X ray Fluorescence in the IAEA and its Member States

In This Issue

Activities in the IAEA XRF Laboratory

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

Application of X ray imaging techniques for studying the morphology of malaria-transmitting mosquitoes

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Introduction

The X ray phase contrast tomography technique was applied to examine the morphology of malaria transmitting mosquitoes in support of the development of the sterile insect technique (SIT) [1, 2]. The aim of the experiment was to detect possible damage induced by the sample preparation procedures, to perform X ray phase-contrast imaging on freshly prepared (not fixed) and live mosquito species, and to test the new beamline set up, which was not yet fully commissioned at the time of the experiment.

Fig. 1. X ray phase contrast imaging set up at the TOPO beamline, ANKA Synchrotron Facility. Left picture shows overall view of the set up, in the right-hand side picture a close up view of the "sample – X ray camera" region is shown.

Experimental

During the current experiment, which was performed in the TOPO beamline, a new cooled and thermally stabilized CCD camera PCO4000 was used. The camera was coupled to a thin layer scintillator screen and optics. A white beam from a bending magnet was used for the in-line X ray phase-contrast imaging. The details of the set up are shown in Fig. 1.

The spatial resolution of the setup was about 2.5 micrometers per image pixel. Relatively poor spatial resolution did not allow imaging of the morphological details at the tissue level. However, due to a large field of view, it allowed for imaging whole live mosquito specimens using relative short exposure times (200-400 milliseconds per image). Selected mosquito specimens were fixed using procedures developed in the Instrumentation Unit (IAEA). The live specimens were hatch from larvae mosquito forms. The larvae culture was prepared in the Entomology Unit (IAEA) two days before departure to ANKA. The hatching of adult mosquitoes took place in the ANKA chemistry laboratory in an isolated hatching cage shown in Fig. 2.

Fig. 2. Mosquito hatching cage installed in the ANKA chemistry laboratory – the source of live and not fixed mosquito specimens.

A series of X ray phase contrast measurements was carried out. The collected data included still images of fixed male mosquitoes representing irradiated/control populations (14/14 abdomens, 15/14 heads), CT scans of whole mosquitoes (3/3), abdomens (5/5), and heads (4/5). Also sequences of phase contrast images (movies) of living specimens (4 male, 3 female, 3 pupae, and one larva) were collected. The CT scans were also performed for not fixed, freshly prepared, female mosquitoes (2). Still images of not fixed male (1) and females (3) were also taken, as well as CT scans of fixed fruit flies (6). Altogether about 208 GB data was collected. In Fig. 3 a few frames from the collected image sequences of living specimens are shown. The frame rate was in the range between 2.5 – 4 frames per second. It was the first experiment in which the interactions between the internal organs of a mosquito

were observed. The collected data showed also damage induced to the sample due to the fixation procedure. This is demonstrated in Fig. 4. The cracks visible in the reconstructed cross-section of a fixed mosquito head are due to a too fast dehydration of the sample. In this picture there are also some artefacts visible. These artefacts could arise from the sample motion during the CT scan or the misalignment/instability of the scanning stage.
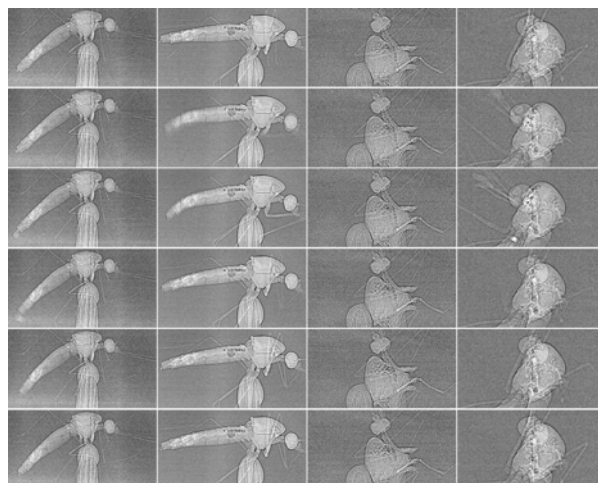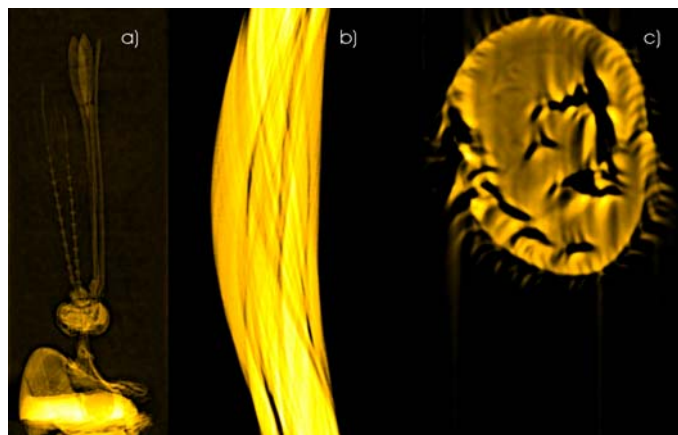

Fig. 3. Individual frames taken out from four X ray phase contrast image sequences showing internal morphology of living mosquito specimens. From left to right: two female and two male mosquitoes, frame rate of 4, 2.5, 5, and 4

frames per second, respectively.

Fig. 4. Left to right: (a) single projection image (phase retrieved) from a series of 1001 projections of a fixed male mosquito head; (b) sinogram build from the 1001 projections at the height of the mosquito head (1150th line in the in the image shown in (a)); c) reconstructed cross-section through the mosquito head – notice the cracks shown as black regions in the reconstructed cross-section).

Conclusions

The ability to perform X ray phase-contrast imaging of live mosquito specimens was confirmed. The collected still images provided data on a relatively large population of mosquitoes. The CT data were very useful to compare selected mosquito species. They

confirmed that the sample preparation procedures are critical for examining the morphological details. The procedures must be further optimized in order to stabilize the sample without inducing significant damage. The most interesting results should be obtained with the high-resolution (~ 0.5 micrometer) set up using the FReloN camera to be commissioned at the TOPO beamline in the 3rd quarter of 2007. If there are differences between the control and irradiated populations of mosquitoes they should show up first at the tissue level. Using the high-resolution setup it should be possible to detect such differences, if present.

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Further information on application of X ray imaging techniques is available from Dariusz Wegrzynek (D.Wegrzynek@iaea.org).

