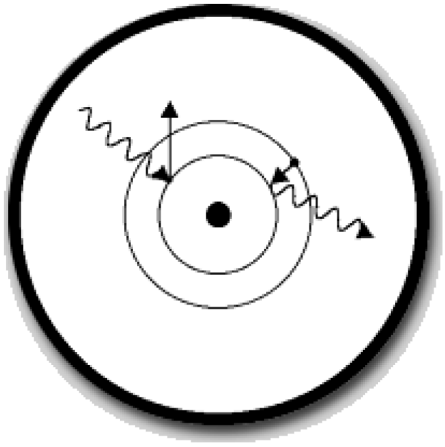
X-ray Fluorescence in the IAEA and its Member States

XRF NEWSLETTER



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Staff involved in XRF activities at Seibersdorf

The XRF Group (called also XRF Laboratory) is a part of the Instrumentation Unit, Physics-Chemistry-Instrumentation (PCI) Laboratory. Currently the following persons are involved in the activities in the field of X-ray fluorescence and ion beam analytical techniques: Samuel Akoto Bamford, Ernesto Chinea Cano and Andrzej Markowicz. In February 2002 Dariusz Wegrzynek will join the XRF Group as the new staff of the IAEA. Occasionally the XRF Group is supported by staff of the Electronics Group of the Instrumentation Unit.

Activities in the IAEA XRF Laboratory

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

Assessment of new detectors for XRF analysis

Recently the following two semiconductor X-ray detectors of potential interest for XRF community were evaluated (with assistance of Mr. Wegrzynek, Poland): cadmium-telluride (CdTe) from Baltic Scientific Instruments and silicon drift detector (SDD) from Ketek. These detectors do not require liquid nitrogen for cooling and operate at temperatures lower than the ambient temperature, maintained by thermoelectrical cooling (Peltier effect). The CdTe detector can be used for detecting hard X-rays and low energy γ photons within the energy range from a few keV up to about 150 keV. The CdTe detector under test (with thickness of 1.5 mm) demonstrated an energy resolution (FWHM) of about 600 eV at 59.5 keV. Some disadvantage of the detector is a pronounced low energy tailing and the presence of intense escape peaks in the high-energy region of the acquired spectra. A major advantage of the SDD is its very good energy resolution at high count rates up to a few hundreds kcps (FWHM around 165 eV at 5.9 keV). However, due to the small thickness of the SDD (300 μm) the application of the detector is limited to the X-rays with energy lower than about 20 keV. Moreover, the SDD is characterised by a rather small sensitive area of about 4-5 mm^2, which in practice requires to combine in one device a cluster consisting of a few single detectors. The spectrometric performance of the SDD appeared to be better, in terms of energy resolution and high count rates capabilities, as compared to other thermoelectrically cooled detectors such as Si-PIN and CdTe detectors.

IAEA mailing list for XRF laboratories

The IAEA Laboratories in Seibersdorf set up an e-mail distribution service for XRF laboratories. The major objective for establishing the world-wide service is to improve communication and facilitate co-operation among XRF laboratories as well as to promote the new applications of the XRF techniques. The e-mail distribution service should enable XRF laboratories, in particular in the developing Member States, to access quickly the information on recent developments in the field of XRF spectrometry, including both fundamental and applied aspects of sampling, sample preparation, instrumentation, quantification, quality control etc. It is also expected that the e-mail distribution service will strengthen the interactions between the IAEA XRF Laboratory at Seibersdorf and XRF laboratories in the Member States. Through this communication channel the Agency's XRF Laboratory expects also to receive an immediate and direct feedback from the XRF laboratories in the Member States including their comments and suggestions related to the future activities at Seibersdorf.

We expect to have on the list the users and developers of the XRF laboratories in developing Member States together with XRF specialists from industrialized countries, including the IAEA experts who often assisted the developing countries in establishing applications of XRF techniques. This might also give a unique opportunity to continue (or renew) a cooperation initiated years ago.

