gypsum which interferes with the sulphur peak. Having a tungsten anode tube at our disposal, the only way to neutralise the calcium lines would be to use very low high voltage on the tube (maximum 4 kV). But below 4 kV HV only the Bremsstrahlung is generated, and the efficiency of the tube becomes rather low which results in time consuming measurements. Therefore we used a higher HV and made tests to optimise the measurement time versus the accuracy of the experimental results.

Using a number of custom-made standards consisting of calcium carbonate and varying concentrations of sulphur it was found that the HV that minimised the measurement time and maximised the results is 15 kV and 200 seconds of measurement. Under these optimised working conditions, archeometrical measurements were carried out on several statues.

Figures 1 and 2 show the measurements for the "Fanciulla di Anzio", an indoor statue housed in the Roman Museum, and for the "Abate Luigi" an outdoor statue located in Vidoni square.

The scatter peaks are not from the primary radiation but are stemming from the Mo secondary target. The blank spectrum has been almost free from any spurious peaks (Teflon cylinders were used to avoid any contributions from the wall material).

Fig. 1. EDXRF measurements for the indoor ancient roman statue "La fanciulla di Anzio"

Fig. 2: EDXRF measurements for the outdoor statue "Abate Luigi".

Slovenia

Applications of X ray Fluorescence spectrometry in biology and food science

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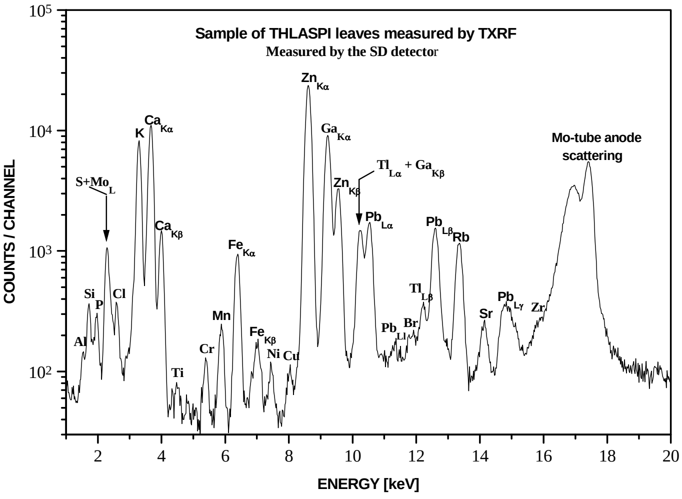
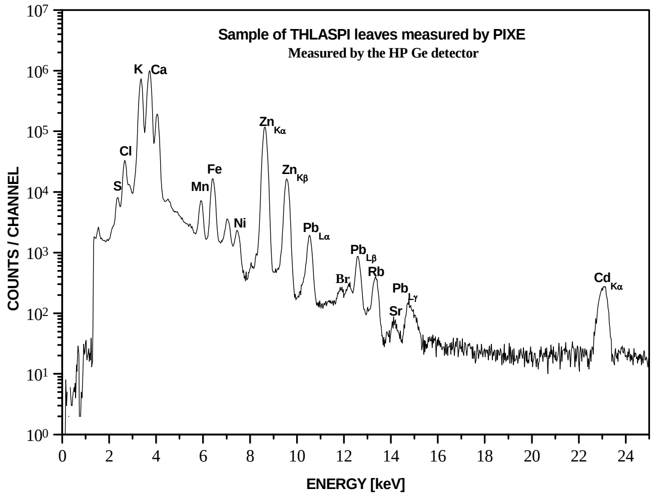
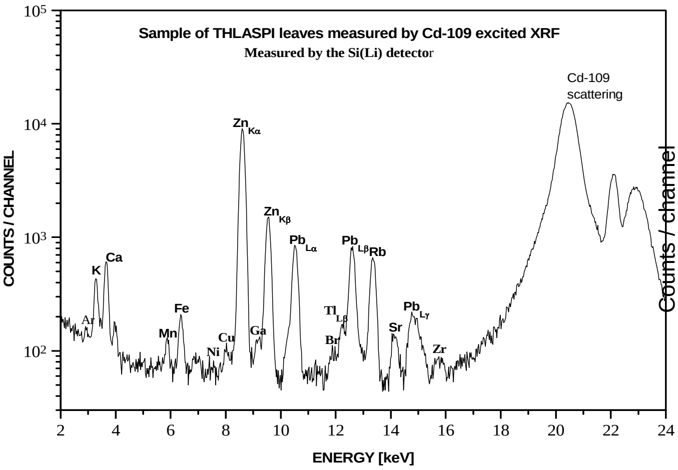
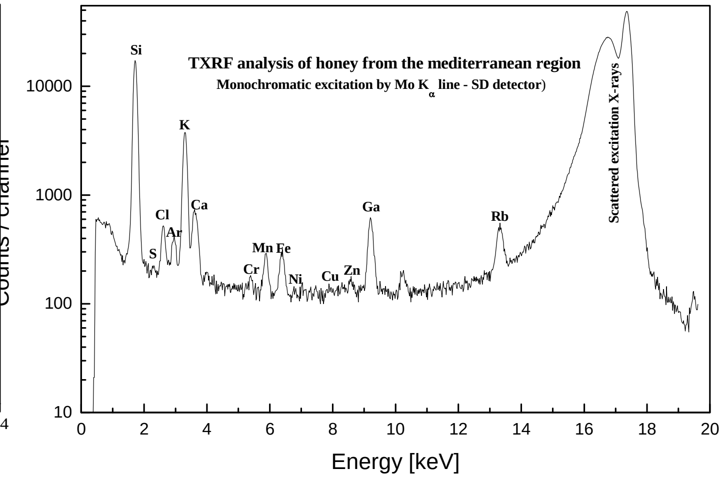
The XRF laboratory at Department of Low and Medium Energy Physics, “Jožef Stefan” Institute, is already more than 15 years involved in development of X ray Fluorescence Spectrometry (XRF) and its applications in different fields. The activities included mainly the development of the quantification software, the assembling of the prototypes of XRF analyzers, and dissemination of the XRF analytical technique among the potential local users for the applications in different interdisciplinary research projects. One of the members of the