International Workshop on X ray Emission Techniques for Forensic Applications

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The Abdus Salam International Centre for Theoretical Physics (ICTP, Trieste, Italy), in cooperation with the International Atomic Energy Agency (IAEA, Vienna, Austria) and the Elettra Laboratory, Sincrotrone Trieste, organised an International Workshop on X-ray Emission Techniques for Forensic Applications from 28 May - 1 June 2007. Forty scientists and practitioners from Albania, Austria, Bangladesh, Belgium, Brazil, Croatia, Egypt, Ethiopia, Germany, Ghana, Greece, India, Italy, Libyan Arab Jamahiriya, Pakistan, Nigeria, Poland, Romania, Sri Lanka, Sudan gathered together at the ICTP to review the current status of and exchange up-to-date knowledge and experience in forensic applications of X ray emission and accelerator-based techniques such as X ray fluorescence (XRF), scanning electron microscopy combined with energy-dispersive X ray spectrometry (SEM/EDS), electron probe microanalysis (EPMA), total reflection X ray fluorescence (TXRF), and ion beam analysis (IBA) including particle induced X ray emission (PIXE), Rutherford backscattering (RBS) and particle induced gamma emission (PIGE). The working definition of forensic science is 'science used for the purpose of the law', hence any branch of science used to resolve legal disputes, including environmental protection, health and safety at work and civil proceedings, but the term is more generally used with the meaning of 'science in the investigation of crime by police and courts'.

One of the major areas of forensic applications of X ray emission techniques is evidence in criminal investigations. These techniques are attractive for forensic applications thanks to their unique features such as: non-destructive character of analysis (essential for archiving the evidence and for making possible further examinations), multi-elemental capabilities, simplicity, speed of operation, ability to analyse unprepared samples, good sensitivity, portability and ability to perform local and bulk analysis [1]. Typical materials analysed by X ray emission techniques to provide forensic evidences include: gunshot residue, paints, glass, oil, car bulb filaments, building materials, sediments, cultural heritage objects, documents etc. [2]. The participants became acquainted with the physical principles, methodology, advantages and limitations of the X ray emission techniques. Special emphasis was on the use of micro-analytical and imaging techniques based on both X ray tubes and synchrotron sources as well as on in-situ methodology by using portable XRF spectrometers [3]. The broad use of accelerator-based methods were also presented, including bomb-pulse radiocarbon dating to determine the time of harvest of illicit drugs, frauds related to wine and food products and ages of corpses related to homicides and mass murders [4].

Below selected forensic applications are presented in detail:

Paint traces

Particles of paint coats are associated with such events like car accidents, robberies or burglaries. They occur, e.g., as micro-fragments of paint coat or visible smears of paint in the form of coloured streaks on the clothing of persons being involved in these events. The aim of examination of paint is to establish the degree of similarity between the sample that includes the paint trace and the sample which originates from the suspect (vehicle, tools etc.). Through identification analysis (often combined with chemical composition characterization) one can determine the type of paint product, its use, producer and year of production. In many cases the fragments of paint have a multilayer structure while paint smears contain one or two layers of painting material mixed together with and sunk into the base, e.g., among the fibres of the fabric. Each layer can be a mixture of various chemical compounds such as polymer binder, organic and inorganic pigments and extenders. This is particularly true for car paints where one type of paint is offered in various colours and shades. Paints of the same colour can also contain a different set of pigments and extenders depending on the producer. Therefore, the elemental composition of the paint sample has to be determined in order to identify pigments and extenders. In this context one of the most powerful analytical techniques is scanning electron microscopy (SEM) combined with energy-dispersive X ray spectrometry (EDXRS) which enables both imaging of the sample and determination of elemental composition. The results of the analysis can be presented in the form of X ray spectra or elemental maps showing distribution of the elements in the analysed objects. The elemental maps are usually qualitative and might lack the sensitivity to display minor differences in the concentrations of the detected elements. Analysis of the very small fragments of paint requires special sample preparation techniques such as embedding into a resin and then cutting into thin slices by using microtome or scalpel. In case of analysis of paint smears the isolation of a paint particle from the substrate is required [5].

Oils

Oil traces are revealed on the clothing of car accident victims as greasy stains, arising as a result of contact between the victim and the chassis of a vehicle. In the course of crime examinations, an oil sample extracted from the fabric is compared with oil taken from the suspected car in order to establish the degree of similarity. Chromatography, IR spectrometry and various methods of the elemental analysis are routinely applied in the examination of oil samples. In particular elemental analysis of oil supports both the identification of oil and assessment of degree of use. Oil contains additives suspended in the hydrocarbon base, i.e., organic compounds like alkylosulphonates, alkylonaphtenates, alkylophenolates or alkylodithiophosphates of zinc, barium, magnesium and calcium which are added to the oil in order to improve its properties. Particular types of oils can be distinguished by the hydrocarbon base as well as by the type and concentration of the additives. When the engine is working the composition of the oil changes, and small parts of metal originating from the wearing away of cylinder, pans, valves and other parts of the oiled engine are transferred to the oil. The amount of the metals depends on usage conditions and technical state of the vehicle.

X ray fluorescence is particularly attractive for the direct analysis of oil samples. In many cases a simple comparison of the intensities of the characteristic X ray lines of such elements like Zn, Ca, P and S in the recorded spectra is sufficient for characterization of oils. The ratios of S/Zn, Ca/Zn P/Zn are also used for identification of oil samples. It was observed that for the used up oil the concentrations of iron, cadmium, lead and copper increased, and the concentrations of these elements can be used to determine a degree of use of oil. Other elements such calcium, barium, magnesium, zinc and phosphorus didn't show any change in concentration. Based on the results for metal contents derived from the XRF measurements a scheme for crime investigation was proposed [6].

Glass

Glass fragments are known to transfer to the clothing of a person breaking a window. They are revealed in cases of traffic accidents, fights or robberies. They have various sizes. Routine examination of glass fragments includes determination of their elemental composition and refractive index. These data can be used by a forensic scientist for comparison of glass samples in order to identify the origin of the glass fragments. The major elements such as Na, Ca, Si and Al are present in all types of glasses at a very similar concentration level. The differences are due to other elements in additives which are used to modify and/or improve the usage properties of the glass. Also impurities in raw materials used in the production process can be responsible for the differences in composition at the trace element level.

The chemical composition of glass can be determined by using many analytical methods. Non-destructive methods are obviously preferred because they allow

analysis of the samples by two or more analytical methods as well as to archive the samples as forensic evidences for future reference/examination. Another desirable feature of the analytical techniques is a possibility to perform multi-elemental analysis of very small samples in order to determine several elements (analytes) simultaneously. All those requirements are perfectly fulfilled by SEM/EDX and XRF techniques. Currently, SEM/EDX is routinely applied for examination of glass fragments. For qualitative analysis a glass fragment is simply placed on a stub and covered with a thin layer of carbon to ensure conductivity. Quantitative analysis requires sample preparation step which usually involves embedding the glass fragment into a resin, polishing to get a flat surface and coating with carbon.

