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XRF Newsletter

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X-Ray Fluorescence in the IAEA and its Member States

In This Issue

Activities in the IAEA XRF Laboratory

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

Determination of elemental concentrations in samples of low mass

A procedure for quantitative analysis of minute, powdered samples has been developed. The procedure uses finely collimated beam of primary X-rays and a scanning X-ray spectrometer for determination of elemental concentrations in samples with masses less than 1 mg. This procedure has been proven useful for examination of the homogeneity of candidate reference materials and for determination of the minimum mass of the material which should be taken for chemical analysis.

The analysis was performed with an XRF spectrometer consisting of 3 kW Mo-anode X-rays tube, liquid nitrogen-cooled Si(Li) detector, thermoelectrically-cooled silicon drift detector (SDD), and a computer-controlled sample positioning stage. The primary beam was collimated down to the diameter of 0.6 mm (FWHM) with a silver collimator. The tube was operated at 20 kV/5 mA and the samples were scanned with measuring time per point ranging from 0.3 s to 1 s, live time. An overview of the measuring geometry is shown in Fig. 1.

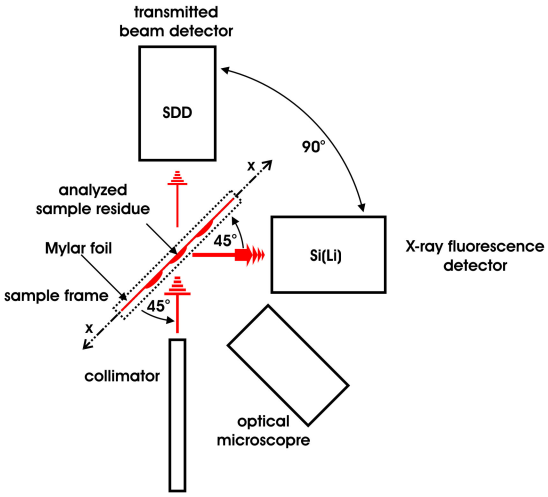

Fig. 1. A scheme of the measuring geometry. The SDD is utilized to measure the energy dispersive spectra of the transmitted beam and the Si(Li) detector collects the X-ray fluorescence radiation excited in the dried residue of the sample at a given position.

The distribution of the transmitted beam intensity and the intensity of Ti-Kα peak in the form of bitmap images are shown on Fig.2.

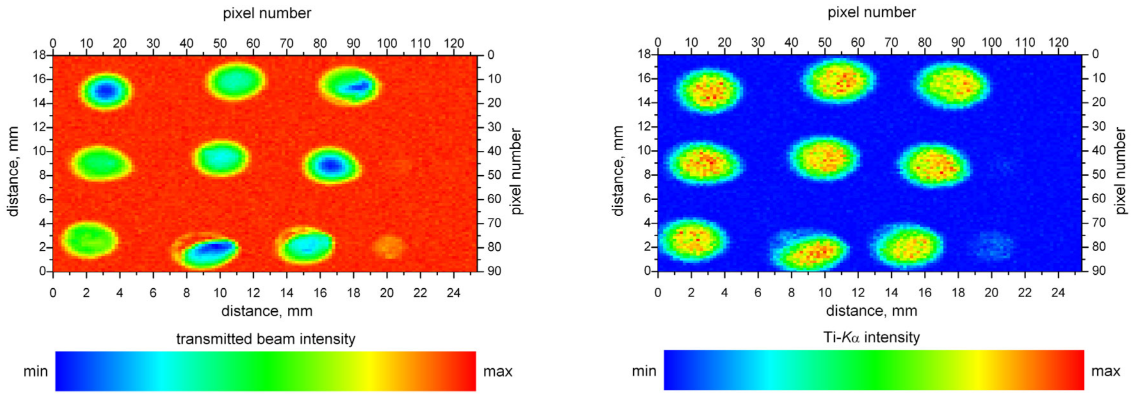

Fig. 2. The distribution of the intensity of the transmitted beam and the intensity Ti-*K*α signal over the scanned area containing the dried residue spots. The nine clearly visible spots correspond to the dried aliquots of the analysed sample. The weak spot in the lower right corner (seen on both images) corresponds to the dried residue of the standard solution. The scanned area was 25.4×18 mm^2 (128×91 pixels).

The cumulative spectra were used to determine the concentrations of elements in the analysed samples (example of the results in Table 1).

Table 1. Elemental concentrations for a standard reference material. The uncertainties of the determined concentrations and the uncertainties of the reference values are shown in parentheses.

