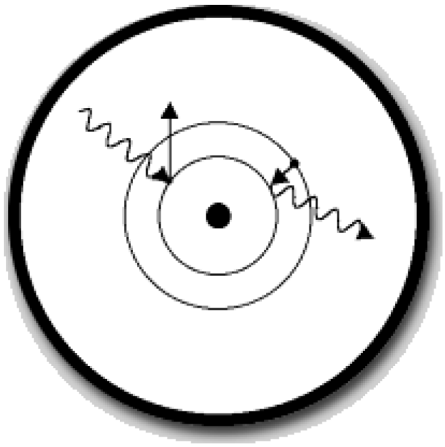
X-ray Fluorescence in the IAEA and its Member States

XRF NEWSLETTER



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CONTENTS

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Activities in the IAEA XRF Laboratory

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

Application of X-ray fluorescence techniques for the determination of hazardous and essential trace elements in environmental and biological materials

Utilization of various X-ray fluorescence techniques (energy-dispersive XRF with polarizing secondary targets, total reflection XRF, direct *in-situ* XRF, and micro-beam XRF spectrometry) was summarised in a paper presented during an International Conference on Isotopic and Nuclear Analytical Techniques for Health and Environment held in Vienna, 10 – 13 June 2003. The performance and detection limits for the different techniques available at the IAEA Laboratories at Seibersdorf as well as their applications for the analysis of soil and water samples, plant materials and airborne particulate matter collected on filters were characterised. Preliminary results of applications of micro-beam XRF technique for studying elemental distribution of heterogeneous samples and investigating the 2D- and 3D-morphology of minute samples were also given.

Further information is available from Samuel Akoto Bamford (S.A.Bamford@iaea.org).

X-ray fluorescence analysis and computerized tomographic imaging with a laboratory micro-beam scanning spectrometer

X-ray tube based, micro-beam X-ray fluorescence scanning spectrometer developed at Seibersdorf some years ago was equipped with two energy-dispersive X-ray detectors (liquid nitrogen cooled Si(Li) and thermoelectrically cooled silicon drift detector) which allow for simultaneous collection of both X-ray fluorescence and transmitted radiation with a spatial resolution down to about 10 μm. Data acquisition is carried out in an automatic way under control of a dedicated software developed in co-operation with the Rudjer Boskovic Institute, Zagreb, Croatia. Data obtained for selected regions of interest are used for on-line mapping of elemental distributions and computerised tomographic imaging. As an example a tomographic reconstruction of a human osteoporotic bone fragment is shown in Fig.1. Silicon drift detector provides the intensities of the transmitted beam which are utilised in the absorption correction methods. The performance of the micro-beam XRF scanning spectrometer and the results of application for characterisation of individual particles will be presented during XVIIth International Congress on X-Ray Optics and Microanalysis to be held in Chamonix, France, 22-26 September 2003.

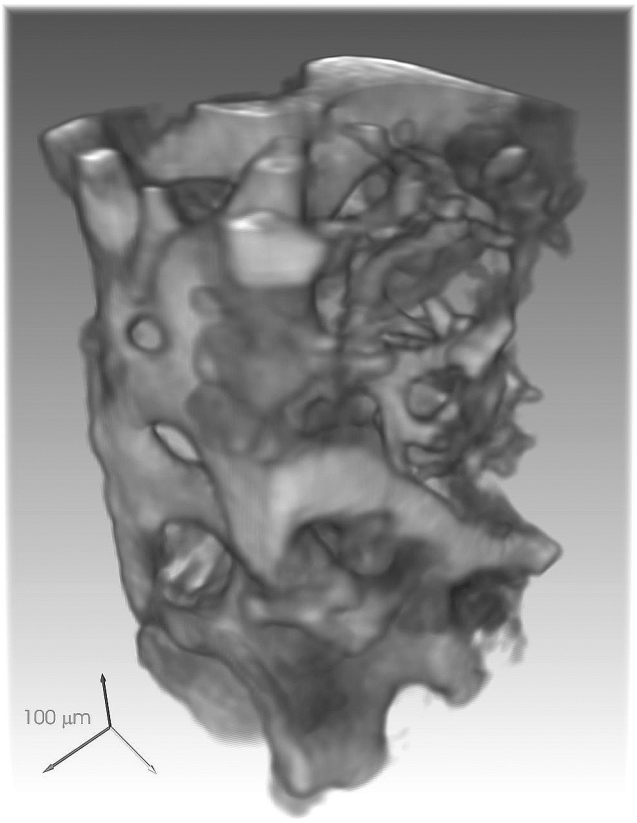

Fig. 1. Tomographic reconstruction of a human osteoporotic bone fragment.