Interpretation of analytical data obtained by SEM/EDX technique often requires application of statistical/ chemometrics methods. Car window glass, car headlamps, external glass of car light bulbs, internal glass of car light bulbs, internal glass of ordinary light bulbs, and sheet glass are investigated by SEM/EDX and a dedicated glass classification scheme based on the concentrations of Al, Ba, Ca, Fe, Pb, Mg, K, Na and Zn. An alternative approach for classification of glass samples is based on a non-statistical method and cluster analysis [7].

Gunshot residue (GSR) analysis

GSR examination is extremely useful in establishing some circumstances of a crime with the use of a firearm. The most characteristic gunshot residues are metallic particles arising from components of the primer with distinctive morphology and size (usually spheres in the micrometer range) as well as specific chemical composition (e.g., Pb, Sb, and Ba in the case of lead ammunition). GSR found around the gunshot hole and on the clothing and body of suspect provide information to define the shooting distance and type of ammunition (and thus the weapon) used. The most powerful and successful technique applied for GSR examination is scanning electron microscopy combined with energy-dispersive X ray analyser (SEM/EDX). Sampling is performed by using aluminium stubs with an adhesive layer of double-sided tape. When the sample has been secured on the stub, an automatic search can be done to identify spherical metallic particles and determine their composition. Based on the results of SEM/EDX, chemometrics methods help in identification of used ammunition. Recently some European forensic institutes decided to develop a database of characteristics of various brands of ammunition which will include the X ray spectra,

morphological features and organic data of particles present in gunshot residues [8, 9].

Miscellaneous materials

XRF spectrometry is applied for qualitative characterisation and screening analysis of complex materials such as sediments from water, soil, body fluids, hair and stomach contents, especially for determination of heavy metals which are components of inorganic poisons. In this context a major advantage of XRF is a possibility to perform in-situ measurements which are essential for fast identification of contaminated areas and proper sampling. The collected samples are next analysed in a laboratory by using atomic absorption spectrometry (AAS) or inductively coupled plasma mass spectrometry (ICP/MS) methods to get quantitative data.

Applications of synchrotron radiation sources

Currently available systems attached to a synchrotron radiation source are highly integrated and can perform microanalysis and micro-tomography to study elemental 2-D and 3-D distributions with a special resolution in the order of a few µm. Moreover, by using a confocal geometry (where both the primary and outgoing X rays are collimated by using capillary optics) depth profiling can also be performed in a non-destructive way with a resolution of about 30 µm. For imaging of low-Z materials an X ray phase contrast micro-tomography based on synchrotron radiation is currently available [10]. The microtomography beam line at the Elettra laboratories in Trieste is shown on Fig. 1.
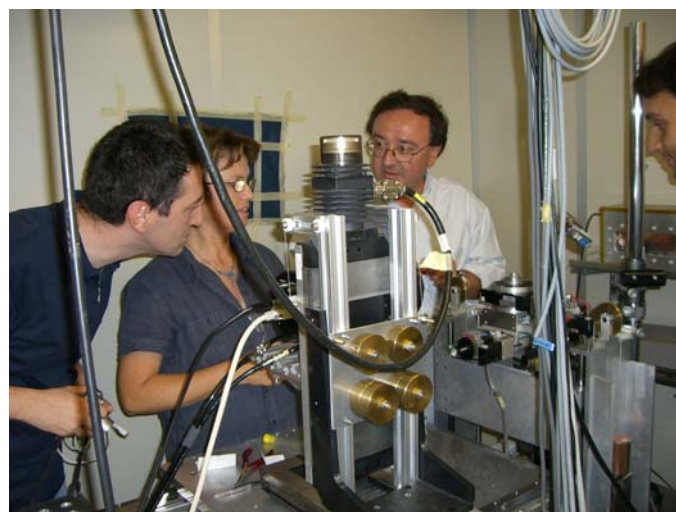

Fig. 1. The microtomography beam line at Eletta (from left to right, L. Rigon, G. Tromba, F. Zanini and S. Favretto).

Portable XRF instrumentation and in-situ measurements

The availability of thermoelectrically cooled semiconductor detectors created a possibility to develop portable XRF spectrometers for in-situ applications. The characteristic X rays of the analytes can be generated by using radioisotope sources (^{55}Fe, ^{109}Cd, ^{241}Am) or low-power X ray tubes. For detection of X rays liquid nitrogen free Si-PIN or Si drift detectors are applied. The primary photon beam can be collimated by using a conventional pinhole collimator or polycapillary lens. In order to reduce absorption of the excitation and characteristic X rays the XRF spectrometer can be equipped with a compact vacuum chamber that allows determination of low-Z elements such as Mg, Al, Si, P, S, and Cl [3]. An example of (trans)portable XRF spectrometer with a vacuum chamber demonstrated during the workshop is shown on Fig. 2.

Fig. 2. Practical demonstration of a (trans)portable XRF spectrometer for in-situ applications during the Workshop in Trieste.

"Authentic Fakes" and "Fake Authentics" - role for XRF techniques

Illegal trade of valuable archaeological objects is a real problem especially in the areas rich in cultural heritage. The contemporary production of museum quality, technologically authentic, and archaeologically documented ceramic artefacts (which are called "**authentic fake**") may well mitigate the demand for the originals and simultaneously improve access to a wider audience. This policy has been adopted a few years ago by the Peruvian government, which set up outlets for high quality 'certified' artefacts in order to reduce the illegal export of pre Columbian antiquities.

Promotion of similar policies was one of the aims of a recently completed EU project (www.cera-med.net)

which involved Greece, Turkey, Spain, Morocco and Jordan. The Hellenic Ministry of Culture, Greece has already adopted such a policy by commissioning "museum quality" ceramic reproductions for sale at the major museum shops [11]. There is of course a potential danger that such high quality reproductions might be artificially aged in order to enter the market as originals. As a safeguard against such cases a label is usually stamped in the body of the artefact. However, such stamps can be easily removed by breaking and reassembling the object. The best signature for "authentic fakes" is a suitable chemical (elemental) tag inserted in the body of the artefact that can easily be detected by non-destructive X ray fluorescence technique.

