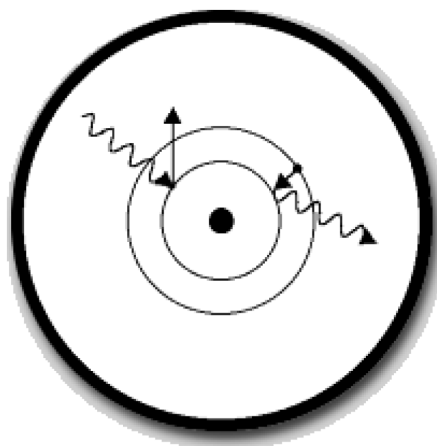


X-ray Fluorescence
in the IAEA and its
Member States

XRF



NEWS LETTER

Prepared by the
Agency's Laboratories,
Seibersdorf

Published by the
International Atomic Energy Agency
Vienna

No. 5

January 2003



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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.

Evaluation of uncertainty of elemental determination using energy-dispersive X-ray fluorescence technique and the emission-transmission method

A detailed procedure for quantification of uncertainty in EDXRF based on the secondary target excitation geometry and the emission-transmission (ET) method was developed. The uncertainty budget included major sources of uncertainty associated to the different steps of the overall analytical procedure such as calibration, sample preparation, measurements, and absorption correction procedure. It was demonstrated that the major contribution to the combined uncertainty comes from the calibration of the spectrometer, determination of mass per unit area and evaluation of the absorption correction factor. In case of trace element determination the uncertainty of the X-ray peak intensity is also an important factor. The approach proposed for quantifying uncertainty can be used for other modes of XRF analysis not only to identify and assess the contribution from the different sources of uncertainty but also to design an optimum analytical strategy to reduce the contribution of the critical parameters. A paper describing the approach and the results obtained for the EDXRF based on the ET method was accepted in the X-Ray Spectrometry Journal. For those interested in this topic the following publication is worth mentioning: S.L.R. Ellison, M. Rosslein and A. Williams, Quantifying Uncertainty in Analytical Measurement, Eurachem/CITAC Guide, Second edition, QUAM:2000. P1.

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

X-ray fluorescence applied for air pollution studies

It is well known that air particulates deposited on a filter form an ideal target for X-ray spectrometry that offers a fairly uniform detection limit, satisfactory speed, economy, and ease of operation. Moreover, XRS can perform direct multi-element analysis of a solid sample without pre-treatment. Quantitative XRF analysis of air particulates collected on filters is usually performed based on a thin-sample technique where both absorption and enhancement are neglected. However, even in such a case one has to check whether the criteria for the thin-sample technique are met. Furthermore, if the samples are of intermediate thickness, a correction procedure has to be applied. One of the simplest approaches is to calculate the absorption factors for all the elements determined based on the thickness and average atomic number of the material deposited. An alternative approach is based on the experimental assessment of the combined absorption properties of the analysed materials for the primary and fluorescent radiation by using the emission-transmission technique. For highly polluted regions and/or long collection time the deposit of the air particulates is of intermediate thickness and one has to consider the contribution due to enhancement effects. The simplest way to assess the effects is to calculate the enhancement factor for the intermediate thickness samples based on the thickness and average atomic number of the deposited material and well known expression for the enhancement factor for thick samples. To assess and correct for the particle size effects two different approaches are available. Since both of them require knowledge of the diameter of the fluorescent particles they can only be used in XRF analysis

of size-fractionated air particulates (collected by using cascade impactors or dichotomous samplers). In case the particle size is entirely unknown, an experimental correction based on two sources of primary radiation of different energy can be used. The procedures used for the assessment and correction of the interfering effects can also be used in support of the calculation of the overall uncertainty of the analytical results. As a quality control (QC) test to verify the accuracy of the conventional XRF analysis based on the correction procedures mentioned above, a total reflection XRF (TXRF) method was used. In this case air particulates were first decomposed in a microwave oven by using HNO₃ and H₂O₂, and next, the aliquots of 5 to 10 µl were placed onto quartz carriers and analysed by the TXRF method. A relevant paper was presented during the American Nuclear Society 2002 Winter Meeting held in Washington, D.C. from 17-21 November 2002.

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

Application of the backscatter fundamental parameter method with simultaneous excitation by ⁵⁵Fe and ¹⁰⁹Cd radioisotope sources

The work (performed in co-operation with Dr. P.J. Potts, United Kingdom) is based on simultaneous excitation with ⁵⁵Fe and ¹⁰⁹Cd sources that results in improved detection limits for low-Z elements as compared to the excitation with ¹⁰⁹Cd source alone. Quantification is based on the fundamental parameter (BFP) method where Ag K-series scattered radiation has been used to correct for the influence of the so-called dark matrix of the analysed samples. The measurements were performed with a portable spectrometer consisting of two annular excitation sources, a thermoelectrically cooled Si-PIN photodiode detector, and a battery operated power supply/amplifier/multi-channel analyser connected to a laptop computer for data acquisition and evaluation. A modified BFP algorithm was implemented in a computer program that was used to calculate the elemental concentrations in loose powder samples. The calibration of the BFP method was performed with a set of samples prepared from pure elements, element oxides or element compounds. A good accuracy was confirmed by the analysis of a few standard reference materials. In the future the scattered radiation from ⁵⁵Fe will be used to reduce the variation of the calibration factors. We hope the dual excitation method will improve the quantitative analysis of irregularly shaped/not flat samples that is a real challenge in *in-situ* applications of XRF technique. A relevant paper was presented at the 51st Denver X-ray Conference held from 27 July-2 August 2002.

