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XRF Newsletter

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X-ray Fluorescence in the IAEA and its Member States

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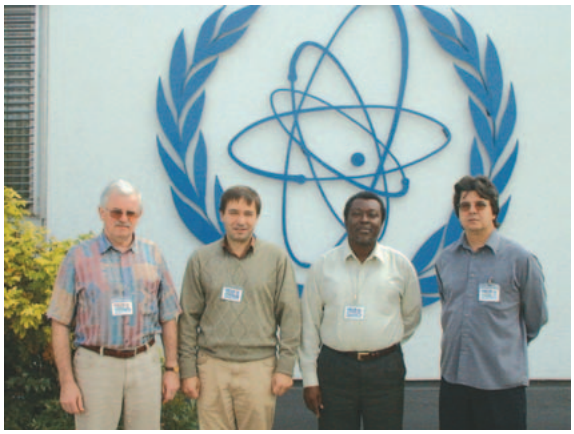
Activities in the IAEA XRF Laboratory



From left: A. Markowicz (Head, Instrumentation Unit), D. Wegrzynek (Leader, XRF Group), S. Bamford and E. Chinea-Cano

The XRF Newsletter is prepared by the Instrumentation Unit of the IAEA Laboratories of Seibersdorf. Current staff of the XRF Group in the Instrumentation Unit is on the photo.

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

In-situ applications of XRF techniques

X-ray fluorescence spectrometry is perhaps the first spectroscopic technique which can be successfully applied in the field and in industrial environments for *in situ* analysis of various materials. A modern, high resolution, portable XRF analyser brings to the field site not only an excellent performance often matching that of the laboratory instrument, but also unsurpassed savings in time and labour, contradicting the popular conviction of the inherent inferiority of portable instrumentation. Field-portable X-ray fluorescence (FPXRF) is an example of a well-balanced compromise between portability, ruggedness, reliability and analytical performance. Simplicity, speed of operation and flexible requirements for sample preparation are among the major features of FPXRF techniques. Major advantages of FPXRF over conventional laboratory-based analysis include: (i) immediate analytical results, which is important for interactive measurement programmes, e.g., assessing sites contaminated with heavy elements, remediation studies (rapid, on-site analyses incorporated into a field study programme provide the possibility of changing the density of sampling at any location, depending

on the results obtained), (ii) non-destructive analysis of objects that can neither be sampled nor removed to the laboratory for analysis, e.g., museum samples, works of art, archaeological samples.

Portable instrumentation can be used for both the direct *in situ* non-destructive analysis of samples and as a "mobile laboratory" transportable to field sites.

In 2000-2003 the IAEA run a CRP on "*In-situ* applications of XRF techniques". The participants of the CRP have developed, adapted and improved several quantitative (and semi-quantitative) methods for *in-situ* measurements. The proposed methods and procedures led to improved precision and accuracy of *in situ* element determination by XRF technique. The following improved correction algorithms and/or improvements in quantification procedures resulted from the CRP:

1. Extension of the range of standard reference materials used for calibration.
2. The use of site specific and matrix matched calibration samples.
3. Improved quantification procedures for analysis of painting's pigments and other objects of works of art.
4. Correction procedures for moisture/light matrix content, and surface irregularity effects.
5. Compensation for differences in size between calibration standards and analysed samples.
6. Method for estimating effective atomic number of analysed samples in support of quantification.
7. Estimation of low-*Z* matrix composition by applying emission-transmission method in support of quality control.
8. Applied corrections for surface roughness, mineralogy and preliminary study of weathering effects in the analysis of rock outcrops
9. Development of partial least squares (PLS) procedures to improve quantification.
10. Modification of a fundamental parameters correction procedure for dual excitation of samples by using ^{55}Fe and ^{109}Cd sources.