Element	Concentrations determined in the low mass (~ 1 mg) samples	Bulk concentration values of the certified reference material
	[wt. %]	
Ti	0.884	0.82
	(0.082)	(0.055)
Fe	7.91	6.8
	(0.24)	(0.3)
	µg/g	
Cr	352	288
	(22)	(50)
Mn	1757	1670
	(58)	(90)

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

Metrological traceability

One of the current efforts of the XRF Group is related to development of a procedure for metrological traceability of the XRF technique. Below there are some thoughts about the topic.

Any analytical technique can produce results. However, for the measurement result to be reliable, it must be comparable to recognized and approved standards. Traceability therefore involves the process of developing and implementing procedures by which quantitative results of an analytical measurement can be traced back to the international standard unit of measurement (SI units). These procedures will have to be developed by the respective laboratories, owing to the differences in analytical facilities, and purposes of the measurements. The International Vocabulary of Basic and General Terms in Metrology defines traceability as

> "… the property of the result of a measurement or the value of a standard whereby it can be related to ***stated references***, usually national or international standards, through an ***unbroken chain of comparisons,*** all having ***stated uncertainties.***"

Traceability of measurement results is one of the requirements in preparing towards Laboratory Accreditation to ISO/IEC 17205. There are a few guidance documents on traceability available, but practical implementation is yet to be distilled out of these documents and harmonized for specific analytical techniques.

Elements of Traceability

In order to support a claim of the establishment of traceability, the following conditions among others, should be met:

1. Analytical results have been linked to known values (reference standards) or accepted methods (reference methods) – ***stated references.***
2. Traceability can be followed through a hierarchy of standards or methods to a measurement scale or unit – ***unbroken chain of comparisons.***
3. An uncertainty budget has been carried out for the significant stages in the measurements and methods used – ***stated uncertainties.***

Since traceability must be an integral part of a quality control system, it is also expected that:

4. Measurement conditions, procedure for calibration, and calculations have been clearly and sufficiently specified and documented.
5. There exist evidence of the implementation of supplementary quality control procedures (internal and external quality control practices such as statistical control charts, participation in intercomparison exercises, and proficiency tests).

Calibration is one of the pathways through which traceability linkage is established. It is an operation that compares the unknown value of the sample of interest with known values (standards) for the purpose of

- ensuring the correct functioning of the equipment (equipment calibration),
- establishing an energy-channel relationship for analyte identity (energy calibration), and
- establishing an intensity-concentration relationship for analyte (method calibration).

The quality of a calibration has a direct influence on the measurement uncertainty of an analytical result. In addition, the correctness of the working equation (method specification) in representing the real situation is assessed through **validation**, and **evaluated uncertainties. Method validation**, therefore, serves as a means for assessing possible sources of error and facilitating their control by elimination, reduction or correction. Validation is carried out taking also into consideration: scope of method, accuracy, sensitivity, selectivity, linear range, and limit of detection. This helps in confirming the adequacy of the method specification. Method validation is realized by carrying out measurements on appropriate reference material or comparison with results of reliable independent methods. This is due to the fact that result values in certified reference materials are of a higher meteorological level than individual laboratory results.

"***Uncertainty*** is the parameter associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand."

It incorporates all components of uncertainty from the various stages of the measurement and the analytical process (uncertainty budget). The uncertainty estimation process may be summarized in the following steps:

- **Specification of measurand**
  This step requires that a clear indication of the measurand, and statement of the relationship between the measurand and the input parameters be provided.
- **Identification of uncertainty sources**
  There is the need to produce a list of possible sources that contribute to the uncertainty on the input parameters mentioned above. It should be borne in mind also, the assumptions and approximations employed in the measurement method and procedure.
- **Quantification of uncertainty components**
  The contribution from each identified uncertainty source must be evaluated separately, or accounted for from existing data
- **Calculation of combined uncertainty**
  The overall uncertainty must be calculated by combining the effects of the significant uncertainty components evaluated.

The establishment of traceability of analytical results forms an integral part in the implementation of a quality system for any analytical/calibration laboratory. The achievement and demonstration of traceability implies that the values of the measurement results are reliable due to the facts that: the accuracy of the values are comparable to that of an accepted national or international standards, degree of uncertainties have been stated, and the results are reproducible.