Below there are some basic features of the mailing list named **naalistxrflabs**:

(i) the list is closed and every subscription to it is done via moderator (A.Markowicz)
(ii) the list is moderated; each message is first sent to the moderator who will re-send it to the whole list
(iii) mails originating only from list members will be accepted for delivery
(iv) each subscriber can unsubscribe from the list without approval.

Everyone is invited to join the mailing list. If you are interested, please kindly send a confirmation e-mail to A.Markowicz@iaea.org. We would be grateful if you kindly distribute the invitation to your colleagues who are involved in any IAEA-sponsored activity related to the XRF techniques. Any suggestions on the functioning of the e-mail distribution service are highly appreciated.

Training opportunities at the IAEA Laboratories at Seibersdorf

The XRF Group at the IAEA Seibersdorf Laboratories, among other activities, provides training in METHODOLOGY and APPLICATIONS of Energy Dispersive X-ray Fluorescence Spectrometry. The major facilities available for training include:

1. Radioisotope-excited XRF spectrometer
2. Tube-excited XRF spectrometer
   - conventional atmospheric-based system, and
   - vacuum-based system
3. Total Reflection XRF spectrometer
4. μ-beam XRF spectrometer
5. Portable XRF spectrometers
6. PIXE/RBS dedicated beam line, located at the Ruder Boskovic Institute (RBI) in Zagreb, Croatia

Training is offered at various levels, and can address the needs of beginners and advanced fellows. Areas covered include X-ray physics, sampling, sample preparation, optimization of instrumental set-up, spectrum evaluation, quantitative packages included in the QXAS software, quality control procedures, and special application projects.
In 2001 fellows and scientific visitors from Portugal, Lebanon, Nigeria, Vietnam, Albania, Zambia, Angola, and Jamaica received training at Seibersdorf.
Further information is available from Samuel Akoto Bamford (S.A.Bamford@iaea.org).
A picture below shows the Agency's PIXE/RBS facility in Zagreb, Croatia.

Fig. 1 Experimental lines of Tandem van de Graaff accelerator in Zagreb, Croatia including Agency beam line.

Implementation of a Quality Assurance system in XRF laboratory

Nowadays Quality Control/Quality Assurance (QC/QA) is inevitable in the functioning of any analytical laboratory. Establishing a Quality Assurance system is however time-consuming and requires special knowledge and experience. The IAEA XRF laboratory at Seibersdorf has been doing considerable efforts to establish QA system. The relevant activities include:

- Writing and approval of a set of Standard Operational Procedures (SOP) and Instructions for sample handling/keeping/tracing, sample preparation as well as calibration and routine checking of the XRF equipment.
- Establishing an electronic (computer based) system for data management, tracing, and storage.
- Establishing a Quality Control System applied to X-ray fluorescence analysis

Currently sets of approved SOPs that cover sample preparation methods for various types of materials prior to TXRF, analysis by TXRF, and calibration and routine checks of EDXRF spectrometers are available. A computer program was written that allows control of the flow of the samples throughout the whole process of analysis. Essentially, it is a database with forms for recording data relevant to the sample, sample preparation, measurement, evaluation of the results, and reporting stages. It gives the possibility for auditing the analytical process at any moment. Links are kept to the calibration, sample spectra and corresponding QXAS files. An automatic data backup program was developed and installed on all PCs associated with the measurements and data evaluation. The corresponding SOPs were drafted and the programs are now being tested. Moreover, the uncertainty budget for the emission -transmission method

was established. For more details on QA system for XRF laboratory, please contact Ernesto Chinea-Cano (e-mail: E.Chinea-Cano@iaea.org).

We are aware that some XRF laboratories in Member States are also interested in introducing QA system and are investing some efforts in this area. Therefore, we kindly invite staff of the XRF laboratories to submit to the Agency a short note for the next issue of XRF Newsletter, on the QA system being in place in your laboratory or being currently introduced, including your views and opinions on the needs, importance and usefulness of QA in XRF laboratories.

X-ray Fluorescence in Member States

As announced before, the XRF Newsletter intends also to present XRF activities in the Member States laboratories. Below there are short communications received from Peoples' Republic of China, Nigeria, Slovenia, Spain and United Kingdom (this section is based on the original submissions, with minor editorial changes).