Moreover, sampling strategies and procedures as well as methods for *in situ* sample preparation and analysis have been elaborated during the course of the CRP. Based on the results of the CRP the following three harmonized guidelines/protocols for *in situ* XRF analysis were compiled:

1. Guidelines for *in situ* sampling and analysis of soils, sediments and rocks
2. Guidelines for using portable XRF equipment for non-destructive analysis of works of art
3. Sample preparation protocol for alloy characterization and scrap metal sorting by field portable x-ray fluorescence spectrometry

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

Quantifying uncertainty in XRF analysis

In July 2004 the Agency published an IAEA-TECDOC-1401 on "Quantifying uncertainty in nuclear analytical measurements". The document is a result of a Consultants' Meeting held in Vienna some years ago. It includes twelve examples of quantifying uncertainty for selected nuclear and related analytical methods such as EDXRF, PIXE, radio-chemical NAA, gamma spectrometry, alpha spectrometry, liquid scintillation counting, and mass spectrometry. Uncertainty in measurements close to detection limits is also covered. Three papers prepared by staff of the Instrumentation Unit at Seibersdorf are dealing with quantifying uncertainty (following the principles of the EURACHEM guide) in EDXRF analysis of thin, thick and intermediate thickness samples.

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

Recent involvement of IAEA in international discussions on air pollution issues

The IAEA has been involved in the participation and discussions at some recent international meetings on air pollution issues. This article therefore seeks to share with you some of the concerns, future directions, and recommendations expressed at the said meetings and also to re-emphasize the IAEA's on-going and planned programmes on air pollution issues.

The Executive Body of the Convention on Long-range Transboundary Air Pollution (LRTAP) had its latest meeting, its 21st Session, in December 2003 at Palais des Nations in Geneva, Switzerland. This Convention is one of the five environmental treaties negotiated by the United Nations Economic Commission for Europe. The protocols already in force are the 1988 NOx protocol, the 1991 Geneva VOC protocol, the 1994 sulphur protocol, the 1999 Gothenburg protocol, the 2003 POPs protocol, and the imminent entry into force of the protocol on Heavy Metals. The activities of the Executive Body for the convention were reported under two main categories: (1) the Cooperative Programme for monitoring and evaluation of long-range transmission of air pollutants in Europe (EMEP), and (2) the Working Group on Effects (WGE). It was noted that whereas the EMEP Eulerian model for integrated assessment provided satisfactory results for sulphur, nitrogen, and ozone, more work needed to be done for modelling of particulate matter. More observational quality data on particulate matter and its composition are required for evaluating and validating the model The WGE also reported on its international cooperative programs dealing respectively with effects on forests, rivers, materials, natural vegetation, integrated effects on ecosystems, and health effects. The contact link: http://www.unece.org/env/eb/welcome.html.

In April 2004, an international workshop on ***Particulate Matter Measurement and Modelling*** was organized through a collaborative program of EMEP, USEPA and Environment Canada at New Orleans, USA. The purpose of the workshop was to review the state of the science and current trends in particulate matter measurement and modelling. Topics discussed included: measurement programs, time-integrated measurements, continuous measurements, emission-based air quality models, receptor-based air quality models, measurement needs, and new directions. A draft of recommendations was presented to the EMEP steering Committee. For further details contact: http://www.emep.int/.

The IAEA also organized a Thematic Planning Meeting on ***The Role of Nuclear Analytical Techniques in Monitoring Air Pollution,*** in Vienna, Austria, June 2004. ***Thematic Planning*** is a process by which specific problems are identified for which the transfer of nuclear technology through technical co-operation can be expected to result in significant impact, because of the distinct advantages of the nuclear technology involved. Field experience and feedback from projects creates an awareness of national, regional and global problems that can be matched with existing nuclear technologies, as well as problems that can be addressed through Agency safety or security services. Thematic planning helps to identify opportunities for immediate application or research, as well as to identify constraints. Participants at this meeting reviewed past and on-going projects of the IAEA on airborne particulate matter, received inputs from other international bodies involved in air pollution studies, and produced a draft of recommendations to the IAEA. The recommendations rationalize why air pollution monitoring using nuclear analytical techniques can play an important role in air pollution monitoring, and seek to assist the Agency in defining its role and contribution to air pollution monitoring for the protection of human health and providing a sustainable environment for development. For further information on IAEA's programs on APM, contact A.Markowicz@iaea.org.

Combined X-ray fluorescence and absorption micro-tomography on U- and Pu-rich particles

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Introduction

Synchrotron X-ray micro-tomography has been used to study three-dimensional (3D) distributions of chemical elements in two U/Pu-rich environmental particles. Simultaneous fluorescence- and absorption tomography measurements have been performed. The recorded absorption images were used to correct the X-ray fluorescence sinograms for self-absorption within the sample. For the U/Pu-rich particle, which was recovered from the sea sediment matrix, a formation of an outer coating layer, made of Fe-rich sediment matrix surrounding the U/Pu-rich core, has been observed. The Pu-rich particle, collected on the surface of the Mururoa Atoll, did not show ongoing embedding of the plutonium element in the strontium-rich coral matrix.