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

XRF Laboratories Database

X-ray fluorescence is one of a few analytical techniques which applications are being promoted by the IAEA. In addition to provision of the equipment, expert services and training under the relevant Technical Cooperation projects, the IAEA disseminates information on the current development in methodology and applications of XRF techniques as well as encourages and facilitates cooperation among the XRF laboratories in both industrialised and developing Member States. Keeping in mind this mandate, the IAEA intends to establish a worldwide database of the XRF laboratories in order to provide its Member States with systematised and comprehensive information on the XRF facilities, expertise, techniques and applications. The XRF Laboratories database will be available on Internet and the Agency will update/extend it systematically. We kindly invite all of you to submit your input to the

database. Electronic version of simple questionnaire to be completed and submitted to the IAEA is available from Andrzej Markowicz (A.Markowicz@iaea.org). We would be grateful if you could inform other XRF groups/laboratories in your institution/country on this initiative and encourage them to submit their input to the XRF database.

Training at the IAEA Laboratories at Seibersdorf

As described in the third issue of the XRF Newsletter published in January 2002, the XRF Group at the IAEA Seibersdorf Laboratories provides training in methodology and applications of energy-dispersive X-ray fluorescence spectrometry. The Laboratory offers excellent training facilities and professional guidelines. The training programmes cover all aspects of XRF including underlying physical principles, sampling, sample preparation, instrumentation, measurements, quantification procedures, QA/QC, and special application projects tailored to the interests and needs of the fellows. The XRF Group is planning to organise at Seibersdorf a group fellowship training programme in methodology and applications of EDXRF analysis (basic level) for 6-8 fellows from 1 April – 30 June 2004. Moreover, individual training programmes and scientific visits can be accepted.

For more information please contact Andrzej Markowicz (A.Markowicz@iaea.org) or Dariusz Wegrzynek (D.Wegrzynek@iaea.org).

X-ray Fluorescence in Member States

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

The Philippines

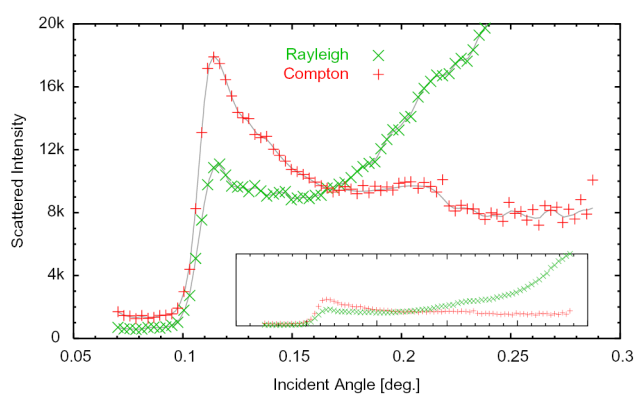
Philippine Nuclear Research Institute, Applied Physics Research Group

X-Ray Scattering Report 2002

Contributor: Virginia S. Calix (vscalix@pnri.dost.gov.ph)

In TXRF spectroscopy the scattered tube characteristic peaks have found variety of uses such as to estimate irradiated sample area, to calculate footprint corrections, and very recently to determine the molecular weight of polymer films. We examined the possibility of using the scattered peaks for thin-film thickness analysis by angle dispersive TXRF (AD-TXRF) for the case of low Z films (e.g., organic or polymer films, and SiO_2 coatings) on a high Z substrate such as metallic materials. For Mo target, the Compton and Rayleigh scattered peaks of the Mo characteristic lines are separated far enough to allow the intensities for each interaction to be extracted. The wide difference in the Compton and Rayleigh scattering amplitudes between the low Z (strong Compton scatterer) film and high Z (strong Rayleigh scatterer) substrate can be used to distinguish between film and substrate scattered signals. The feasibility of the method is illustrated for the case of a protective SiO_2 layer on a Gold mirror. The sample is of a high quality optical grade surface finish ($\lambda/20$) so effect of surface roughness is minimal. The critical angles of the film and substrate are far from each other thus providing a considerable angular range to observe the standing wave and/or intensity oscillations. The plot in the figure shows that the Compton intensity exhibits the interaction between the standing wave and the film.