laboratory has participated as consultant and expert in many IAEA technical assistance projects, has trained a number of IAEA fellows, and lately participated also in few coordinated research projects organized by the IAEA. It is necessary to mention that according to our opinion the role of the IAEA in promoting and supporting the XRF technique and its applications in our laboratory and elsewhere in a number of member states was very important for the training of staff in the field of nuclear spectrometry and also in applications based on the XRF elemental analysis. This technique is extremely well suited to familiarize the users with different aspects of nuclear spectrometry, and also in numerous applications of the mentioned analytical technique in different applied and scientific fields, including environment, industry, geology, biology, food science, archaeology and cultural heritage, development of new materials, etc. It is only to regret that the support of the IAEA to the initiated XRF projects, in spite of their potential benefits, is not any more considered as a priority.

Our objective here is to present briefly two applications of the XRF elemental analysis, which we recently started: applying the XRF analysis after sample excitation by radioisotope sources, X ray tubes in the standard and the total reflection modes (TXRF), as well as by PIXE and microPIXE. The fluorescence X ray spectra shown below are typical examples of data and information on basis of which all the applications were realized. It is obvious that the use of the techniques, which produce the above spectra require a good knowledge of the nuclear spectroscopy, and also skills to adjust the experimental set-up including the source of fluorescence excitation, selection of appropriate X ray detection system (geometry of experiment), as well as proper sampling and sample preparation, considering the characteristics of a large variety of different materials to be examined. And finally one needs to define the application and establish good collaboration with the users and/or scientists in a number of interesting fields. We would like to present here just two examples of such a comprehensive approach to the application of XRF analysis.