Experimental

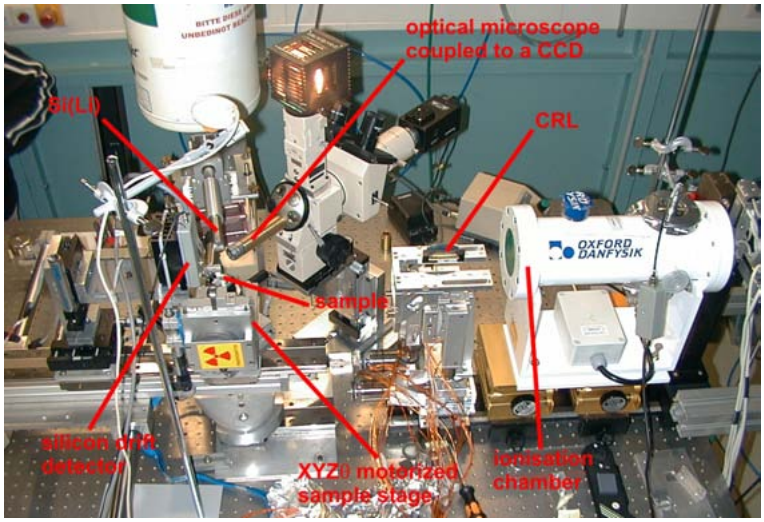

Fig. 1
A picture of the X-ray micro-tomography spectrometer set up at the ANKA, Fluo-Topo beamline.

The X-ray micro-tomography spectrometer designed by the IAEA laboratories Seibersdorf, Austria has been set up at the Topo hutch of the Fluo-Topo beamline at ANKA (Fig.1).

A multilayer monochromator was used to provide a monochromatic synchrotron x-ray beam at 18.83 keV for the determination of plutonium, uranium and the matrix elements distributions in individual particles. Focusing of the beam to a spot size of about 5µm was performed by means of a compound refractive lens (CRL), offering the required pencil-beam geometry for X-ray fluorescence micro-tomography. A fast silicon drift detector (SDD) allowing acquisition at high count rates was placed behind the sample to collect photons from the transmitted beam. The Si(Li) semiconductor detector, for detection of X-ray fluorescence photons, was mounted in the orbital plane at 90 degrees to the incoming beam. The samples were mounted on a XYZθ translation/rotation stage, allowing to perform lateral scans of the sample as well as a sample rotation by 360° necessary for fluorescence tomography. The data acquisition system consisted of 3 multichannel analyzers for collecting transmitted photons, fluorescence photons and monitoring the incident beam. Acquisition time was set to 0.15/0.10 s (Si(Li)/SDD) per pixel.

Results

The distributions of elements in two particles were investigated: in a U/Pu-rich particle recovered from the sea sediment near Thule, Greenland, and in a Pu-rich particle embedded in a coral matrix, collected in the Mururoa Atoll. The particles were scanned in pencil-beam geometry [1, 2]. For each particle, 64 area projections, separated by 5.625 degrees, consisting of 64 by 10 pixels were collected simultaneously in X-ray fluorescence and X-ray absorption

modes. The horizontal beam spacing was 19 μm and 11 μm for the Mururoa and the Thule particles, respectively. The corresponding vertical beam spacing was equal to 42 μm and 20 μm. The 3D distributions of Pu, U and the matrix elements (Sr and Fe) were reconstructed (see Fig. 2). A preliminary method of absorption effect correction was applied [3]. As can be noticed the Thule particle, recovered from the sea sediment, has been partially encapsulated in the Fe-rich sediment matrix during its long residence in the seabed. The Mururoa particle, recovered from the surface of the coral atoll, was found to be attached to the coral matrix (represented by Sr) only from one side. It suggests that the merging of plutonium with the matrix material occurred during the nuclear test explosion, the source of this particle.