Another aspect is identification of "**fake authentics**" defined as either a contemporary reproduction that is promoted as or claimed to be authentic or a heavily retouched, repaired/ reconstructed artefact that is promoted as original. Since almost all original archaeological/historic works of art are subjected to some form of conservation, the chemical tagging of the conservation material would allow identification of the conservator and provide effective protection against substitution and counterfeiting. In this context XRF technique is the ideal analytical tool for implementation and enforcement of the relevant policies [11]. The systematic adoption by major museums of the policy of elemental tagging for subjected to conservation original antiquities, works of art and technologically authentic "museum quality" replicas sold at museum shops should also have a substantial economic impact.

Conclusions

Laboratories involved in forensic applications should demonstrate a high standard of analytical performance and comply with international QA/QC standards like ISO 17025 preferably through a formal accreditation. Combined use of nuclear and related analytical techniques is often inevitable to characterize the materials. Profound knowledge and practical skills in forensic statistics are also critical for proper interpretation of the results in order to provide reliable forensic evidence. For successful forensic applications of XRF techniques strong interactions between the law enforcement agencies and nuclear analytical scientists are required.

Acknowledgements

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Further information on the IAEA contributions presented at the Workshop is available from Andrzej Markowicz (A.Markowicz@iaea.org).

First Research Coordination Meeting under Coordinated Research Project on Unification of Nuclear Spectrometries: Integrated Techniques as a New Tool for Material Research

During the last years the IAEA supported a substantial number of laboratories in Member States in establishing nuclear spectrometry facilities for various applications. These laboratories are being used in support of applied research, teaching and education in nuclear science and technology as well as for providing analytical services for industry, environmental pollution monitoring, study of cultural heritage, food and agriculture, human health etc. In most cases nuclear analytical techniques such as energy dispersive X ray fluorescence (EDXRF), particle induced X ray emission (PIXE), particle induced gamma emission (PIGE), Rutherford backscattering (RBS), etc. are used independently and provide information on a specific characteristic of the analysed materials. In order to characterise the materials in a comprehensive way or to improve the quality of the analytical services provided by laboratories, a combined use of a few techniques is often required. In order to coordinate the research

efforts of laboratories towards better integration and unification of nuclear spectrometries, a new Coordinated Research Project (CRP) has been proposed under the project D.3.03. "Improvements in nuclear spectroscopy applications". One of the major areas of integration is application of synchrotron radiation sources for X ray micro-fluorescence, micro-diffraction, X ray microscopy, micro-tomography, and absorption techniques used for elemental analysis, 2-D and 3-D imaging and chemical speciation. In general, integration and unification of nuclear spectrometries can be observed at the level of instrumentation including hardware and software components, measurements and data collection, data processing and data interpretation. The CRP is a joint effort of the Instrumentation Unit, IAEA Laboratories Seibersdorf and the Physics Section, Division of Physical and Chemical Sciences; the responsible officers are Mr. A. Markowicz and Ms. F. Muelhauser, respectively.

The First Research Coordination Meeting under the CRP was held in Vienna from 16 – 20 April 2007. The participants from Argentina, Australia, Austria, Belgium, Croatia, Cuba, Germany, Greece, Italy, Slovenia, United Arab Emirates and United States of America attended the meeting. Major objectives of the meeting were to: (i) review the progress in current research activities related to the CRP, (ii) discuss/prepare a consistent programme for the development of integrated instruments and methodologies, (iii) exchange information on the research undertaken in participating laboratories with relevance to achieving the objectives of the CRP, and

(iv) review future directions and possibilities for this CRP and beyond.

During the meeting, a visit to the IAEA Seibersdorf Laboratories was organised to introduce the participants to the research work conducted there and to demonstrate the training facilities available to the IAEA Member States.

At the RCM, participants presented their individual progress reports submitted to the IAEA. The activities planned for the forthcoming years were discussed in details. Current status of the outputs under the CRP is summarised in Table 1.

Table 1. Current status of the CRP outputs (as of April 2007).

Expected output	Current status
Integrated and multifunctional instruments with technical documentation	BEL1: micro-XRF + micro-Raman accomplished BEL2: EPXMA upgraded to achieve low Z elements detection and implementation of X ray grazing emission CUB: XRD refurbishing and EDXRF automation in progress GRE: PIXE+XRF chamber under construction ITA: XRF portable equipment optimized for analysis of work of arts
Software packages for handling and operation of multifunctional instruments	AUL: PIXE module is nearing completion BEL1: XRF+XRD 2D-scanning + tomography processing CRO: Software in progress (PIXE+XRF) CUB: XRG control and XRF measurements accomplished ITA: Dedicated software for gold and painting layer analysis
Integrated software packages for data processing and presentation	AUL: Methodology for inclusion of PIGE software into existing PIXE package has been determined BEL2: MonteCarlo simulations implemented for EPXMA quantification CRO: Software in progress (PIXE+XRF) CUB: Software in progress GRE: Software in progress for combining PIXE and XRF excitation modes SLO: Software in progress
Improved analytical methodologies based on combined use of various nuclear spectrometries	ARG: Completed the combination of (TXRF+XRD) and (SEM-EDX) techniques for use in pigments. AUS: SR-TXRF+SR-XANES, micro-XRF+XANES under development AUL: Improved matrix corrections for multiple samples has been demonstrated manually (automation to follow) BEL1: 3D-micro-XRF+micro-XANES successfully tested BEL2: Characterization of different materials by combined use of EPXMA, micro-Raman, EPXRF, XRF CRO: Preliminary measurements with X ray source within the PIXE chamber, trying t optimize the geometrical set-up GER: Successful test of 3D-micro-PIXE at Ljubljana and Paris ITA: For pre-Colombian gold analysis (Au-Ag-Cu) samples prepared and instrumentation optimized. SLO: TXRF + XRF + micro-PIXE use in analysis accomplished UAE: sampling methodology for XRD, optical absorption, XPS for spin-tronic application established. USA: Data acquisition parameters set, samples identified and measurements initiated

Expected output	Current status
New applications of nuclear spectro-metries for better characterisation of materials	AUS: Preliminary results obtained in aerosol characterization and bone + cartilage studies BEL1: Micro-tomography + 3D-micro-XRF successfully applied UAE: Optical absorption applied on band gap studies. USA: Initiated studies on 3D-micro-XRF
Research papers, reports, conference contributions	ARG: 1 training course organized, 2 contributions to conferences submitted, 1 paper submitted AUS: 1 in preparation AUL: 1 conference contribution submitted. BEL1: 2 papers submitted GER: 2 papers submitted GRE: 2 papers submitted, 3 contributions to conferences submitted SLO: 1 paper submitted
Providing improved fundamental understanding of physical phenomena	AUL: Investigating different contributions to bremsstrahlung background for PIXE. AUS: Investigation of absorption phenomena in TXRF-XANES GRE: Obtained data on Resonant Raman Scattering cross sections under evaluation ITA: Evaluation of XRF characteristic emission intensity ratios UAE: Information on band gaps gathered by using optical absorption

Conclusions

The meeting was focused on X ray based analytical methods although the excitation methods were varied and included ion beams, X ray tubes and synchrotron radiation. A broad range of nuclear methods which can be integrated to improve analytical information were identified. These include EDXRF, XRD, XPS, PIXE, PIGE, RBS, XAS, SEM-EDS and so on, together with 2D and 3D elemental and structural imaging capabilities.