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

Final Research Co-ordination Meeting on "In-situ Applications of XRF Techniques"

Final Research Co-ordination Meeting (RCM) under Co-ordinated Research Project (CRP) on "In-situ Applications of XRF Techniques" was held in Vienna from 8-12 September 2003. The participants from Albania, Argentina, Belgium, Democratic Republic of China, Ghana, Hungary, Italy, Pakistan, Poland, Romania, Slovenia, United Kingdom reviewed the activities and research outputs of the CRP, with a special emphasis on improvements in quantification and correction procedures as well as on harmonised operating procedures for selected in-situ applications, including alloy characterisation and metal scraps sorting, non-destructive analysis of works of art, analysis of soils, sediments and rocks. Technical document with the results of the CRP will be available in the last quarter of 2004.

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

X-ray Fluorescence in Member States

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

Austria

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A new TXRF vacuum chamber with sample changer

A new vacuum chamber with sample changer for TXRF was designed and built by the X-ray group of the Atominstitut. The main features are: a silicon drift detector with 140 eV energy resolution at 5.9 keV, compact handy design and electrical cooling (no liquid nitrogen is required). A 12 position tray built inside the vacuum chamber allows multiple sample handling. Measurements under vacuum with monochromatic excitation using a multilayer monochromator are thus possible. The complete system includes X-ray generator and X-ray tube with Mo anode, a closed circuit cooling system, vacuum chamber, monochromator unit, sample changer including controller and 12 quartz reflectors, detector, amplifier, and MCA. The software allows automatic measuring cycles, spectra are stored in QXAS format. The standard configuration includes a Mo-tube, but the system is flexible to be adapted for Cu or Cr anode X-ray tube, allowing the more efficient excitation for low-Z elements. Fig. 1 shows the setup (called WOBISTRAX) excluding generator and PC.

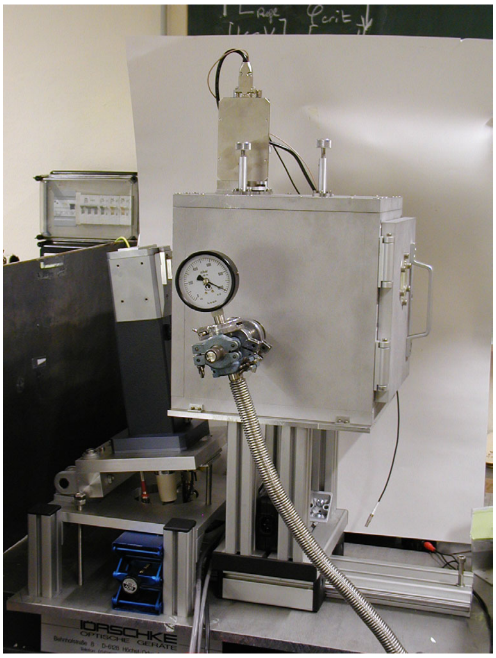

Fig. 1. WOBISTRAX overall view.

Fig.2. WOBISTRAX sample changer.

The performance is shown in Fig. 3, where a spectrum of a 900 pg Rb sample is presented, excited with Mo-Kα radiation, 50 kV and 40 mA, 100 s measuring time. This spectrum shows the excellent background conditions which led to detection limits of 0.7 pg after peak evaluation with QXAS, extrapolated for 1000 s. Fig. 4 shows a spectrum of a real sample, 10 µl of NIST 1643c SRM, water sample were dried on a reflector. The concentrations of the trace elements are in the µg/l range.

Rough pump vacuum of 10-2 mbar in the TXRF chamber reduces the background from air as well as the Ar-K line at 2.96 keV., that further improves the detection limits. Low Z elements down to Na can be measured, because there is no absorption of low energy fluorescence radiation from low Z elements in air and reduced absorption in a 8 µm Be window of SDD detector. However, for more efficient excitation a Cr anode X-ray tube has to be used. With an ultra thin window detector the detectable element range can be extended down to Oxygen.

WOBISTRAX fulfils the Austrian safety regulations for full radiation protection and can be operated outside control area. One set-up was successfully installed at ICENS, Kingston, Jamaica under the IAEA TC project. It will be used for trace element analysis of environmental samples (soils) and medical samples (blood).