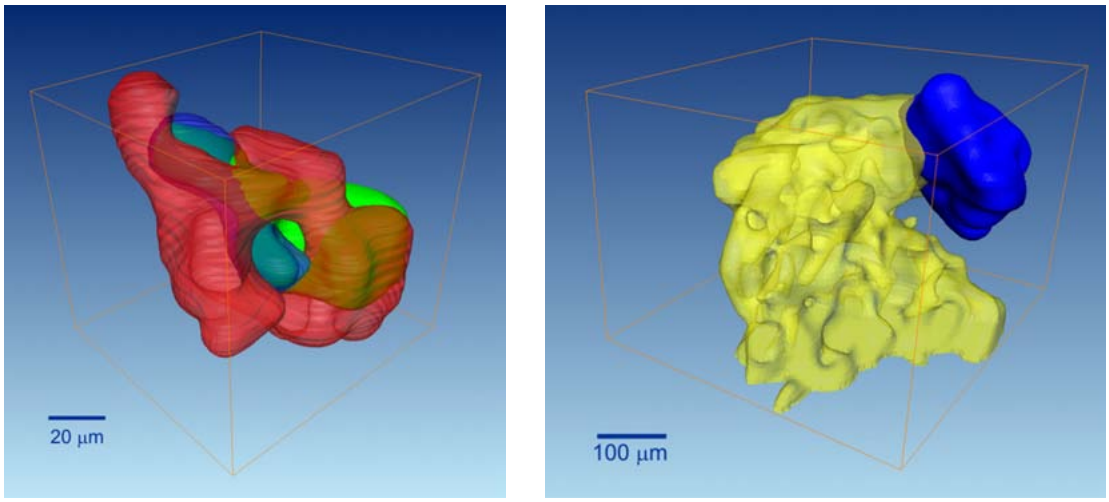

Fig. 2

Left: reconstructed distribution of elements in U/Pu-rich particle recovered from sea sediment, Thule, Greenland. The plutonium (blue) and uranium (green) are coated with iron (red) rich sediment matrix. Right: distribution of plutonium (blue) and strontium (yellow) in a particle collected at Mururoa Atoll.

Acknowledgements

This work was funded by the Austrian Science Fund (FWF) project number P 15740 and by the Agency's Laboratories Seibersdorf, IAEA, Vienna, Austria.

References

11. Kak A.C., Slaney M., Principles of Computerized Tomographic Imaging, IEEE Press, 1998.

12. Wegrzynek D., (2001) X-ray Spectrom. 30, 413-418.

13. Wegrzynek D., Markowicz A., Bamford S., Chinea-Cano E., Bogovac E., (2003) X-ray fluorescence analysis and computerized Tomographic imaging with a laboratory Micro-Beam Scanning Spectrometer, presented during 17th International Congress on X-Ray Optics and Microanalysis, September 22-26, Chamonix Mont-Blanc, France

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

X-ray Fluorescence in Member States

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

Argentina

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[(3)]Instituto Nacional de Tecnología Industrial

1. "Low Impurities in Scleroglucan Aqueous Systems: Removal Processes Control by Total Reflection X-Ray Fluorescence Analysis".

The aim of this work was to use the determination of trace elements by total reflection x-ray fluorescence (TXRF) for the performance study of three final purification methods of polysaccharide systems. TXRF shows two indispensable advantages to accomplish this study: the small quantities of sample required for the analysis and the avoidance of digesting the organic material. Aqueous scleroglucan systems with only impurity traces were studied, from diluted solutions to gels. The most efficient purification process was selected for each range of concentration.

2. "XRF-Analysis of Micronutrients in Endive Grown on Soils with Sewage Sludge"

A simple and fast method was developed for determining traces of Fe, Mn, Cu, Cr, Ni, Zn and Mo in endive using wavelength dispersive X-ray fluorescence spectrometry. Plants were grown in different sewage sludge compositions for 60 days in greenhouse conditions. The samples were compacted and analyzed after drying, milling and homogenization. The difficulty in obtaining certified standards with similar composition as the endives, was solved by preparing synthetic standards using cellulose as the basic component. The results were compared with those obtained by atomic absorption spectrometry. Good agreement for all elements was obtained. The detection limits were found to be: Fe = 1μg g^{-1}, Mn = 3μg g^{-1}, Cu = 2μg g^{-1}, Cr = 5μg g^{-1}, Ni = 1μg g^{-1}, Zn = 1μg g^{-1} and Mo = 3μg g^{-1}. These results permitted the evaluation of the potential use of sewage sludge as agriculture amendment.