A very broad range of applications covering many research areas have been identified, such as study of cultural heritage, environmental pollution monitoring, human health, biology, solid state physics and development of new materials. It was concluded that the progress to-date is consistent with the work plans as agreed under the awarded research agreements and research contracts.

Further information on the 1st RCM is available from Andrzej Markowicz (A.Markowicz@iaea.org).

Announcement on Update of the X ray Fluorescence Labs Mailing List

The X Ray Fluorescence Labs Mailing List is an e-mail based discussion and exchange forum that provides the scientific community of the IAEA Member States with a centralized Internet address through which questions, ideas, comments and answers related to various fields of XRF analysis can be rapidly distributed to a list of (subscribed) individuals and institutions by electronic mail. In the scope of this forum, XRF analysis includes all techniques which make use of the induced X rays to characterize the elemental composition of a particular sample.

The naalistxrflabs was recently updated and is now hosted in a new server. Technically, the list is now managed using GNU Mailman, which is a powerful and highly configurable package. From the point of view of the list members the main difference is that the forum address is slightly different. A new positive feature is online archive that holds all the traffic list and can be browsed. Also the list members have now the possibility of personalizing several settings that affect their subscription. All the details are on the list page at the following address:

http://lists.iaea.org/mailman/listinfo/naalistxrflabs

We believe that these changes will improve the quality of our list, but if you have any suggestions or comments, please, do not hesitate in posting them or contact directly the moderator (naalistxrflabs-owner@lists.iaea.org). Participants are encouraged to

actively take part in the discussions, seek or provide advice and post comments and contributions.

We are looking forward to have fruitful discussions and exchange of experiences through the naalistxrflabs.

X ray fluorescence in Member States

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

Italy

Analysis of paintings and alloys with portable EDXRF-equipments

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In the last years, portable EDXRF equipments have been employed to analyze paintings and alloys. The portable equipments are mainly composed of Ag- or W-anode small size X ray tubes, working at the voltage of 30 - 35 kV and current of 100 µA, thermoelectrically-cooled Si-drift or Si-PIN detectors and pocket pulse-height analysers.

Following studies have been carried out:

a) non destructive inspection for the study of the painting technique and for restoration support on the "Sacra Conversazione" from Palma the Old in Belgrade (Serbia).

b) restoration of the Bronze Sphere on top of the Cupola of Saint Peters' Basilica in Rome.

c) analysis of pre-Columbian gold alloys from the Royal Tomb of Sipán, Lambayeque, Peru.

a) In 2006 the Italian Ministry of Foreign Affairs started a co-operation project with the Republic of Serbia. The aim of the project was to improve the skills of the Serbia restoration experts by offering a "hands on" work on the study and restoration of a painting of the sixteenth century kept in the Royal Palace in Belgrade. The use of a portable XRF system was mandatory in the planning of the work. As a matter of fact the non destructive XRF elemental analysis appeared to be appropriate to identify most of the pigments used by the painter. The following pigments were identified: copper blue (azurite), cobalt based blue (Thernard blue, a restoration colour), red and dark ochre, orpiment,

copper green, white lead, white zinc (restoration colour) and the presence of red lakes and lapis lazuli, the last two not directly characterised. By using a portable XRF system more than seventy points of the painting (approximately 1.7 meter high and 1 meter wide) were analysed. Just to compare the difference among non destructive analysis and destructive analysis (stratigraphic analysis in this case) the latter was fulfilled with 7 sampling. The XRF is nowadays perhaps the best way to analyse the full complexity of a precious painting in a truly non destructive manner. In Fig. 1 the painting and the XRF system are shown.

b) After the death of Michelangelo the building of the cupola of the Vatican Basilica was still not fulfilled. Works to complete the cupola started again during the pontificate of Sisto V (1585). Architect Giacomo della Porta, with the help of Domenico Fontana and 800 workers completed the job not before 1593 when the lantern on which cusp he placed the globe was ended. In the frame of the restoration work started in 2005, non destructive analysis with two portable XRF systems were carried out in the inside and outside of the sphere.

Fig. 1. The XRF system in front of the analysed painting in Belgrade

The globe is placed at a height of 131 meter having a 2.5 meter diameter and a weight of 1862 kg. It is composed of 36 plates soldered together in situ. The measurements carried out in such extreme conditions showed the high level of stability and reliability of the new generation of portable instruments equipped with miniaturised low power x ray tubes and SDD detectors. Inside the globe 31 quantitative measures, 21 on the plates, 7 on the solders and 3 on the repairs were performed. Several measurements were also performed on the outside gilded surface to drive the restoration procedure. The most interesting result is that the soldering of the 36 plates was with autogenous welding, this means that the composition of the plates and of the soldering was the same. In Fig. 2 the outside measurements are shown.

Fig. 2. Outside XRF measurements on top of the Cupola of Saint Peters' Basilica in Rome

c) During March 2007, pre-Columbian gold alloys from the Royal Tomb of Sipán have been analyzed, with the help of scientists from the "Universidad Mayor de San Marcos" in Lima (Prof. Angel Bustamante and Julio Fabian), the "Universidade Federal do Rio de Janeiro" in Rio de Janeiro (Prof. Ricardo T. Lopes, Marcelino Anjos and Cristiane Calza), the "Museo Tumbas Reales de Sipán" (Walter Alva, Luis Chero, Fidel Gutiérrez, Marco Seclén and Rosendo Dominguez) and from the QALLTA – Centro de Investigacion por la Preservacion y Promocion del Patrimonio Cultural, Lima (Dr. Mercedes Delgado). About 250 X ray spectra were collected for about 50 objects of gold, gilded copper and gilded silver.

Figure 3 shows a mask from the IV Century A.D. approximately, which represents one of the most important gold objects from the Museum of Sipán. It is composed of two soldered parts (the front and the rear of the head). The rear side was possibly made with the same basic alloy as the front side, by simply adding copper. The two parts were then soldered using an Ag-Cu alloy.