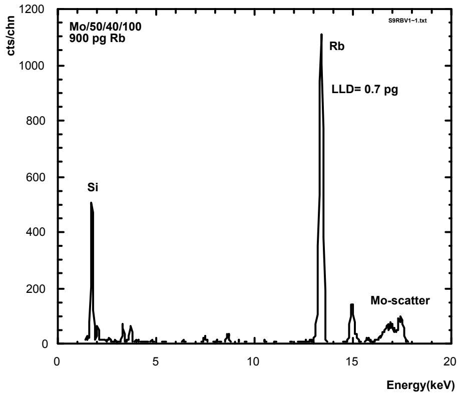

Fig. 3. Spectrum of 900 pg Rb showing Detection Limit of 0.7 pg when using Mo-Kα excitation 50 kV and 40 mA, 1000s.

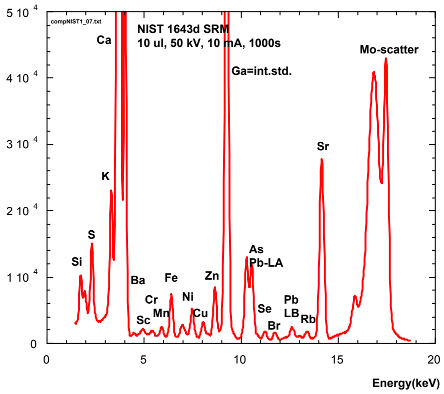

Fig. 4. Spectrum of NIST 1543 water sample, 10 µL.

Greece

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The Laboratory of Material Analysis (LMA) of the Institute of Nuclear Physics (INP) at the National Center for Scientific Research (NCSR) "Demokritos", has been involved very actively during the past few years in the development, evaluation and analytical application of portable X-Ray Fluorescence (XRF) instruments, applied in particular for the non-destructive analysis of cultural materials. The study, conservation and preservation of cultural materials are considered nowadays issues of main concern for countries and international cultural organizations. Due to the strong interest and motivation from archaeologists, conservators and archaeometrical scientists in Greece and elsewhere, a large network has been developed involving the LMA and archaeologists/conservator scientists from Museums (Benaki Museum in Athens), Cultural Foundations (Thera Foundation P. Nomikos), the Greek Ministry of Culture-Conservation Department, Foreign Schools in Greece (American School of Classical Studies, French School of Athens), Universities (Department of Conservation of Antiquities & Works of Art in the Technological Educational Institution of Athens, University of Cincinnatti, Universite de Paris I, Pantheon Sorbonne), private sectors (THETIS, Thetis Authentics - Science and Techniques for Art History Conservation Ltd) and Institutions (Centre de Recherché et de Rastauration des Musees de France, LNS-INFN, LANDIS group). A variety of cultural materials/artifacts have been examined so far, including ceramic vases with colored decoration(1), bronze artifacts(3), wall-painting pigments(4,5), traces of polychromy on marble sculptures, Gold and Silver ancient jewelry(6), Gemstones, Roman Coins(7).

Our research and analytical applications of the in-situ XRF analysis have been focused so far on the following: 1) optimum selection and integration of portable XRF instrumentation for improving analytical and sensitivity range 2) evaluation of the potential of in-situ XRF analysis to provide specific answers to archaeometrical/conservation problems on various kind of cultural materials 3) complementary role of the in-situ XRF analysis to other recently developed analytical techniques based on portable instrumentation (XRD, PIXE-alpha), and 4) dissemination of the proper use of the XRF technique in the field of conservation science through training courses for conservators.

The LMA has designed, developed, evaluated and used in-situ for archaeometrical research the following portable XRF spectrometers:

1. A portable tube excited XRF spectrometer:

It consists of a PIN detector (XR-100T, Amptek Inc.), a Rh-anode side-window X-ray tube of 50 Watt power with 125 μm Be window (Model XTF5011, Oxford) and an MCA for data acquisition (MCA8000A, Amptek Inc.). The X-ray tube spectrum can be filtered, by inserting a composite set of different materials. Two laser pointers were mounted in the set-up in such a way that the intersection point of their beams coincides with the cross-point of the incident X-ray beam and the detector axis. The spectrometer head is attached to an X-Y-Z stage allowing a movement of about 20 cm in the X-Y directions, whereas in the vertical axis a movement from 30 cm up to 160 cm is possible in order to analyse large objects (pigments on wall-paintings, marble or bronze statues).

2. A portable radioisotope induced XRF spectrometer

It includes two point radioactive sources, a Cd-109 and an Am-241 coupled with a PIN X-ray detector (XR-100T, Amptek Inc). The X-ray source and the detector were mounted in a compact geometry that optimises both excitation and detection conditions. The irradiated area was restricted by proper collimation to about 3-4 mm^2.