3. "Study of a novel labelled scleroglucan macromolecule"

The aim of this work is to present a method to label the scleroglucan macromolecule without altering its properties. A fast and simple chemical reaction is presented here to label the polysaccharide scleroglucan to simplify its detection in static or dynamic experiences. The selected conditions of the chemical reaction permit the substitution of a few –OH groups of the polymer with iodine atoms. The quantification of the labelled macromolecule is possible by Radioactivity or Total Reflection X-Ray Fluorescence techniques, according to the used iodine isotope. These techniques were adjusted to their use in labelled (with ^{127}I or ^{131}I) scleroglucan solutions. A comparison of the physical properties of solutions of the labelled product and of the original polymer was done. Rheological behaviour, average molecular weight, polydispersity and density were tested and no major differences were found.

4. "Soil characterization by energy dispersive x-ray fluorescence: sampling strategy for "in situ" analysis"

This work describes a sampling strategy that will allow the use of portable EDXRF instruments for "in situ" soil analysis. The methodology covers a general approach to planning field investigations for any type of environmental studies and it was applied for a soil characterization study in the zone of Campana, Argentina, by evaluating data coming from an EDXRF spectrometer with a radioisotope excitation source. Simulating non-treated sampled as "in situ" samples and a soil characterization for Campana area was intended. "In situ" EDXRF methodology is a powerful

analytical modality with the advantage of providing data immediately, and allowing a fast general screening of the soil composition.

Morocco

CNESTEN (Centre National de l'Energie, des Sciences et des Techniques Nucléaires), B.P. 1382, R.P. 10001, Rabat, Morocco.
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The X-ray Fluorescence Laboratory of Elemental Analysis Unit (UAE) at National Center of Nuclear Sciences, Techniques and Energy has been involved in many studies and an IAEA Research Contract since its installation under an IAEA TC project and CNESTEN funds. The analytical techniques applied are conventional ED-XRF using both Mo X-ray tube and radio-isotopes sources (Fe-55, Cd-109 and Am-241) excitation systems, and TXRF with a monochromatic excitation using W/C multilayer crystal. HPGe and Si(Li) detectors coupled with Canberra and Ortec integrated signal systems are used. The missions of XRF laboratory are focused on 3 main activities : applied research in geochemistry and environment, analytical services and training. The last activity concerns student preparing Doctorate and IAEA trainees. With these facilities, we participated in several projects: air pollution monitoring, geochemistry of bassins (sediment, water and suspended particulate matter), medicinal plant characterization, bio-monitoring, heavy metals in blood of children, etc…

Staff of the XRF Laboratory include the Unit's Head Moussa Bounakhla, two scientists : Anas Doukkali and Khalid Embarch ; three superior technicians : Khalid Fathi, Mounir El Hassani and Rachid Touhami ; and three research students.

Example of TXRF application: Analysis of Aerosol samples by Total Reflection X-Ray Fluorescence Technique

The aim of this work is to adapt the Total Reflection X-Ray Fluorescence (TXRF) technique to the analysis of aerosols collected on reflectors usually used for PIXE. Aerosols were collected on quartz reflector plates. We used these reflectors instead of filters to allow a direct measurements without any digestion. 2 cascade impactors with 7 stages had been used for the collection. The particles are deposited separately according their sizes. This is very important for assessment of impact of air pollution on human health.

In order to prevent and/or to reduce the bounce-off effect on reflector, we used Vaseline oil which improved the coating technique. Petroleum in cyclohexane, or paraffin in toluene (as recommended by the manufacturer of the impactor) could be alternatives.

The following elements could be found after 3 hours of collection on the premises of CNESTEN (moderate pollution), and quantified with usual precision and accuracy after more elaborate calibration: S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, Br, As, Rb, Sr, Zr, Ba, Pb. For spectral reasons, Ga or Y were used as internal standard. The volume, concentration and acid concentration (ca. 10%) of the internal standard solution have a great influence on the quantification (re-dissolution of the collected aerosol, in case of pipetting after collection) and should be studied carefully. The calibration of the TXRF spectrometer with a new sample reflector holder plate, for both reflectors with the usual diameter of 30 mm and the smaller one as used in the impactor stages, was established for a concentration range of 5-30 ppm (not adequate for some elements in the collected aerosols).

