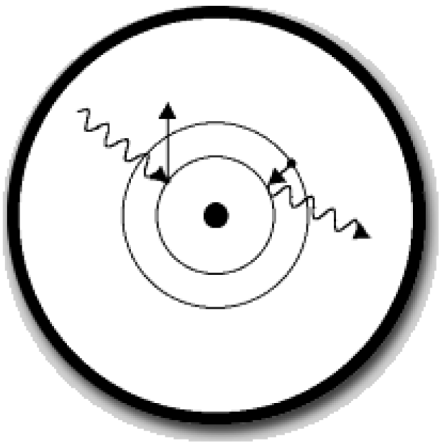
X-ray Fluorescence in the IAEA and its Member States

XRF NEWSLETTER



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Activities in the IAEA XRF Laboratory

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

Development of portable XRF spectrometer for in-situ study of works of arts

A portable XRF spectrometer based on a small size, low power X-ray tube and a thermoelectrically cooled Si-PIN detector was developed and constructed (with assistance of Ms. A.Mendoza, Cuba). The spectrometer provides an opportunity for direct and secondary target excitation. By choosing a proper target and/or filter one can optimise the excitation conditions for selected element(s). A set of different collimators provides the primary photon beam in the range of 1 mm -1 cm in diameter. The portable XRF spectrometer (see Fig. 1) was successfully applied to study a variety of works of art in the Kunsthistorisches Museum in Vienna (in collaboration with Dr.M.Griesser). It was used in support of investigation of the painting technique of old master paintings and provenance of ancient Etruscan mirrors. The results helped the Museum experts to answer a number of art historical and archaeological questions.

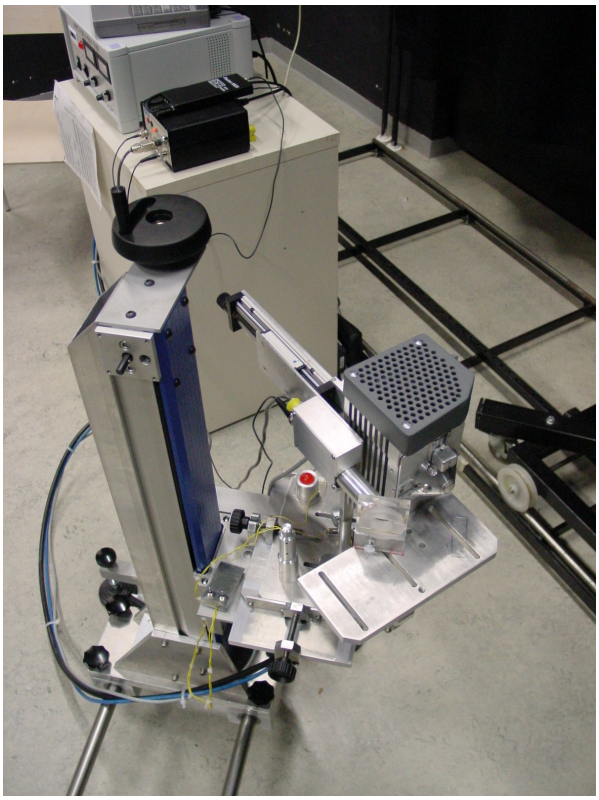

Fig. 1 Portable XRF Spectrometer based on a low power X-ray tube and thermoelectrically cooled Si-PIN detector

X-ray microfluorescence analysis of depleted uranium (DU) particles

A capillary-based X-ray microfluorescence system (see XRF Newsletter No.1, Dec. 2000) was used to analyse a number of DU particles in soil samples collected in Kosovo. The magnetic particles containing DU were first isolated and glued on a plastic holder by using a silicone compound. Coarse and fine scanning was performed with a primary photon beam of 0.7 mm

and 30 micrometer in diameter, respectively. The elemental distribution maps revealed "hot" spots containing DU in the size range of a few hundreds - a few micrometers.

First Research Co-ordination Meeting (RCM) under Co-ordination Research Project (CRP) on "In-situ applications of XRF techniques"

Eleven participants of the CRP on "In-situ applications of XRF techniques" from Albania, Belgium, Peoples' Republic of China, Ghana, Hungary, Italy, Mongolia, Pakistan, Poland, Slovenia and United Kingdom attended the first RCM held in Vienna from 12-16 March 2001. The participants presented their individual progress reports and assessed the present status of the CRP including both the activities and outputs. The research activities under the CRP focus on

(i) optimisation and standardisation of sampling procedures,
(ii) improvements of performance of field portable XRF (FPXRF) instrumentation,
(iii) improvements in quantification procedures,
(iv) extension of applicability range of FPXRF, and
(v) preparation of operating procedures for selected applications.