We examined the performance of the IAEA TXRF spectrometer, which is intended for fixed angle use, in variable incident angle mode. For angle stepping the most important component of the spectrometer is the three-micrometer-legged sample support and tilt mechanism that acts like a lever—two micrometers acting as the fulcrum, the third acting as lever handle. Small and precise angle step can be performed by turning only the lever handle micrometer in one direction (to avoid backlash). However, this movement also causes the sample to be displaced below/above the incident beam which in turn causes intensity fall-off as the sample is brought away from the beam and an error in angle due to the incident beam being non-parallel. We developed a procedure to determine these systematic errors from the Compton and Rayleigh scattered peaks of Mo- $K\alpha$ and Mo- $K\beta$ of an angle scan of a blank SiO_2 . From the intensity of the scattered peaks the intensity-fall off with displacement can be evaluated. From the ratio of the Mo- $K\alpha$ and Mo- $K\beta$ scattered peaks the slight angle deviation due to displacement can be measured.



Mo- $K\alpha$ Compton and Rayleigh scattered peaks of a SiO_2 film on a Gold substrate versus incident angle.

Spectrum analysis in AD-TXRF differs from that of the traditional TXRF. In AD-TXRF, the study of one sample angle scan requires several energy spectra (having similar appearances) to be analyzed. We developed a Python module for non-linear least squares spectrum fitting having an embedded Fortran code in the inner loops for speed. With this module, fast (execution speed) Python scripts customized to analyze a particular series of similar looking spectra can be written easily. The spectrum model is organized in an object oriented manner such that the model is conceptually just a list of objects of spectrum components (e.g., peaks and backgrounds) and constraints objects (e.g., objects that constrain peak widths to system resolution). During fitting, a spectral model can be easily modified by adding or removing components to/from the list without affecting the state of the other components. This allows a model to be quickly adapted to changes in spectrum appearance such as when total reflection effects begin to manifest.

Spain

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Contributors: C. Roldán (Clodoaldo.roldan@uv.es); J.L. Ferrero.

The study of patrimonial works by non-destructive techniques has wakened up great interest because they allow the analysis of unique pieces without attempting their integrity. The Archaeometry Unit (UA) of the Instituto de Ciencia de los Materiales of the Universidad de Valencia (ICMUV) has carried out EDXRF analyses for the identification of forged works of art using portable instrumentation. In addition to the detection of forged works of art, EDXRF may help to obtain information of the art pieces that could be important to determine its value.

In recent works we have presented some examples of the use of the EDXRF spectrometry to obtain information that can be important to value a work of art. First, we have applied this technique to detect fakes in some paintings which could be attributed to Joaquín Sorolla. The comparison of the EDXRF spectra of these paintings with a database of well-known Sorolla's paintings (database made by the UA) gives additional arguments to judge about the originality of the work. The fact of detecting titanium in "*Carros en la Playa*" of the Museo de Bellas Artes de La Habana makes almost impossible that this painting was painted by Sorolla. In "*Portrait of Two Children*" we have detected zinc as the most important element, which is not observed in our database. This could indicate that this work is also a fake although it is not a conclusive argument.

In addition, the EDXRF technique has been found helpful to determine the degree of originality of a work of art because it is sometimes able to distinguish between the original part from the author and latter modifications from restorations. This has been used in the - "*Fondo de Lucillo Funerario Gótico de la Iglesia de San Esteban de Cuéllar*" among other works of art. The use of EDXRF analysis to obtain technological information of the process involved in producing the work of art for paintings and for gold-plated pieces has also been made. Finally, as example of the potential applications of the EDXRF analyses, we have reconstructed the original tonality of a degraded region of the oil on canvas paint "*Coronation*" (anonymous, s. XVIII) by comparing its EDXRF analyses with some patterns.

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2. M. Ardid, J. Ferrero, D. Juanes, C. Roldán, M. Crespo, M.E. Pernet, M. Marzal, M. Burke, S. Rovira, R. Vives. Identification of forged works of art by portable EDXRF spectrometry. *50th Annual Conference on Applications of X-ray Analysis*. Denver, Colorado, USA, 2002.
3. J.L. Ferrero, C. Roldán, D. Juanes, J. Carballo, J. Pereira, J.L. Lluch, C. García; M. Ardid. Reconstruction of the original tonality of a blue degraded smalt from the measurement of the relationship Co/Pb with a portable EDXRF spectrometer. *ART2002, 7th International Conference on Non-destructive Testing and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage*. Antwerp, Belgium, 2002.

Publications of potential interest to the XRF community:

1. P.J. Potts, A.T. Ellis, P. Kregsamer, J. Marshall, Ch. Strelis, M. West and P. Wobrauschek, Atomic spectrometry update. X-ray fluorescence spectrometry, *J. Anal. At. Spectrom.*, 2002, 17, 1439-1455
2. G. McGranahan and F. Murray, eds., "Air Pollution and Health in Rapidly Developing Countries", Earthscan, March 2003 (www.earthscan.co.uk)
3. Guidelines for Air Quality, World Health Organization, Geneva, 2000

XRF Newsletter No. 5

The XRF Newsletter is issued twice a year by the IAEA Laboratories in Seibersdorf.
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Printed by the IAEA in Austria,
January 2003

03-00137