3. A portable semi-micro XRF spectrometer

It consists of a low power X-ray tube, a Si-PIN X-ray detector (XR-100CR Amptek Inc.) of 25 mm^2 crystal area and 300 μm crystal thickness, an optical microscope for visualization of the analysed spot and several mechanical parts necessary for the alignment and mounting of the aforementioned components. The exciting source of the μ-XRF equipment is a 1.6W battery operated end-window X-ray tube with a grounded Au anode initially manufactured for medical purposes. The Be probe's end external cover is made of a Tungsten-Copper alloy rod and a Pt disc collimator having a pin-hole of 240 μm. The Tungsten-Copper alloy tube is placed on an X-Y positioning stage. Visualization of the analysed object is performed by using an optical microscope. The detection limits from 0.25 to 0.55 ng for the elements in the range from Ca-Cu were obtained (at 1000 s measuring time). In the near future, polycapillary lenses will also be tested in order to improve spatial resolution (down to a few tens of microns) and to further improve the absolute detection limits.

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Hungary

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XRF and XANES analysis of hot/cold particles complemented by mass sensitive analysis for source identification

The Health and Environmental Physics Department of KFKI Atomic Energy Research Institute (AEKI) has strongly cooperated with the Institute for Transuranium Elements (ITU) of the European Commission to develop complementary micro-analytical techniques that are capable to determine the presence of low specific activity, long lived radioisotopes in environmental samples. The abundance of such particles can be very low in the environment, like the sediments of the Irish sea or particles from crashed atomic bombs. With optimal sample preparation 1 out of 10^5 particles can be identified. Further the small concentration of actinides in the particles can be determined by single particle analysis X-ray emission methods (EPMA or μ-XRF). The combination of conventional particle analysis techniques like EPMA and laboratory micro-XRF available at AEKI enables to locate sample areas with elevated actinide concentration and further synchrotron radiation XRF and XANES analysis reveals the quantitative trace composition and valence state of the actinide. After relocation of the analysed particle the nuclide composition can be determined by ITU's CAMECA IMS 6f secondary ion mass spectrometer. With the combination of the above high sensitivity techniques 10^{-13} g of long lived radioactive isotope can be determined.

<u>*See also*</u>:
S. Török , J. Osán, L. Vincze, S. Kurunczi, G. Tamborini, M. Betti, Characterization and speciation of depleted uranium in individual soil particles using microanalytical methods, Spectrochim. Acta B, in press.

Spain

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Instrumental facilities of the ICMUV include: a Total-reflection X-Ray Fluorencence (TXRF), a static and a portable Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometers. These equipments are employed in the field of the art and archaeometry, and some applications in this area are implemented. The portable EDXRF spectrometer is advisable to perform "in situ" and on-line analysis in a multidisciplinary environment, the static EDXRF equipment is good to perform analysis on paper and metal pieces. The TXRF spectrometry is the best technique for very sensitive analysis of trace elements in micro-samples. Using the last technique we have analyzed the cottons used by the restorers in the different steps of the restoration process; it appeared that the method is a good tool to study the composition of different layers and zones of the work of art.

Current projects include:

1. Analysis of valuable antique ceramics that can be investigated only when the analysis does not result in any damage. EDXRF measurements with portable instrumentation provide non-destructive analysis that completely eliminates sampling. An alternative method to determine the overglaze or underglaze pigment decoration is the microscopic examination of a ceramic cross section, but this examination requires sampling and damage to the physical integrity of the object. The aim of our work is to apply non-destructive technique ensuring the physical integrity of the object. We have proposed a portable EDXRF spectrometer to identify the underglaze and overglaze pigment decoration of ceramics on the basis of different values for the ratio between the Pb(Lα) line from the main element of the glaze cover and the Kα lines from the main elements (Co, Mn, Ni) found in the pigment, when the angle of the incidence radiation is varied. If the position of the detector is fixed, these ratios (Pb(Lα)/Co(Kα), etc.) increases with the angle for

underglaze decoration, and decreases for overglaze decoration. Six Valencian ceramic sherds have been studied by using this method, revealing the underglaze and overglaze decoration.

2. Non destructive EDXRF analysis of the mural paintings from the “Salón de Cortes” in the *Palau de la Generalitat Valenciana (s. XVI-XVII).* Six mural paintings are systematically analyzed in more than 100 points with EDXRF portable equipment. The pigments are analyzed in order to determine their composition and to discover non documented restorations.
3. Non destructive analysis of paper and engravings by EDXRF spectrometry.

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Publications of potential interest to the XRF community

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