The RCM concluded that the activities undertaken by the individual Research Agreement/Research Contract holders are consistent with the objectives of the CRP and a significant progress has been made. The next RCM is planned for the beginning 2003. Report of the RCM is available from A.Markowicz, IAEA Laboratories, Seibersdorf upon request.

Improvements in software for X-ray microfluorescence and total reflection XRF (TXRF) systems

A procedure for generation arbitrary gradient color scales suitable for single element X-ray images was developed and implemented in the existing data acquisition software for X-ray microfluorescence analysis (with assistance of Mr. M.Bogovac, Croatia). In order to implement the procedure a graphical user interface for color selection and an additional code to handle the colors were developed. The procedure improved the quality of presentation of the experimental results in the form of the elemental distribution maps. A comprehensive manual for X-ray microfluorescence software was also prepared.
Automatic adjustment of a spectrum modifier in TXRF system was developed (also with assistance of Mr. M.Bogovac, Croatia) by implementing several new features in the existing TXRF software.

Voigt peak shape profiles in evaluation of the energy-dispersive X-ray fluorescence spectra

The AXIL computer program for the evaluation of X-ray spectra was extended (with assistance of Mr. Wegrzynek, Poland) to take into account the broadening of peaks of K-series of high-Z elements (Z>50) due to increasing contribution of the natural line width. This effect has to be considered in the determination of such elements as W, Au, Pb, U via K-series characteristic X-rays. The so-called Voigt function obtained by convolution of the natural line profile (given by the Lorentz function) with the Gaussian detector response function was implemented into the AXIL computer code. The relevance and importance of fitting the X-ray spectra of K-series radiation of high-Z elements with Voigt peak shape versus Gaussian approximation was thoroughly examined by using simulated and measured spectra. The experimental XRF spectra were obtained by using a high voltage X-ray tube with tungsten

anode (130 kV/65W) and a Ge detector. The fitting procedure and the results obtained are described in a paper submitted to the X-Ray Spectrometry journal.

X-ray Fluorescence in Member States

As announced in the first issue, the XRF Newsletter intends also to present XRF activities in the Member States laboratories. Below there are short communications received from Belgium, Hungary, Madagascar and Poland (this section is based on the original submissions, with minor editorial changes).

Belgium
Micro and Trace Analysis Center (MiTAC), University of Antwerp (UIA)
Contributor: Dr. Jasna Injuk

The Micro and Trace Analysis Center (MiTAC) of the University of Antwerp has got six different XRF equipment for micro and/or in-situ applications used by four different research groups. In addition, X-ray emission systems are available in one electron microprobe and in one scanning electron microscope. As a part of MiTAC, the research group (headed by Prof. Van Grieken) is devoted to various forms of analytical chemistry, with special emphasis on microscopic methods for nondestructive analysis and materials characterization. In the group, special attention is dedicated to fundamental and methodological research of micro and trace analysis and their applications in environmental and conservation issues and in material science.

Current projects, concerning the use of XRF are summarized below:

- Air-sea exchange of nutrients for the North Sea
- Deposition of heavy metals and nutrients over water surface due to anthropogenic processes: case of Lake Balaton, Hungary
- Study of air pollution in urban and remote sites in South Africa
- Transboundary aerosol pollution between France and Belgium
- Personal and indoor exposure to fine and ultrafine particulate matter and its relationship to short-term changes in cardiovascular and respiratory health
- Study of the transport and deposition fluxes of heavy metals in the Tisza river (Hungary) after the recent massive pollution event
- Source apportionment of dust particles in ambient air over The Netherlands
- In-situ X-ray fluorescence analysis for archaeological objects
- Evaluation of Minipal XRF unit for aerosol and sediment analysis
- Optimization of wavelength-dispersive XRF for aerosol analysis
- Environmental effects on important cultural heritage monuments in Greece and Bulgaria
- Deposition of aerosol particles on art objects in the "Royal Museum of Fine Arts", Antwerp, Belgium

Hungary
KFKI Research Institute for Particle and Nuclear Physics
Contributor: Prof. Z. Szökefalvi-Nagy