Further information is available from Dariusz Wegrzynek (D.Wegrzynek@iaea.org)

Proficiency test (AirFilt 2003)

A proficiency test for the laboratories involved in a TC project RAS/7/013 on "Improved Information about Urban Air Quality Management" has been organised. Sets of filters artificially loaded with air dust and blank filters were distributed to the laboratories in Australia, Bangladesh, China, India, Indonesia, Republic of Korea, Malaysia, Mongolia, Myanmar, New Zealand, Pakistan, Philippines, Singapore, Sri Lanka, Thailand and Vietnam in February 2003. The participants were requested to determine as many elements as possible by using the established and proved analytical techniques (such as XRF, PIXE, NAA) which are routinely used in their laboratories for the analysis of air particulate matter collected on filters. The final report of the proficiency test is expected to be ready for distribution in November 2003.

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

IAEA mailing list for XRF laboratories and electronic version of XRF Newsletter

As already announced in the XRF Newsletter No.3 (January 2002) the IAEA Laboratories in Seibersdorf set up an e-mail distribution service for XRF laboratories with a major purpose to

improve communication and facilitate co-operation among XRF laboratories as well as to promote the new applications of the XRF techniques. In this context we kindly ask all subscribers to send us the updated e-mail addresses in case any changes took place recently. Moreover, we ask all recipients of the XRF Newsletters to submit their e-mail addresses that enables us to prepare and distribute the electronic version of the publications in the future.

The requested details should be sent to Andrzej Markowicz (A.Markowicz@iaea.org)

Data acquisition software for X-ray microprobe

Modified data acquisition software for X-ray microprobe was developed by the XRF Group with assistance of Mr. M.Bogovac, Croatia. The software consists of data acquisition (scanning and calibration), automatic positioning and micro-movement of sample, data reduction and evaluation. The acquisition software was designed in order to support different measurement set-ups that are applied in low-energy nuclear physics. The modified software described in user's manual on "Data Acquisition for X-Ray Microprobe", IAEA, Computer Manual Series No.17, 2002, supersedes the first version entitled "Microanalysis Data Acquisition and Control Program" published under Computer Manual Series, No.9 in 1996, and is freely available from the IAEA upon request.

Further information is available from Dariusz Wegrzynek (D.Wegrzynek@iaea.org).

XRF Laboratories Database

A worldwide database of the XRF laboratories including XRF facilities, expertise, techniques and applications is being established on the IAEA Laboratories web site. The XRF laboratories that didn't submit their input to the database are kindly requested to complete a simple questionnaire available in electronic version from Andrzej Markowicz (A.Markowicz@iaea.org) upon request.

Collaborative "Bronze Art Project"

Most bronze art statues and art objects found in Europe contain lead. This problem has received recent attention, leading to the "The Eureka Project" which seeks, among other things, to find a substitute bronze alloy that is lead-free. In connection with the above, the XRF laboratory in Seibersdorf is collaborating with the XRF Group at the Atominstitut in Vienna in "The Bronze Art Project" with the following objectives:

1. To contribute towards law-enforced change of the classical bronze alloy composition aiming at elimination of the use of lead in bronze production process.
2. Design of a portable x-ray fluorescence spectrometer for the "on the spot" analysis of art works.

In relation to the above, analysis of two NIST bronze standards (NBS 1151, NBS 1108) and eight different bronze samples received have been carried out. The x-ray fluorescence analysis at Atominstitut was done with a Tracor TN 5000 spectrometer. This spectrometer uses a Rh anode low power X-ray tube and a Si(Li) detector with resolution 150eV at 5.9keV. It is equipped with sample changer for maximum load of 10 disc-like samples of 30 mm in diameter. The samples are analysed in direct excitation geometry utilizing a set of filters. In bronze alloys the expected detection limits are in the range from about 0.01 %. The samples were also analysed by using an energy dispersive x-ray fluorescence spectrometer available at the IAEA Laboratories, Seibersdorf, Austria. This is a SPECTRO X-Lab 2000 x-ray fluorescence spectrometer consisting of a 300W oil-cooled x-ray tube with Pd anode

combined with 5 secondary targets for efficient excitation of elements from atomic number Z=11 (Na) to Z=92 (U). The measuring geometry is optimised fully utilizing the effect of polarization of x-rays scattered on secondary target to improve signal to noise ratio. The x-ray fluorescence radiation is collected by Si(Li) detector with a resolution of 150eV. Up to 20 samples can be loaded in the spectrometer and analysed in a fully automatic way. Manual fine-tuning of the analysis process is also possible. The elements identified and quantified are Ni, Cu, Zn, Sn, Sb, and Pb. Initial results obtained by both Laboratories in the analysis of the bronze standards and samples were in good agreement.