Application of X ray fluorescence spectrometry in plant biology and phytoremediation studies

Biospheric pollution by metals has accelerated dramatically during the last few decades, mainly due to mining, smelting and manufacturing, and the treatment of agricultural soils with agrochemicals and soil sludge. Because engineering-based remediation methods such as soil excavation, soil washing or burning, or pump and treatment systems are very expensive and in many cases not ecologically acceptable (Raskin and Ensley, 2000) [1], there is an urgent need for development of cheaper and environmentally friendlier technologies of cleaning and remediation of metal contaminated sites. In the last decade extensive research has been conducted to investigate possibilities for the use of ‘metal hyperaccumulating plants’ for extracting metals from moderately polluted soils (Ernst, 2005) [2]. Today more that 440 plant species are known to hyperaccumulate more than 10,000 mg kg-1 of Zn and Mn, 1,000 mg kg-1 of Al, As, Se, Ni, Co, Cr, Cu and Pb, and more than 100 mg kg-1 of Cd (Baker and Brooks, 1989[3]; Reeves and Baker, 2000[4]), while for up to two orders of magnitude lower concentrations of the mentioned elements are detected in non-accumulating plants (Adriano 2001) [5]. Because plant biological processes are ultimately solar driven, phytoremediation is on average tenfold cheaper than engineering-based remediation methods, however to increase the efficiency of phytoremediation technologies, it is important to learn more about the specific plant physiological processes involved, including plant metal uptake, translocation and tolerance (compartmentation, complexation) mechanisms, plant–microbe interactions and other rhizosphere processes (Lasat, 2000) [6].

The studies of our research group are mainly focused on resolving the mechanisms of Cd, Zn and Pb uptake, localization and coordination in organs and tissues of Cd, Zn and Pb hyperaccumulating Thlaspi praecox (Figure 1).

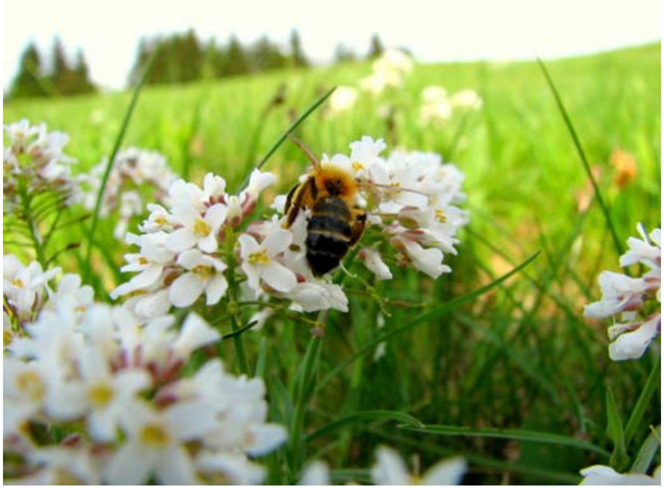


Fig. 1. *Thlaspi praecox* Wulfen (Brassicaceae)

Using standard energy dispersive X ray fluorescence spectrometry (EDXRF) and total reflection X ray spectrometry (TXRF) we have determined that T. praecox has an outstanding capacity of accumulating Cd. Up to 7430 mg kg-1 dry weight (DW) has been detected in its shoots (Vogel-Mikuš et al. 2006)[6] and up to 1350 mg kg-1 DW in its seeds (Vogel-Mikuš et al. 2007) [7]. In addition high capacity of Zn as well as Pb accumulation has been shown for the shoots (Vogel-Mikuš et al. 2006, 2007) [6,7]. The discovery of T. praecox outstanding capacity of hyperaccumulating metals has raised questions about the mechanisms of tolerance at tissue, cellular and molecular level. After improving the procedure of sample preparation using cryo-fixation, which enables preservation of element distribution in tissues as close as in vivo, as well as satisfactory preservation of sample morphology (Vogel-Mikuš et al. 2008) [8], the mechanisms of tolerance at the tissue and cellular level were partly revealed by element localization studies using micro-proton induced X ray fluorescence (PIXE) at micro-analytical centre of Jožef Stefan Institute (head dr. Primož Pelicon) (Vogel-Mikuš et al. 2008) [9]. In the leaves of T. praecox plants collected in their natural environment Cd, Zn and Pb showed different localization patterns, with intensive Zn accumulation found in epidermis, particularly in the symplast of large vacuolated epidermal cell, while avoiding accumulation in guard cells of leaf stomata (Figure 2, 3). Cd and Pb were on the other hand also intensively accumulated in the mesophyll (Figure 2), with higher Cd concentration found in symplast, while higher Pb concentrations were found in apoplast (Vogel-Mikuš et al. 2008) [9]. Strong correlation between sulphur and Cd localization in the mesophyll indicated Cd coordination to sulphur ligands to be an important mechanism of tolerance to Cd at molecular level (Vogel-Mikuš et al. 2008) [9].