Some reference papers published in Proceedings and International Journals :

- *Elemental Analysis of Moroccan Marine Sediments using INAA and XRF*

M.Bounakhla, A. Sabir, M. Labraimi, A. Ait Haddou, A. El Hamdaoui , M. Bahlouli, M. El Maghraoui, P. Kump
IAEA-SM-344/97, Harmonization of Health Related Environmental Measurements using Nuclear and Isotopic Techniques (Proc. Symposium Hyderabad, India, 4-7 November 1996), IAEA, Vienna, (1997)

- *The CNESTEN ED-XRF spectrometers- sensitivity, calibration and Application to geochemistry*

Rahmani, M. Bounakhla, F. Benyaich and A. Saadane
Journal of Advances in X-ray Analysis, Vol.44, Proceedings of 49th Annual Conference on Application of X-ray Analysis, 31 July – 4 August 2000, Denver, Colorado, U.S.A

- *Air pollution assessment of Salé's city (Morocco)*

M. Bounakhla, A. Fatah, K. Embarch, R. Azami, A. Sabir, A. Nejjar, R. Cherkaoui, A. Gaudry
J. Phys. IV France 107 (2003) 211-214

- *Determination of some heavy metals (Fe, Cu, Zn and Pb) in blood by total reflection X-ray fluorescence*

M. Bounakhla, A. Doukkali, K. Lalaoui, B. Attrassi, H. Aguenaou
J. Phys. IV France 107 (2003) 203-206

- *Comparison of 14 MeV-NAA, k0-NAA and XRF for air pollution bio-monitoring*

A. Senhou, A. Chouak, R. Cherkaoui, M. Lferde, A. Elyahaoui, T. Elkhoukhi, M. Bounakhla, K. Embarch, X. Bertho, A. Gaudry, S. Ayrault, D. Piccot,
Journal of Radioanalytical and Nuclear Chemistry, Vol 253, N°2, (2002) 247-252

- *TXRF interest for metal determinations in water pollution: case of Bouregreg river"*

A. El Hamdaoui, S. Cohen-Jonathan, M. Bounakhla, P. Duboi et M. Ibn Majah
Cahiers de l'Association Scientifique Européenne pour l'eau et la santé . Volume 7 - N° 1-2002 (p. 15 à 22)

Slovenia

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In the past year we were involved in the analysis of organic samples. The TXRF technique with the monochromatic excitation was found to be very useful in the analysis of bee honey and botany samples (leaves, roots, seeds, etc). Previously mainly the AAS was utilized and just few elements were selected to be measured. With TXRF all the elements from Si to Pb were determined and only Cd in case of low concentrations was measured by AAS. In study of the physiology processes in plants, correlations between different elements are also important. The results of this work will be published in three papers in addition to two to three diploma thesis. Another achievement was the construction of the XRF analyser with 1 mm diameter excitation beam, which can be used in museums and art galleries. It is equipped with the video camera, which is used to position and control the analysed spot. For excitation a 50 W X-ray tube is used and spectrometry is based on a Si-PIN detector.

For another user, which is involved in sorting of disposed metals, an analyser was constructed using a 3 W cold cathode X-ray tube and Si-PIN detector. The system is small, light, and practical for fast analysis also in-situ.

Spain

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Contributors: C. Roldán (clodoaldo.roldan@uv.es), J.L. Ferrero

Instrumental facilities of the ICMUV include: a Total-reflection X-Ray Fluorescence (TXRF), laboratory and portable Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometers. These equipments are employed in the field of the art and archaeometry.

Current projects are:

EDXRF analysis of blue pigments used in Valencian ceramics.

EDXRF analyses of cobalt-blue pigments were made on 73 pieces of Valencian ceramics from the beginning of the 14th century up to 20th century. These ceramic samples have the pigment decoration applied together with a tin opacified lead glaze cover on the clay body. The comparison between EDXRF spectra from coloured and non-coloured areas provides information about the pigment composition. The following elements: Mn, Fe, Co, Ni, Cu, Zn and As are identified as characteristics of the blue pigments. Different association of these elements as well as correlation with the chronology of the samples were found. These results can be used for identifying the different types of cobalt ores employed in the manufacture of the blue pigments to study their provenance.