Peoples' Republic of China
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Contributors: GE Liangquan, LAI Wangchang and LIN Yanchang

The report is dealing with the investigation of sampling methodology to determine the concentration of elements in soil or rocks by using field portable XRF (FPXRF) analyser.

In mineral exploration and prospecting proper sampling is a critical step for a reliable *in situ* analysis. Based on the distribution features of mineralized elements in rock or soils, and the requirements of geological and geochemical prospecting, the sampling methodologies were developed for the following four cases of *in situ* FPXRF analysis:

a) *In situ* measurement of natural soil
The developed procedures are only applicable for a portable XRF probe which is placed directly on the surface of natural soil. A number of well defined measurement steps are to be followed.

b) *In situ* measurement of natural rock
In *in situ* measurements of primary rocks, an examined surface must be "fresh" and smooth as much as possible. In order to obtain representative results, three to five measurement points should be selected at the investigated area at a distance of 0.5 - 1 m.

c) Measurement of soil samples in the field
In mineral exploration, an FPXRF analyser is usually used as a stationary instrument in the field, just like a mobile analytical laboratory. The XRF analysis includes sampling soil samples, preparing samples for XRF analysis and measurement according to established protocols.

d) Measurement of well-prepared rock samples
The sampling methodologies for rock samples are basically similar to those applied for soil samples.

In recent years, our group successfully applied *in situ* FPXRF technique for the determination of Au, Ag, Cu, Pb, Zn and Sn in geological prospecting and exploration. In particular, satisfactory results were obtained for geological and geochemical prospecting of gold. Although gold abundance in rocks or soil (about 10^{-9}) is far below the detection limit of FPXRF, some other elements closely related to gold mineralization, such as Cu, Zn, As and Pb, can be determined in the field with portable XRF instruments. More than twenty large mineralized areas were evaluated by using *in situ* FPXRF technique, and some of them were eventually identified as middle of large-scale mineral deposits.

The work was supported by the IAEA, Research Contract No. 11305/R0, and China Geological Survey, Project No. 20002010002116, 200120120083. For more details please contact Dr. GE Liangquan.

Nigeria

Centre for Energy Research and Training, Ahmadu Bello University, Zaria
Contributor: I.I. Funtua

The Centre for Energy Research and Training, Ahmadu Bello University, Zaria has got three EDXRF systems with isotopic sources (Fe-55, Cd-109, Am-241), secondary target and total reflection. These facilities are used for training, research and provision of analytical services.

Training is provided for students of Chemistry, Geology, Physics, Chemical and Metallurgical Engineering at both Undergraduate and Postgraduate levels. The samples analysed consist essentially of geological, biological, water, and steel and alloy materials.

Research activities are carried out in areas of mineral studies[1], environmental studies (air, water, biological and geological materials)[2,3,4] and optimization of measurement protocols[5].

Analytical services are provided for small-scale prospectors and miners of mineral ores (most importantly for Nb-Ta ores). With Cd-109 source the Nb-Ta ores are analyzed along with major constituents such as Mn, Fe, Ti and Zr and impurities and/or contaminants such as W, Pb, Th and U within an hour (including sample preparation and quantitative analysis). This is a competitive advantage as at present no other analytical facility offers this service with the same speed. The benefit is that it offers the miners the opportunity to classify their ores into either a Nb or Ta ore[6], it is important from the commercial point of view (different prices and help to take a proper decision). Other analytical services include the determination of trace elements in rock and sediment samples for the Nigerian Geological Survey, Nigerian Mining Corporation and Oil Companies.

The XRF group has participated in different projects organized by the International Atomic Energy Agency (IAEA), Vienna such as Intercomparison survey of XRF Laboratories and Intercomparison analysis of marine sediment and biological samples.