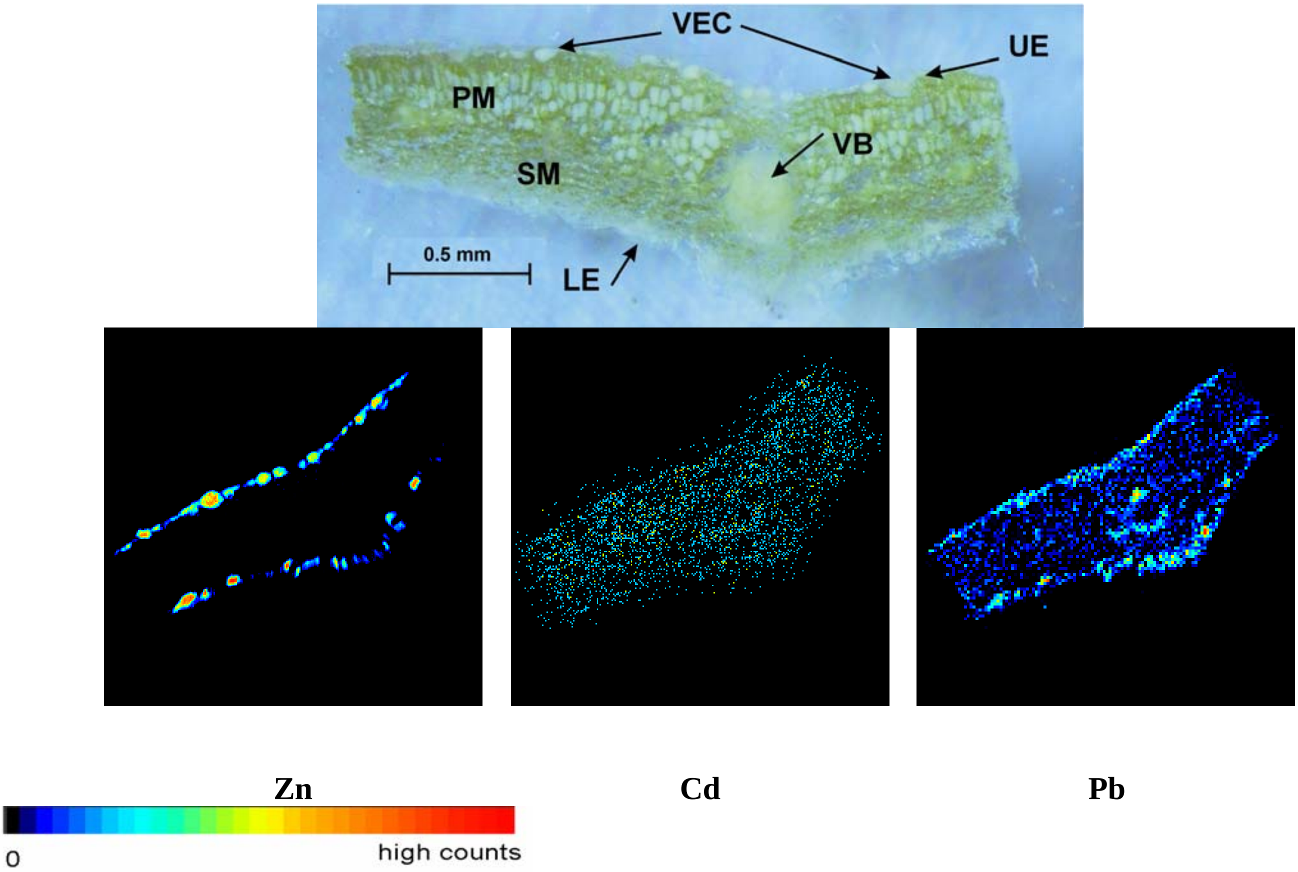


Fig. 2. Light microscopy photography of cryo-fixed and freeze-dried leaf cross-section of field collected T. praecox and qualitative elemental maps of Zn, Cd and Pb in leaf cross-section. UE, upper epidermis; PM, Palisade mesophyll; SM, spongy mesophyll; LE, lower epidermis; VB, vascular bundle; VEC, vacuolated epidermal cells. (Vogel-Mikuš et al. 2008; Plant, Cell & Environment © Wiley-Blackwell, with permission).

However further studies of Cd coordination in T. praecox tissues using extended X ray absorption fine structure (EXAFS) at the European synchrotron radiation facility (project EC 398, head Dr. Iztok Arčon) showed that Cd is mainly bound to weak oxygen ligands in mesophyll so as in epidermis. Therefore vacuolar sequestration (Figure 3) of Cd was proposed as a main detoxification mechanism in leaves of this metal hyperaccumulating plant (Vogel-Mikuš et al. 2009) [10]. Micro-PIXE element localization studies in T. praecox seeds revealed Cd to be mainly accumulated in epidermis of cotyledons, away from the future photosynthetically active tissues (Vogel-Mikuš et al. 2007) [7]. Further coordination studies using EXAFS revealed two thirds of Cd to be bound to sulphur, namely thiolates (Cd-S-C coordination) and one third to phytate (Cd-O-P coordination), indicating that prevailing tolerance mechanism to Cd in embryonic tissues is its binding to strong sulphur or phytate ligands. In addition the results also indicated that Cd may be transported into the seeds by two routs, first bound to thiolates and second probably mimicking