The results are the following:

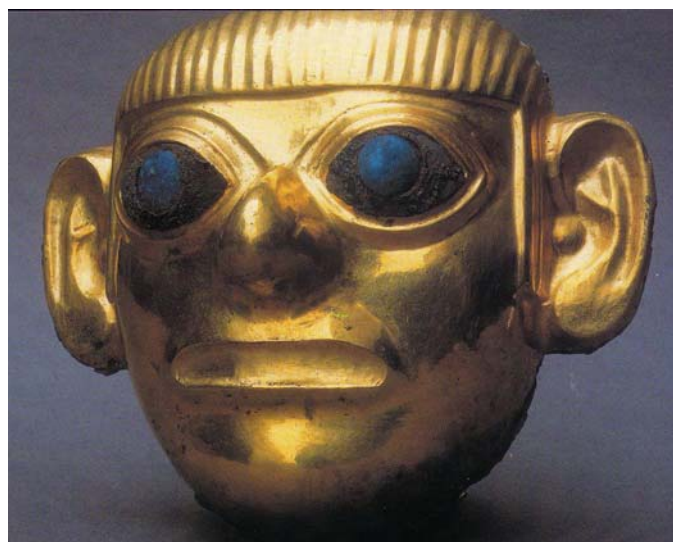|	Au(%)	Ag(%)	Cu(%)
Front side	74.6±1.0	23.1±0.8	2.3±1.4
Rear side	60.8±1.0	23.2±1.0	16.1±1.7

Fig. 3. Pre-Columbian gold mask from the Museum of Sipán

Morocco

Activities in the field of XRF at CNESTEN

I. Examples of TXRF applications

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1) TXRF instrument

To determine concentrations of heavy metals in support of environment studies, we set up a TXRF module with a 2 kW power fine-focus X ray tube with a molybdenum anode operating in most cases at 30 mA and 50 kV. X ray beam is monochromatized by using a multilayer (W/C) crystal. The fluorescent X rays of the sample are detected by a Si(Li) detector with a resolution of 165 eV at 5.9 keV and next analyzed by a Canberra S100 multi-channel analyzer card coupled to a computer for data storage and analysis.

2) Assessment of Air Pollution and its Impact on Human Health in Kenitra's City (Morocco)

The main objective of our present work is to assess the air pollution level and to evaluate its effect on urban population of Kénitra's city living close to the sources of pollutants. For this purpose, we proposed two methodologies: (i) determination of the concentration of gases by absorption of UV light, and (ii) collection of air particulate matter on filters by using dichotomous sampler. Particles were separated according to their size:

- The breathable particles (PM10) have a diameter between 2.5 µm and 10 µm

- The inhaled particles (PM2.5) have a diameter lower than 2.5 µm.

Elements have been determined by using Atomic Absorption Spectroscopy and Total Reflection X ray fluorescence (TXRF).

Our results show that the concentrations recorded in the sites of survey for PM, Lead, Cadmium Nickel and Sulphur Dioxide (SO_2) exceed the norms recommended by the World Health Organization and the European Union.

The pollutants observed in the sites of study influence air quality and have serious negative impact on human health.

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

The main purpose of this work is study of the interactions between nutrition (micronutrients heavy metals like Fe, Zn, Cu) and toxic heavy metal such as Pb in blood of children living in Gharb region of Morocco. This region receives all pollution carried by the Sebou river coming mainly from industrial activities. A rapid and simple analytical procedure was used for the determination of Fe, Cu and Zn trace amounts in blood by total-reflection X ray fluorescence technique. Digestion of blood samples was done in microwave oven by using a mixture of HNO_3 and H_2O_2. The accuracy of measurements was verified by using certified materials. The concentration of Cu was found to be normal in all samples ($\cong 1$ ppm) which ruled out any interaction between this element and the others. On the other hand, amounts of Fe and Zn varied considerably, suggesting an interaction between Fe and Zn. However, amount of Pb in blood was below 50 ppb, suggesting that no interaction exist with this metal and micronutrients.

II. WD-XRF Applications

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Figure 1 shows a simplified schematic of the WD-XRF spectrometer installed in CNESTEN. This spectrometer is used for carrying out elemental analysis especially in environmental and geochemistry studies including determination of heavy metals and major elements in sediments, water and aerosols. Some of the recent applications in our laboratory are described below.
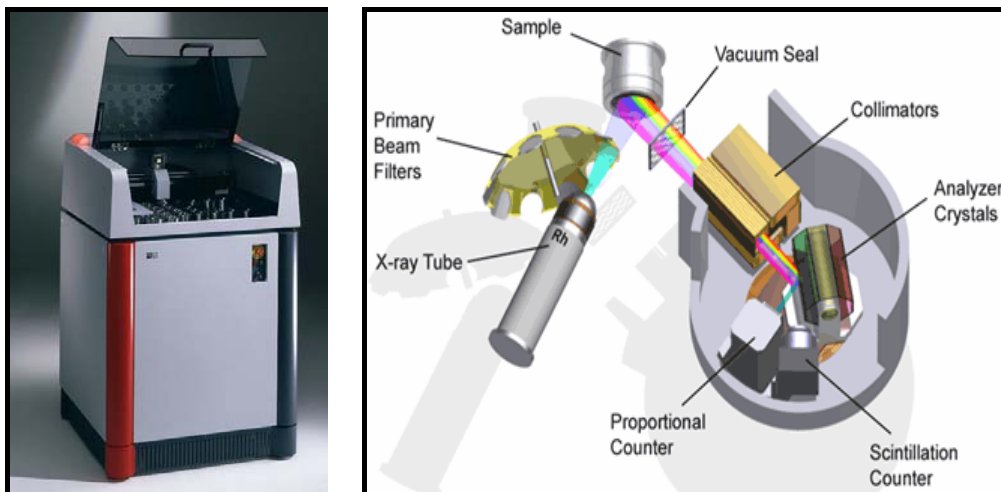
Fig. 1. S4 Pioneer WD-XRF Spectrometer. On right, the chamber installed inside the S4 Pioneer.

1. Determination of heavy metal contents in soils irrigated by wastewaters in Meknes's region

The study area was located along the Oued Boufekrane river (Meknes) which is loaded by domestic and industrial wastewaters. Concentrations of Al, Fe, Cr, Cu, Ni, Pb and Zn in soils, sediments and water samples collected along this river were determined using WD-XRF technique. A multivariate statistic approach (Principal Component Analysis, PCA) was used to interpret the obtained data. This method allows to identify correlations among the different groups of metals and the ratios between natural and anthropogenic sources. The main conclusions are:

For sediments and water

The variability of Al, Fe, Cr and Ni in sediments and Al, Fe and Ni in water, associated to the same factor, is controlled by anthropogenic source (industrial activities). The concentrations of Cu, Zn and organic matter (determined by loss on ignition) in sediments, and Cu and Zn in water, grouped in the same factor, are controlled by another anthropogenic source (human and urban activities). Pb is isolated in another factor indicating that this element is associated with anthropogenic activities such as the pottery industries (Pb is used for glass ceramic fabrication).