Instrumentation includes two PIXE beamlines at a home made 5MV single-ended Van de Graaff accelerator. The first is equipped with a small vacuum chamber containing only one sample at a time for standard PIXE analysis[1]. The special vacuum-lock system allows sample

changing in 30-60 sec. The beam-stopper of the chamber can be replaced either by a narrow tube with 8μm Kapton exit window for non-vacuum analysis[2], or by a special extension for PIXE induced XRF (PIXRF)[3]. The second beamline contains a dedicated chamber for automatic linear PIXE scanning of samples, first of all polyacrylamide gel electrophoretograms containing separated proteins in narrow bands (PIXE-PAGE technique)[4]. This chamber accepts only a horizontal, high resolution (145 eV for Mn Kα line) DSG Si(Li) detector, while at the first beamline, the vertical Canberra 3777E Si(Li) detector of 185 eV energy resolution can also be used. The PIXE-PAGE measurements are controlled by a dedicated MCA card and software combination, the standard PIXE spectra are off-line evaluated by the program packages AXIL and GUPIX.

Using a New England Nuclear (USA) ring source holding radioisotope excitation head XRF analyses[5] can also be performed. For practical reasons a vertical Canberra detector is generally used in these measurements, but a proper support allows to use the horizontal one, too. For excitation ^{109}Cd and ^{241}Am NEN ring sources are used. For *in situ* analysis of art and archaeological objects a portable spectrometer containing thermoelectrically cooled Amptek Si-PIN detector is under construction.

Projects:

- Environmental and biomedical analysis, PIXE-PAGE study of metalloproteins (supported by EU as Work-package No. 6 of the KFKI Condensed Matter Research Center (Centre of Excellence)
- Investigation of L-subshell ionisation, study of the chemical effects on the Kβ/Kα intensity ratio with PIXE and XRF
- External beam analysis of art and archaeological objects (COST G-8 Action)
- In situ characterisation of paint layers of large art and archaeological objects (supported by IAEA as a part of Co-ordinated Research Project "In situ application of XRF techniques")

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References:

[1]Le Huong Quynh, I. Demeter K. Hollós-Nagy and Z.Szőkefalvi-Nagy, PIXE measurement of the Cadmium content in animal tissues, Int.Journal of PIXE 2 (1992) 397-403

[2]I.Gyódi, I. Demeter, Katalin Hollós-Nagy, I. Kovács, and Z. Szőkefalvi-Nagy, External-beam PIXE analysis of small sculptures, Nucl.Instr.Meth. B 150 (1999) 605-610

[3]Le Huong Quynh, I.Demeter and Z.Szőkefalvi-Nagy, PIXE Induced XRF Analysis of Trace Amounts of Iron in Pure Copper Matrix, Nucl.Instr.Meth. B49(1990)566-568

[4]Z.Szőkefalvi-Nagy, Cs. Bagyinka, I.Demeter, Katalin Hollós-Nagy and I.Kovács, Speciation of metal ions in proteins by combining PIXE and electrophoresis, Fresenius J. Anal. Chem. 363 (1999) 469-473

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Madagascar

Institut National des Sciences et Techniques Nucléaires (INSTN)
Contributor: Prof. R. Andriambololona

Madagascar is one of the island in the Indian Ocean. The country is situated 20°S, 45°E near the African continent. The Institut National des Sciences et Techniques Nucléaires, INSTN (created by the Director General Prof. RAOELINA ANDRIAMBOLOLONA) applies nuclear and related techniques for peace, sustainable development and protection of the environment.

Staff of the XRF department include the department's head Dr. RANDRIAMANIVO Lucienne, three assistants: Dr. RAKOTONDRAMANANA Hery Tiana, Dr. RASOLOFONIRINA Mamiseheno and Ms RASOAZANANY Elise O. (M.Sc.) and three research students.

The XRF activities at the Institute are to fulfill the following three missions: training, research and analytical services. Training provides a relevant module for the students who prepare their Masters in nuclear physics. The XRF department applies the total reflection XRF (TXRF) and the conventional XRF based on X-ray tube with a molybdenum anode. The Ultra-LeGe and Si(Li) detectors with a resolution of 130eV and 160eV at 5.9keV, respectively, are used for both techniques. The most important aspect in research activities is the monitoring of environmental pollution (air, water and soil). Concerning the analytical services, the XRF techniques are used for quality control of foodstuffs (e.g., fish products, drinking water) and other types of samples (e.g., ores).