Upcoming relevant meeting

Second (final) Research Co-ordination Meeting (RCM) of the IAEA's Coordinated Research Project on "*In-situ* applications of XRF techniques" will be held in Vienna from 8 – 12 September 2003. The purpose of the meeting to be attended by the participants from Albania, Argentina, Belgium, China, Ghana, Hungary, Italy, Pakistan, Poland, Romania, Slovenia and United Kingdom, is to review/discuss the results obtained under the CRP and to prepare a draft of the final report. It is expected that the RCM report will include harmonised and optimised sampling procedures, complete operating procedures for selected in-situ applications as well as reliable quantification methods. The report will be available for distribution at the beginning of 2004.

X-ray Fluorescence in Member States

During the last months we received the contributions from Nigeria, Spain and Hungary on the current XRF and related activities. Below there are short communications based on the original submissions (with minor editorial changes only).

Nigeria

Environmental Research Laboratory (ERL) of Physics Department, Obafemi Awolowo University, Ile-Ife

Contributors: H.B Olaniyi, I.B. Obioh, J.O. Ojo, O.K. Owoade (*oowoade2001@yahoo.com), F.S. Olise*

Environmental Research Laboratory (ERL) has got EDXRF system with total reflection module. These facilities are used for training, research and analytical services. Training is provided for Physics, Chemistry and Geology for both undergraduate and postgraduate students. The samples analysed in our laboratory include environmental, geological, biological, water, steel and alloy materials.

The Research activities are carried out in support of environmental studies for air, water, soils and plant materials and optimisation of measurement protocols.

We provides analytical services for the determination of major and minor elements in small-scale prospectors and miners of mineral ores with major constituents such as K, Ca, Ti,

Cr, Mn, As, Pb and Zr. Presently we are monitoring environmental pollution due to toxic heavy metals in industrial workplaces.

Other analytical services rendered by the laboratory include determination of trace elements in Nigerian bitumen samples, determination of toxic heavy metals like Ti, Cr, Mn, Fe, Cu, Zn, As, Pb, Cd, Hg in various stages of dam water in Ile-Ife- the university community.

The laboratory also offered analytical services to other research institutions, Universities, governmental agencies, geological and environmental assessment companies.

ERL group is currently participating in different projects/conferences organized by the International Atomic Energy Agency (IAEA), Vienna with the following papers presented:

(1) Determination of atmospheric concentration of toxic metals along urban motorway in two Nigerian cities using TXRF technique

(2) Assessment of Occupational Exposure to Toxic Metals in some Paint and Secondary Iron and Steel Industries in Lagos, Nigeria using TXRF Technique.

One of the postgraduate projects already completed is on Determination of Concentration of Toxic Metals in the Ambient Air in Lagos and Ile-Ife, Nigeria, using Total Reflection X-ray Fluorescence Technique.

Spain

Unidad de Arqueometría. Instituto de Ciencia de los Materiales de la Universitat de València (ICMUV), Apdo. de Correos 2085, E-46071 Valencia

Contributors: J.L. Ferrero, C. Roldán (Clodoaldo.Roldan@uv.es)*

Study of patrimonial works by non-destructive techniques has wakened up great interest because they allow the analysis of unique pieces without affecting their integrity. The Archaeometry Unit of the Instituto de Ciència de los Materiales de la Universitat de València (ICMUV) has carried out EDXRF analysis in support of identification of forged works of art using portable instrumentation. The comparison of the EDXRF spectra of these objects with a data base, which contains the spectra and compositions of well-known originals, gives evidences to detect fakes. In addition to the detection of forged works of art, EDXRF may help to obtain information on the art pieces that could be important to determine their value. For instance, knowledge of the degree of originality is very important. Although the authenticity of the work can be clear, it could have been degraded and repainted or rebuilt. The EDXRF technique can help to distinguish between the original parts of the works and latter modifications. Another application is to obtain technological information about the process of making the work of art and the state of preservation.

References:

J.L. Ferrero, C. Roldán, D.Juanes, J. Carballo, J.L.Lluch, R. Vives,
Study of old master prints with portable EDXRF spectrometry; to be published in *Nucl. Instr. and Meth.* B, 2003

C. Roldán, J. Coll, J.L. Ferrero, D. Juanes,
Identification of the overglaze and underglaze cobalt decoration of ceramics from Valencia (Spain) by portable EDXRF spectrometry; to be published in X-ray Spectrometry. 2003.

M. Ardid, J. Ferrero, D. Juanes, C. Roldán, M. Crespo, M.E. Pernett, M. Marzal, M. Burke, S. Rovira, R. Vives,
Identification of forged works of art by portable EDXRF spectrometry, to be published in *Advances in X-ray Analysis*.