For soils

The association of Al, Fe, Cr and Ni in the same group is related to lithogenic factors. Pb and Zn grouped in the second factor with high loadings are considered to be controlled by lithogenic origin (presence of sulphides in parent rocks). Cu included univocally in a factor is controlled by agricultural practices.

2. Variations of Pb concentrations with distance from main highway

The impact of road traffic on Pb concentrations was confirmed and established in many studies. In this section, we try to evaluate the spread of this impact on soil samples located at the vicinity of a main highway. To accomplish this goal, a set of soil samples was collected at different distances from a main highway, and analyzed by WD-XRF. Fig. 2a and 2b illustrate variation of Pb concentrations versus distance from the main highway. Pb concentrations are high at sampling sites close to the highway and they become constant at 200 meters from the highway where impact of road traffic is not significant.
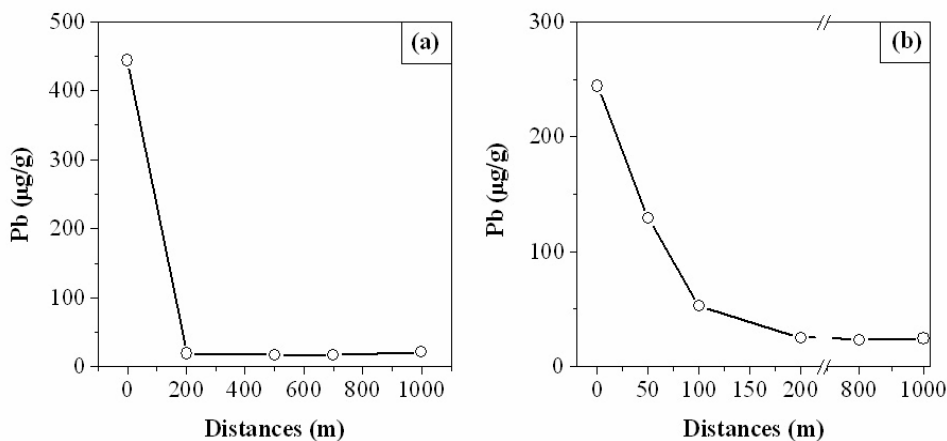
Fig. 2. Pb concentrations at different distances from two different main highways.

Slovenia

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Activities in the XRF Laboratory of Jožef Stefan Institute

Design and construction of the laboratory and/or portable XRF analyzers

Three prototypes of X ray analyzers were constructed so far. One of them is based on radioisotope excitation of fluorescence radiation and other two employ for excitation air cooled X ray tubes of 50 W and 3 W, respectively. The X ray spectrometers attached to these analyzers utilize Si PIN X ray detectors. The 3 W X ray tube-based analyser is portable but for in-situ applications needs the AC power generator. The portable analyzer with ECLIPSE II 3W X ray tube is shown in Fig. 1.

Fig. 1. X ray tube-based portable XRF analyser

Communication between the analyzer and the computer is through the USB port and all the commands are available in the LABVIEW window environment. Using the mouse it is possible to adjust the excitation parameters for the tube, put the HV On/Off, adjust the spectrum acquisition parameters, i.e. start and stop acquisition, save the spectrum, etc. But it is also possible to identify automatically the elemental lines in the spectrum, analyze the spectrum, and perform the quantification utilizing few different models. These are based on the absorption in the total and residual matrix, which is defined by two parameters. The LABVIEW window is shown in Fig. 2.
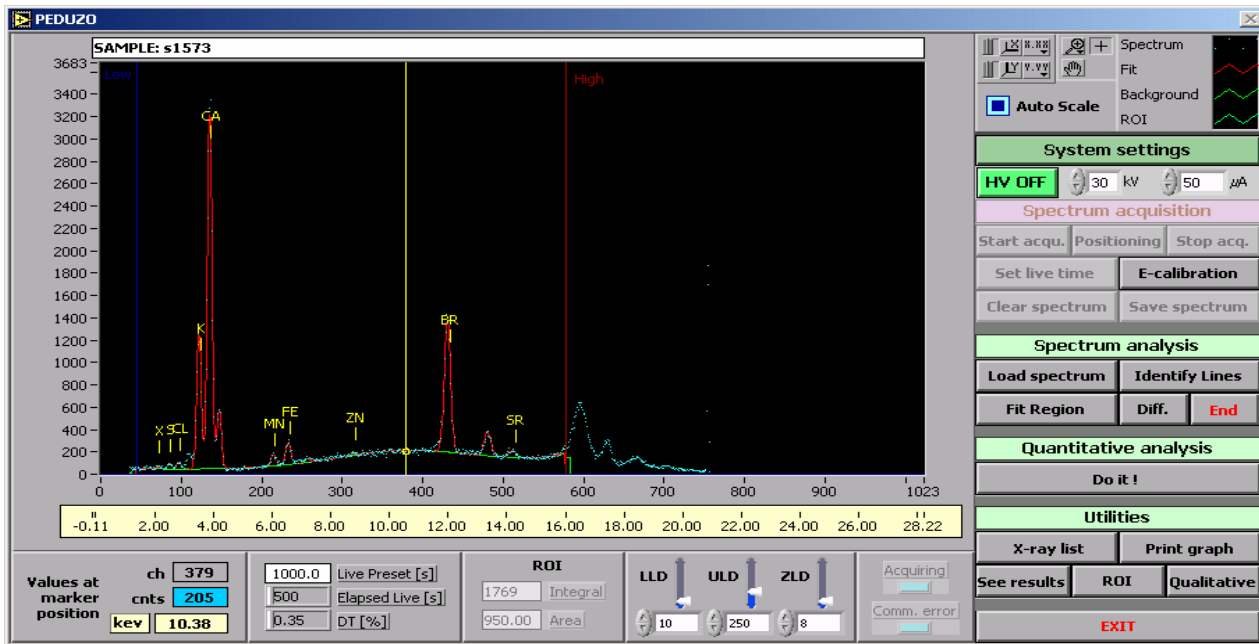
Fig. 2. Example of LABVIEW window