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2. Funtua, I. I. and Oyewale, A. O. (1997). Elemental composition of Traditional Eye-Makeup (*Kwalli*) in Nigeria. *Journal Chemical Society of Nigeria*, vol. 22, pp160-163.
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Slovenia

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Contributors: P. Kump and M. Necemer

Research and development activities include:

- development of quantification software for radioisotope and tube excited X-ray fluorescence spectrometry, based on use of fundamental parameters and emission-transmission method
- development of sensitive XRF technique for aerosol analysis, utilising excitation at small incident angles
- development of fast semi-quantitative analysis of samples in powder form by TXRF
- designing and manufacturing of portable XRF systems with radioisotope and tube excitation for use in archaeometry and for the analysis of pigments on paintings.

Applications:

- analysis of geological samples (geochemistry applications)
- determination of P, S, Cl, K, Ca and some heavy metals in animal food (hay, grass silage and maize silage)
- routine aerosol analysis in urban areas close to industrial facilities
- analysis of pigments from old paintings and other artefacts by TXRF
- analysis of vines and bee honey for the contents of S and some heavy metals by TXRF
- analysis of thin layers (Ti, Cr, Ni, and Zn) used for anticorrosion protection

Spain

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The Archaeometry Unit (UA) of the Material Science Institute of the Valencia University (ICMUV) has carried out, by using a portable EDXRF equipment, analysis of works of art located in museums, churches, excavations, etc., along the whole Spanish territory. A close collaboration with the responsible for the artistic patrimony has been reflected in the realization of technical and analytical reports about the state of conservation, alterations and composition of the analyzed artistic patrimony.

The XRF activities of the UA include study of the following objects:

- Iberian polychrome sculpture on stone (collections of the Museo Arqueológico Nacional, Madrid and the Museo of the Alcudia, Alicante).
- Pigments of altarpieces from the XIV to XVI centuries (collections of the Museo de Bellas Artes of Valencia and Museo Nacional de Arte of Cataluña, Barcelona).
- Mural paintings from the XIV-XVI centuries.
- Iberian silver works (collections of the Museo of Alcoi, Alicante).
- Paintings on canvas from Joaquín Sorolla, XIX-XX centuries (collections of the Hispanic Society of America, Museo de Bellas Artes of Valencia, and Museo Nacional de Bellas Artes de Cuba).

A portable EDXRF system used for the analysis is extremely versatile, easy in operation and it allows to carry out both *in situ* and laboratory measurements in non-destructive and non-aggressive way, to provide the results often in real time. The instrument consists of an X-ray excitation source (X-ray tube) coupled to semiconductor detectors (Cd(Zn)Te or Si-PIN) by means of a mechanical device, and a pocket multi-channel analyser. To restrict the irradiated area on the sample the output X-ray beam is collimated by a 2 or 5 mm plastic collimators.

United Kingdom
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The analytical laboratories in the Department of Earth Sciences, The Open University, support a wide range of research projects involving geochemical investigations of igneous and metamorphic rocks. One of the techniques that supports this research is wavelength dispersive X-ray fluorescence where a small analytical group has developed procedures for the determination of major and trace elements in silicate rocks to high accuracy and precision. The quality of these data is supported by regular participation in the GeoPT proficiency testing programme. Work has also been undertaken in the development of the portable X-ray fluorescence technique for the *in situ* analysis of rocks and lithic archaeological artefacts. Applications to date, have involved applications of the technique to the characterisation of contaminated soil at a medieval lead smelter site, hazards associated with arsenic contamination at a heritage mineral processing site (both with the University of Sussex), and the provenancing of neolithic stone axes (with Dr Olwen Williams-Thorpe). A contribution is also being made to a project lead by Prof. George Fraser at the University of Leicester in the development of a portable XRF instrument to be flown on the Beagle 2/Mars Express mission to the surface of Mars in 2003.

Book of potential interest to the XRF community:

- Rene E. Van Grieken and Andrzej A. Markowicz, Eds., Handbook of X-RAY SPECTROMETRY, Second Edition, Revised and Expanded, Marcel Dekker, New York, 2002, 1016 pages.

Other publications:

- P.J. Potts, A.T. Ellis, P. Kregsamer, J. Marshall, Ch. Streli, M. West, and P. Wobrauschek, Atomic Spectrometry Update. X-ray Fluorescence Spectrometry, J. Anal. At. Spectrom., 2001, **16**, 1217-1237
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