Non-destructive analysis of paper supports used in prints

In paper based works of art it is not possible to separate the support from the work of the author. Then, the maximum knowledge of the support in this kind of works is desirable. In this work, Energy Dispersive X-Ray Fluorescence (EDXRF) was used to determine the elemental composition of a set of European and Oriental papers from the 20th

century and an Arabian paper from the 14th century. These papers were manufactured with different production techniques and used as support for writing, drawing and printing. Normalised fluorescence yields of the elements to the weight of the paper show that there are some correlations between its elemental composition and the type of paper, provenance and use. Therefore, the Energy Dispersive X-Ray Fluorescence (EDXRF) technique could be used for a better characterization and classification of the paper supports used in prints.

References:

C. Roldán, J. Coll, J. L. Ferrero
EDXRF analysis of blue pigments used in Valencian ceramics from the 14th century to the modern times. To be published.

M. Ardid, J.L. Ferrero, M. E. Pernett, C. Roldán, R.Vives
EDXRF study of paper supports used in prints. Presented in the EXRS-2004 Conference. Alghero (Italy), 6-11 July, 2004.

Validation of X-ray fluorescence technique (summary of a relevant paper)

One of the most important challenges that the X-ray fluorescence community is facing in the recent years is the validation of the analytical techniques. Nevertheless, due to the inherent difficulties of XRF methods in this respect and probably because it is a rather cumbersome task, the amount of published works is not very abundant. To illustrate, notice that a quick internet search for "analytical (method validation)" produces some 16,600 records, but a search for "xrf analytical (method validation)" returns only 855 hits (~5%). In this context the appearance of dedicated papers in the specialized literature is of special interest. That is the case of a very recent article by P. Morgenstern, L. Bruggemann and R. Wennrich entitled "Validation of an X-ray methodology with environmental concern" (Spectrochimica Acta Part B 59 (2004) 185–197). This work has the benefit of being, both a practical guide and sound theoretical assay. It should be remembered that "doing a thorough method validation can be tedious, but the consequences of not doing it right are wasted time, money, and resources" (J. Mark Green, Analytical Chemistry 1996, (68) 305A-309A)

As it is well known, method validation is the process of proving that an analytical procedure is suitable for its intended use. Methods need to be validated or revalidated:

- before their introduction into routine use;
- if there is a change in the conditions for which the method has been validated;
- if the method itself changes outside the original scope.

Although, in the ISO/IEC Guide 25 the chapter on the validation of methods lists nine validation parameters, for practical purposes a particular subset can be used. In the discussed paper, validation was carried out in terms of precision, trueness, measurement uncertainty, limit of detection and test for homogeneity of the sample material. Thus the method was validated:

- for screening of contaminated sediments and soils to investigate anthropogenic impacts;
- to get an insight in both the sources of environmental pollution and the distribution of analytes in contaminated areas;
- to examine and optimize remediation processes.

Yet, the validation is challenging. The most important problems are associated to the large ranges of analyte concentrations as well as unexpected changes of the sample morphology and matrix composition. The authors applied a matrix correction algorithm to the raw data and obtained linear relationships between the corrected fluorescence intensity and analyte concentration, therefore they make use of the tools of regression analysis as a base to quantify the performance capabilities of the analytical method.

The major components were calibrated using a set of diluted (fused with $Li_2B_4O_7$) reference materials, whereas for the trace elements pellets (20% wax) were employed. The authors noted that special care have to be taken when selecting the reference materials.

The results of the statistical treatment of the corresponding data indicated that, in general, for all analytes the precision is substantially influenced by sample preparation. The dependence of the precision on the concentration was evaluated and it was shown that from certain concentration (~100 mg/kg) precision behaves asymptotically and can be regarded as a constant.

The authors' conclusions:

- Steps toward the validation of XRF analysis can be performed with relatively reasonable effort applying tools of regression analysis in consideration of the recommended guidelines.
- The application of validation procedures to the experimental data yielded reliable information about precision, measurement uncertainty, limit of detection and trueness with reference to the whole concentration range and within the scope of matrices defined by the used reference materials. Both the estimation of the validation parameters and the examination of trueness were performed by regression analysis applied to scatter diagrams (certified vs. measured concentration values), which are on the one hand based on the calibration samples and on the other hand on a set of additional reference samples not included in the calibration routine.
- The results of the validation procedures meet the requirements to quantify the performance of the used XRF method (including the influence of sample preparation) and to examine the investigated calibration strategy with regard to fitness for purpose.
- Concerning the determination of traces of heavy metals, the test procedures yielded according to the expectations somewhat increased values for the limits of detection (~5 mg/kg) and combined measurement uncertainties (~3 mg/kg), as commonly reported with respect to specified types of matrices.
- Orthogonal regression analysis applied to the validation data indicated trueness for nearly all analytes of interest.