Zn transport by binding to nicotianamine and further while entering the embryonic tissues to phytate (Vogel-Mikuš et al. 2009) [10].

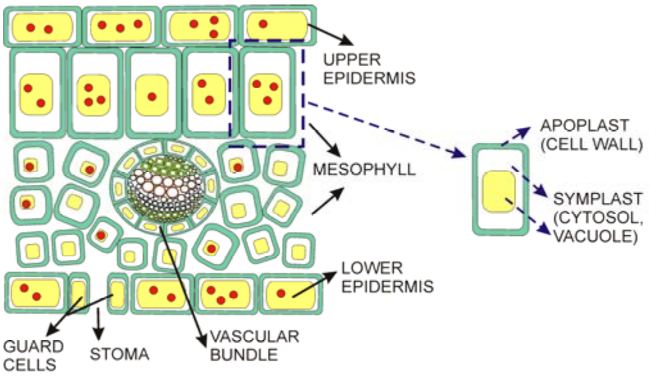


Figure 3. A model of vacuolar sequestration of Cd (indicated by red circles) in leaves of T. praecox. The majority of Cd is localized in symplast of epidermal and mesophyll cells, while avoiding accumulation in guard cells of leaf stomata. In symplast Cd is mainly sequestered in vacuoles, away from metabolically active cytosol.

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Determination of botanical and geographical origin of Slovenian honey

Characterization of honey as a commercial product is a demanding task, which was initiated in the E.U. in response to consumer demands. Beside the quality, the determination of geographical and botanical origin was also demanded, which initiated the establishment of the corresponding regulations in a number of member states. Honey regulation in the E.U. [2] states that the botanical and geographical origin of the product must be printed on the label. The control of commercially sold honey therefore requires the determination of parameters that unambiguously establish the origin and also the quality of honey.