The XRF department participated in different projects organized by the International Atomic Energy Agency (IAEA-Vienna) such as Technical Co-operation project (TC-project 2001-2002 Ref: MAG007/02), Co-ordinated Research Project (CRP 98- CRP 99 Ref: MAG 10 023).

Poland
University of Mining and Metallurgy , Department of Radiometric Analyses
Contributor: Dr. M. Lankosz

The research activity of the Department of Radiometric Analyses comprises both the theoretical and experimental work on the utilization of X-ray radiation. The analytical techniques developed at the laboratory embraced Energy Dispersive X-ray Fluorescence Spectrometry (EDXRS), Total Reflection X-ray Fluorescence (TXRF), micro-beam X-ray Fluorescence Analysis (μ-beam XRF) and Proton Induced X-ray Emission (PIXE) technique.

The μ-beam XRF technique is continuously upgraded and used for examination of local concentration of elements in various materials. This technique was successfully applied to study radial gradients of titanium and bismuth in gradient refractive index materials. A simple procedure with the use of scattered primary radiation from molybdenum anode of X-ray tube was developed to determine local concentration of metals in polymer matrices. Recently, the μ - XRF spectrometer, utilizing capillary optics (tapered capillary with spatial resolution of about 25 μm) was adapted to perform computerized micro tomographic (CMT) imaging of small objects. The CMT imaging measurements in absorption and X-ray fluorescence modes were performed.

In the recent years the TXRF technique was applied for trace analysis of various biological and environmental samples as well as for the examination of the historical objects. This method was

successfully used for elemental analysis of specimens of metallophytes (plants and insects). The TXRF technique was also used for simulation study on the deterioration of various kinds of the sandstone due to the influence of artificial acid rain. Both EDXRF and TXRF techniques were used to investigate elemental composition of the peat cores from Poland and Austria. The applicability of TXRF for analysis of elemental composition in ancient objects for archaeology and archaeometry was investigated. The relevant examples include nondestructive characterization of the alloy used for manufacturing of the XVIIIth century gorget, analysis of the composition of ancient silver coins and medieval pigments.

PIXE method was applied for determination of major and trace elements in tissue samples from selected part of human central nervous system. This information is used in studies of pathogenesis of neurodegenerative diseases. The distribution of S, Ca, Fe, Zn and Cu in samples from different part of human central nervous system was determined. The effect of patient's age on accumulation of the elements in human brain was investigated. For determination of concentration of trace elements in human body fluids the TXRF technique was applied.

More details concerning research and staff of the Department of Radiometric Analyses are available on following Web Page address: www.ftj.agh.edu.pl.

Books of potential interest to the XRF community:

- R. Cesareo, X-ray Physics: Interaction with Matter, Production, Detection, La Rivista del Nuovo Cimento, Bologna, 2000
- J.L.Schnoor, Environmental Modelling. Fate and Transport of Pollutants in Water, Air and Soil, Wiley, New York, 1996
- K. Janssens, F.Adams, A.Rindby, Eds., Microscopic X-Ray Fluorescence Analysis, John Wiley & Sons Ltd., Chichester, UK, 2000
- R.B. James, P. Siffert, Eds., Room Temperature Semiconductor Detectors, Proceedings of the 11th International Workshop on Room Temperature Semiconductor X- and Gamma-Ray Detectors and Associated Electronics, IAEA, Vienna, Austria 11-15 October 1999, Elsevier Science B.V., 2001

Announcement of Proficiency Test

The IAEA Seibersdorf Laboratories organise a world-wide proficiency test designed for the XRF laboratories involved in analysis of various materials. Proficiency test is considered as one of the most effective ways for a laboratory to monitor and assess its analytical performance. It can be used as a way to identify the results with unsuspected bias and to improve the quality of the analytical services provided. The IAEA proficiency test involves distributing to participating laboratories (tentatively by the end of October 2001) a sample of environmental origin with established homogeneity and composition. The laboratories are requested to analyse the sample using established technique following their analytical procedures. It is expected that the results will be returned to the organisers tentatively before the end of February 2002 for evaluation according to recognised international procedures based on z- and u-scores. The final report of the proficiency test should be ready for distribution in the third

quarter 2002. All interested in the proficiency test are requested to contact A.Markowicz, IAEA Labs, Seibersdorf.

The XRF Newsletter is issued twice a year by the IAEA Laboratories in Seibersdorf.
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