For more information please refer to the original paper.

Publications of potential interest to the XRF community

[1] IAEA-TECDOC-1401, Quantifying uncertainty in nuclear analytical measurements, IAEA, July 2004.

[2] M. Cullen, Ed., Atomic Spectroscopy in Elemental Analysis, Analytical Chemistry Series, J.M. Chalmers, A.J. Handley (Eds.), Blackwell Publishing, Oxford, UK, 2004.

[3] M. Martini, M. Milazzo and M. Piacentini, Physics Methods in Archaeometry, Volume 154 International School of Physics "Enrico Fermi", IOS Press, Amsterdam, 2004

[4] B.W. Wenclawiak, M. Koch, E. Hadjicostas (Eds.), Quality Assurance in Analytical Chemistry, Springer, Berlin Heidelberg New York Tokyo, 2004.

[5] Quality system implementation for nuclear analytical techniques, IAEA, Vienna, Training Course Series No. 24, July 2004.

Announcement of Vienna University of Technology: Atominstitut and Institute of Solid State Physics on *"Summer School in X-ray fluorescence Analysis"*

Topics: Wavelength dispersive XRF, Energy dispersive XRF and Total reflection XRF

General: In the run of this Vienna Summer School of XRF a workshop will be organized comprising EDXRS, TXRF and WDXRS practical exercises, fundamental experiments and analysis of various samples. This workshop will be held at the Atominstitut and the Institute of Solid State Physics of the Vienna University of Technology.

Supervisors: Christina Streli, Peter Wobrauschek and Michael Mantler.

Program: The workshop will be held in 5 days, each day covering an individual topic

- WDXRS of a set of samples
- EDXRS of the same set of samples
- TXRF chemical analysis aerosols, orchard leaves and water samples
- TXRF of ultra traces on Si wafer surfaces.
- Sample preparation techniques.

The workshop will be organized in a 2 hours theoretical introduction and explanation of the actual days program, followed by the 6 hours hands on practical exercises in the lab under the supervision of instructors. Small working groups of 2-3 participants will be organized for the measurements with the respective XRS equipment.

The following X-ray equipment is available

- EDXRF: Tracor Northern TN 5000 (Thermo-Electron Corporation)
- Wafer analyzers: Atomika models 8010 and 8030 (FEI)
- TXRF: with Atomika EXTRA II (FEI) and Atominstitut special TXRF chambers including light element analyzer, Atominstitut Micro XRF with a polycapillary in a vacuum chamber
- Wavelength dispersive equipment: ARL 8060 (ATI) and Siemens SRS 303AS

The goal of the workshop is to perform each day the qualitative and quantitative analysis of several samples and comparison of the results with certified values or among different techniques.

The final is a short briefing and response in discussions with the supervisors and a certificate of participation in this **Summer school in XRF**.

Time: 11-15 July 2005

Location: Vienna, Austria University of Technology

The number of participants is restricted to 10-15 and the acceptance is made due to first come first serve principle. For details contact us and read the homepage updates "Summerschool"

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IAEA Proficiency Test for XRF laboratories

The IAEA Laboratories at Seibersdorf will organize the world-wide proficiency test designed for the XRF laboratories involved in the analysis of various materials.

Proficiency test is 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 test involves distributing to participating laboratories sample of biological origin with established homogeneity and known composition. The laboratories are requested to analyze the sample using established techniques following their analytical procedures. The results must be returned to the organizers (tentatively by the end of January 2005) for evaluation according to recognized international procedures based on z- and u-scores. The final report of the proficiency test will be distributed to the participants not later than 3 months after submission of the results. Based on the results of the proficiency test each participating laboratory will be able to assess their analytical results by using the specified standard of performance and, if appropriate, to identify discrepancies and to correct their analytical procedures. All the results submitted under the proficiency test will be treated as fully confidential.

In case you are interested in taking part in the proficiency test please inform A. Markowicz (e-mail: A.Markowicz@iaea.org) immediately. The laboratories which confirm their willingness to join the exercise will receive all necessary details on the material for the analysis and the reporting instructions.

IAEA International Atomic Energy Agency

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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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