The botanical and geographical origin of various sorts of honey produced in Slovenia was investigated by the analysis of mineral content using the Total reflection X ray Fluorescence spectrometry (TXRF), followed by chemometric evaluation of the analytical results. A total of 271 samples of major sorts of Slovenian honey, such as chestnut, lime, flower, acacia, forest, spruce and fir, were collected from bee-keepers all around Slovenia in years 2004, 2005, and 2006. Slovenia is geographically small, but pedologically and climatically diverse country, which offers a number of possibilities for the study of mineral content of bee-honey and other natural products due to influence of mentioned diverse natural conditions. Selecting some key elements (K, Cl, Rb, Mn and Zn) from the mineral content of bee honey, and employing statistical analysis by using Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA), it was possible to discriminate between different sorts of honey and in combination with other parameters such as stable isotopes, % of water, pH, % of lactones, diastase number, % of sugars etc., also their geographical origin. It has been established that the combination of multi element analysis by TXRF, and chemometric treatment of obtained data, represent a simple, fast and cheap approach for characterisation of bee honey according to its botanical and geographical origin .

Botanical origin of each sample of honey is usually determined by sensory and pollen analysis. It is interesting to compare the preliminary classification of honey with the results of LDA analysis of elemental content (Fig. 1), which roughly separates analysed samples as nectar honey (accacia, lime, flower and chestnut) and honey-dew honey (forest, fir and spruce). A good separation of accacia and chestnut samples was found, whereas the separation between lime and floral samples showed that the harvested honey was mixed. The same was true for the forest, spruce and fir honeys.

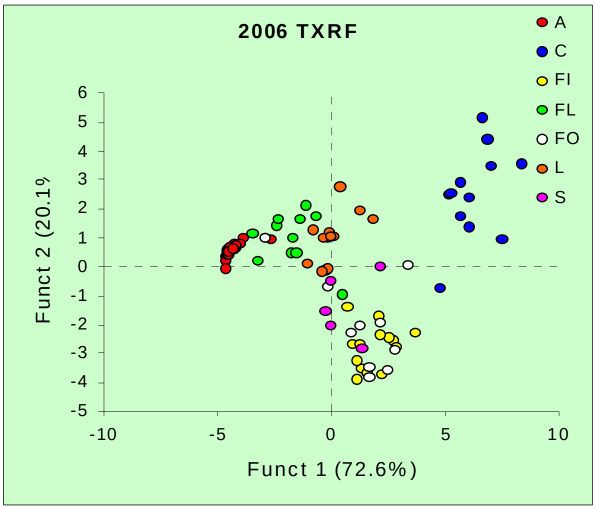

Fig. 1. LDA performed with concentrations of Cl, Ca, K, Mn, Zn and Rb for the production years 2006, with 90 honey samples corresponding to seven different sorts. The graph by the first two discriminant axes represents 92.7 % of the total variance of six variables. Symbols are as follows: A – acacia, FL– floral, L - lime, C – chestnut, FO – forest, S – spruce, FI – fir.

The main reason for the rather indistinct separation of the botanical origin of honey samples by sensoric and polen techniques was the assumption that each honey sample is a pure type. The elemental analysis of honey by TXRF offers more information regarding the botanical origin of honey than classical sensory technique [2]. It namely discriminates between the mixed types of honey, which are produced during the coinciding harvesting periods on different nectar and/or honey dew sources.

Fig. 2 and 3 show results of determination of geographical origin of Slovenian honey. Honey samples were separated according to the production location into four natural-geographic macro regions: Alpine, Dinaric, Pannonian and Mediterranean regions. The adopted regionalization of Slovenia to four natural-geographic regions [3] was primarily based on the analysis of rock, surface relief, climate, vegetation, and land use.