Hungary

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Reinstallation of the "Hamburg proton microprobe" in the KFKI Research Institute for Particle and Nuclear Physics (KFKI RMKI), Budapest, Hungary

The "Hamburg proton microprobe" was introduced to the international PIXE community at the 5th International Conference on PIXE and its Analytical Applications" in 1989[1]. The "home made' device was connected to the 2 MV Van de Graaff accelerator at the University of Hamburg and beam diameter of 3×4 μm^2 on the specimen surface at a current of 2 nA was easily obtained. Later the beam spot diameter was further reduced down to ~ 1 μm still with proton current of a few hundred pA. In the following twelve years the microprobe was extensively used for environmental analysis, these applications and the continuous innovative development of the microbeam were strongly connected with Dr.Manfred Niecke.

By help of the new scientific contacts initiated by the EU supported KFKI Condensed Matter Research Center of Center of Excellence we were informed in July of 2001 that the whole accelerator laboratory would be finally closed at the end of August 2001. After intensive e-mail discussions and a one-day-visit in Hamburg an agreement of research co-operation was signed on the 10th of September 2001 between the Department of Experimental Physics of the University of Hamburg and the KFKI RMKI. According to the agreement the complete Hamburg proton microprobe was gifted to KFKI RMKI. In return, free access to the reinstalled microprobe was provided for Dr. Manfred Niecke in the frame of common research projects.

In two weeks the microprobe was dismantled, packed and launched to KFKI RMKI. For lack of sufficient room in the usual target-hall, a special vibration-free supporting base extending into the adjoining hall of our heavy ion cascade accelerator had to be built. The support also has equalized the more than 1 m level difference between the two rooms. In March and September 2002 Dr. Niecke spent one month each in KFKI RMKI. Thanks to his very effective contribution and supervision, the instrument was successfully reinstalled and restarted during this rather short time. As a part of the dedicating ceremony of the relief of Professor Károly Simonyi, the builder of the first particle accelerator in Hungary, the "Budapest microprobe" was introduced to the public on 17 October, 2002. That time the characteristic spot size of the 2 MeV proton beam on the target surface was about 10 μm, that is about ten times larger than it was in Hamburg. As the result of the fine adjustments, improvements initiated by Dr.Niecke's third one-month visit in March 2003, for today the beam spot size is about 3×5 μm^2 with beam current of 5-600 pA. The focusing procedure

was successfully adapted for 2.5 MeV proton beam, too. The target chamber contains several detectors. Behind the target at 0^o a Si(Li) detector of large sensitive area, a surface barrier detector, a Faraday cup or an optical microscope can be placed alternatively. Another Si(Li) detector is located with an angle of 120^o with regard to the beam direction. At 135^o a channeltron has been placed to enable secondary electron images to be seen on a live display scope. Strong focusing, target positioning, beam scanning, data collecting and acquisition are all PC controlled. In spite of the rather different beam optics of the RMKI 5 MV Van de Graaff accelerator, we hope that the beam size could be further reduced by optimizing the position and size of the object slit, and by proper mu-metal magnetic shielding. Besides fine adjustments, technical improvements, reduction of vibrations, and calibration for quantitative analysis, research applications in different topics will also be started (monitoring the environmental pollution by measuring the distribution of the heavy elements in the otolithes, single particle analysis of aerosols, study of corrosion of cement in acid environment, etc.).

Reference:

[1]D.Grossmann, J.P.Koopman, M.Niecke, and J.Schöttler, The Hamburg proton microprobe: application in environmental analysis, Nucl.Instr.Meth. B 49 (1990) 495-500

Publications of potential interest to the XRF community

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2. D.C. Adriano, Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability and Risk of Metals, Springer-Verlag, 2001 (ISBN 0-387-98678-2)
3. D.Wegrzynek, A.Markowicz and E.Chinea-Cano, Application of the Backscatter Fundamental Parameter Method for *in situ* Element Determination Using a Portable Energy-dispersive X-Ray Fluorescence Spectrometer, X-Ray Spectrometry, 32, 119-128 (2003)
4. S.A. Bamford, M. Jaksic, Z. Medunic, D. Wegrzynek, E. Chinea-Cano and A. Markowicz, Extending the Quantitative Analytical Capabilities of EDXRF Technique for Plant-Based Samples, accepted in X-Ray Spectrometry (2003)
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7. D.Wegrzynek, A.Markowicz, E.Chinea-Cano and S.Bamford, Evaluation of the uncertainty of element determination using the energy-dispersive X-ray fluorescence technique and the emission-transmission method, X-Ray Spectromentry, 32, 317-335 (2003)

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