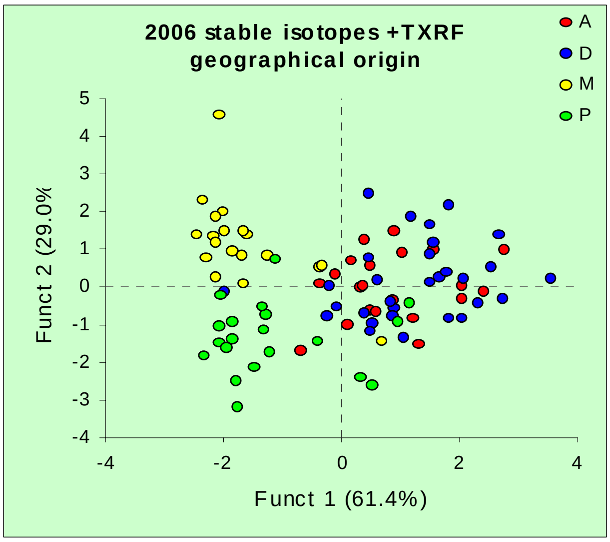

Fig. 2. LDA performed with concentrations of Cl, Ca, K, Mn, Zn and Rb and isotopic values (δ13C) in bulk and protein of honey and values (δ15N) in protein of honey of the production year 2006, with 90 samples of different sorts of honey originating from four geographical regions. The graph with the first two discriminant axes representing 90.4 % of the total variance for nine variables. Symbols are as follows: A – alpine, D– dinaric, M- mediterranean, P-panonic.

It was found out that only the data on elemental content were not sufficient for the separation of honey samples into four geographical regions [1], but it should be performed at least in combination with stable isotope analysis parameters in order to discriminate between Alpine-Dinaric, Pannonian and Mediterranean regions. In Fig. 2 the results of such discrimination of 7 various sorts of honey from the year 2006 into 3 geographical regions is presented. More significant and accurate classification was achieved when data of several physico-chemical parameters of a single sort of honey were analyzed with LDA. In this case (Fig. 3) rather good geographical separation into four regions was achieved considering a set of 22 physico-chemical parameters of only chestnut honey samples.

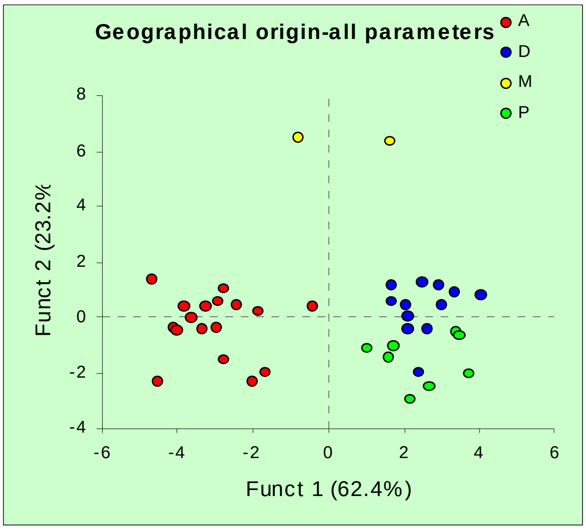

Fig. 3. LDA performed with concentrations of Cl, Ca, K, Mn, and Rb, isotopic values (δ13C) in bulk and proteins content of honey, and by values (δ15N) in proteins, % of water, pH, electrical conductivity, % of lactones, diastase number, % of praline etc. from the production years 2004-2006, applied to 39 honey samples of chestnut originating from four different geographical regions. The first two discriminant axes representing 85.6 % of the total variance for 22 variables. Symbols are as follows: A – alpine, D– dinaric, M-mediterranean , P-panonic.

It seems that the above mentioned inexpensive analytical approach by the TXRF, combined with multivariate statistical analysis is promising also in applications of other food products, like nutrients, food supplements, additives etc. By such an analysis the quality control and determination of geographical origin, production location and authenticity could be established.

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United Arab Emirates

United Arab Emirates' National X ray Fluorescence Laboratory

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The United Arab Emirates (UAE) is currently experiencing an era of accelerated development and expansion in all aspects of civil activities. Huge industrial, as well as, construction projects, evident to the casual observer, have resulted in the creation of environmental conditions that need continuous monitoring. In addition to that, wide interest in the heritage and archaeological findings in the UAE, have necessitated the establishment of a national scientific laboratory capable of analyzing a variety of samples non-destructively, with high accuracy and a minimum amount of sample preparation.

X ray fluorescence (XRF) is one of a number of methods that are suitable for the type of analysis required. XRF is widely used for chemical analysis, particularly in the investigation of metals, glass, ceramics and building materials, and for applications in environmental sciences, geochemistry, forensic science and archaeology. Moreover, XRF has the advantage of low cost of instrumentation and maintenance over similar techniques.

As a result, the UAE, in cooperation with IAEA, is establishing a national X ray fluorescence laboratory (NXFL), hosted by the University of Sharjah, for environmental and cultural heritage applications. The 3 years project was approved by the IAEA under Technical Cooperation Program (Project UAE 0006). Scientists from two institutions, University of Sharjah (UoS) and American University of Sharjah (AUS), will be involved in establishing the lab, training the staff, running outreach workshops within the country and supervising the operation of the laboratory. The core of the scientific team is composed of four professors with excellent knowledge of the subject and extensive experience in utilizing X ray techniques in material science.

NXFL National X-ray Fluorescence Laboratory
المعمل الوطني للأشعة السينية

The NXFL aims at serving the needs of all relevant national organizations such as museums, environmental protection agencies, universities, local industries, art galleries, customs and boarders authorities. Laboratory facilities will be utilized for the analysis of samples pertaining to: archaeological and heritage artefacts, environmental contaminants (e.g., heavy metals) in air, water or soil, in addition to forensic evidence and new industrial materials. Furthermore, the laboratory will provide technical support as a center of excellence, to research groups from other national and regional universities, and operate as a national training center for the technique of X ray fluorescence.

Already the NXFL team has established a national network that includes most of the governmental and private agencies related to environmental and archaeological activities. The lab will help in solving many problems by assisting in the enforcement of the established environmental laws and standards, and investigate historical artefacts together with other archaeological scientific techniques.

The laboratory will host a state of the art micro-EDXRF system and the necessary material preparation equipment. It is also planned to include an X ray diffractometer (XRD) in the near future, in order to integrate the results of both analytical techniques in the field of cultural heritage and environmental issues. At the same time the team of investigators of this project has submitted a proposal to carry out research at a synchrotron facility to utilize the possibility of integrating μ-XRF, μ-XRD and μ-XANES. Integration of the three techniques will provide important information about charge elemental analysis, spatial distribution, and chemical states of particulate air pollutants, particularly heavy elements. Initial phase of the laboratory operation will concentrate on the installation and testing of instrumentation, while simultaneously building a national user network through various activities such as seminars, workshops and symposia, aimed at promoting the lab and its capabilities. As part of the project's competence building plans, the lab team has already been involved in a number of workshops and seminars that were conducted in the last few months including: a workshop at the AUS in collaboration with the IAEA under the ARASIA regional technical cooperation project RAS1010 on Application of nuclear and X ray techniques in art and archaeology; a training course organized in the UAE by UNESCO under its International Center for the Study of the Preservation and Restoration of Cultural Property (ICCROM) project, and a workshop on applications of XRF organized at UoS by the Radiation Science and Technology research group. A team member participated in the regional training course on nuclear techniques in art and archaeology, held at the IAEA laboratories at Seibersdorf in April 2009. During the summer of 2009, three scientists from UoS and AUS will spend five weeks at an XRF training center in Canada on fellowships from the NXFL project. In addition, two team members will visit some major scientific research centers in the USA and Canada to observe the latest sample preparation and analysis techniques.

Thereafter, the NXFL will actively engage in forming joint projects and analyzing samples on user demand. Moreover, regional institutions and organizations will be invited to make use of the facilities either for analysis or staff training.

Publications of potential interest to the XRF community

Fundamentals of Environmental Sampling and Analysis, Chunlong Zhang, John Wiley and Sons, New York, 2007

Aerosol Sampling. Science, Standards, Instrumentation and Applications, James H. Vincent, John Wiley and Sons, New York, 2007

Analytical Chemistry. Theoretical and Metrological Fundamentals, K. Danzer, Springer, 2008

IAEA
International Atomic Energy Agency

XRF Newsletter No. 17
July 2009

The XRF Newsletter is prepared twice a year by the IAEA Laboratories in Seibersdorf. Correspondence and materials to be considered for publishing should be sent to:

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1400 Wien, Austria

Printed by the IAEA in Austria,
July 2009

09-29231