Development of quantification software

The upgrading of the QAES (Quantitative Analyses of Environmental Samples) quantification software was one of the important activities in the laboratory. The procedure of using the emission – transmission method at single energy in order to determine the absorption in the sample as a whole was refined. In a new software not only the intercept but also the slope of the absorption curve in the log-log presentation of residual matrix is obtained and compared with the typical low-Z residual matrices as shown in Fig. 3. From measured absorption in the total sample with Cu target and tube excitation, the concentrations of measured elements in an organic sample as well as the residual absorption was determined.
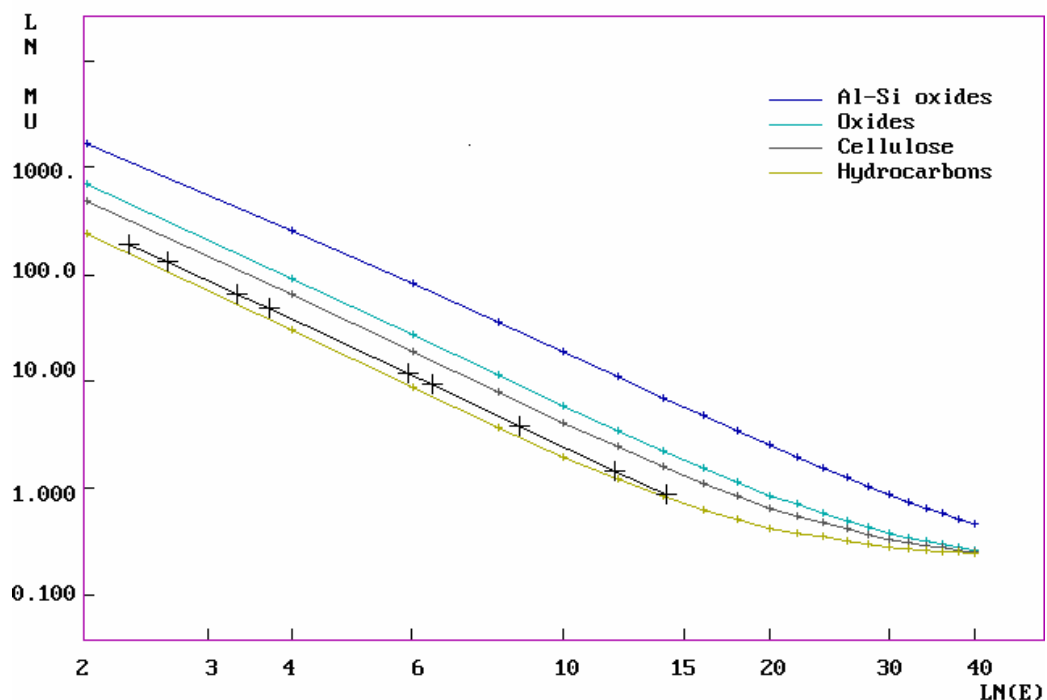

Fig. 3. Experimental absorption in residual matrix compared to few typical matrices

TXRF module with monochromatic Mo K$_\alpha$ excitation and practical applications

In order to reduce the scattered radiation in TXRF analysis of organic but not digested and pre-concentrated materials, the system with mono-chromatic excitation was designed and constructed. It is shown in Fig. 4.
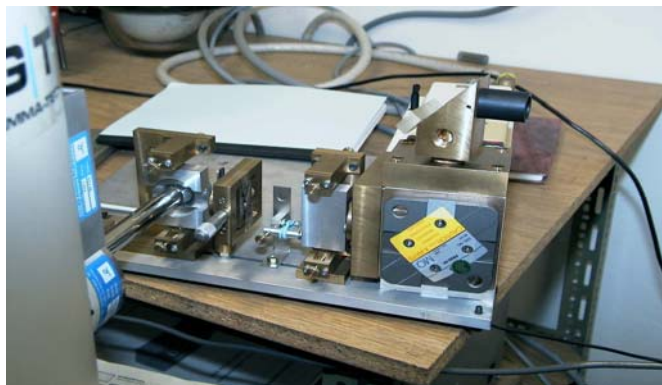

Fig. 4 TXRF module

At the moment the applications of TXRF for the analysis of bee honey and hyper accumulating plant material are in progress.

The analysis of mineral content of honey, namely of the elements S, Cl, K, Ca, Mn, Fe, Ni, Cu, Zn, Br, Rb, and Pb in a large number of honey samples is in progress. By combining these data with measurements of isotopic ratio $^{13}C/^{12}C$, and some other physical and chemical characteristics of honey, the determination of the geographical and botanical origin of honeys is planned to be obtained. The purpose of this investigation is the certification of honey origin, authenticity and quality, which is important in order to control the imports of lower quality of honey to markets of EU [1].

The physiology of metal hyper accumulating plants is important in order to establish the mechanisms of transport of poisonous heavy metals from the soil to the roots, shoots, leaves, and seeds of the plants [2]. Because the concentrations of heavy metals in plant organs are preconcetrated by more than one order of magnitude relative to the soil, these plants can be successfully utilized in remediation of strongly polluted soil, e.g., at sites of old mines.

References

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[2] VOGEL, K, PONGRAC, P, KUMP, P, NEČEMER, M, REGVAR, M. Colonisation of a Zn, Cd and Pb hyperaccumulator Thlaspi praecox Wulfen with indigenous arbuscular mycorrhizal fungal mixture induces changes in heavy metal and nutrient uptake. Environ. pollut. (1987). [Print ed.], 2005.

Spain

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During the last decade the Material Science Institute of the Valencia University (Spain) has been involved in the development, evaluation and analytical applications of XRF spectrometry in the field of study of Cultural Heritage objects . Our research activities in the last year are carried out in support of archaeometric studies and have been focused on:

a) *Analyses of Neolithic pigments from Valencian sites***,** in collaboration with the Prehistory and Archaeology Department of the Valencia University (Dra. I. Domingo, Dr. P. García).

The mineralogical characterization and elemental composition of red colouring materials from the valencian sites of Cova de l'Or, Cova de la Sarsa and Cova Fosca (Vall d'Ebo, Valencia, Spain) were made by SEM-EDX, XRD and XRF. The data demonstrate the use of two different kind of colouring materials during the Ancient Neolithic in the Valencian region: haematites and cinnabar. It is the first time that the presence of cinnabar in samples from Valencian neolithic sites has been confirmed. The characteristics and geographical distribution of these two minerals refer to different strategies to obtain and, probably, use them. More details are available from:

- "Nuevos datos sobre el uso de materia colorante durante el Neolítico antiguo en las comarcas centrales valencianas". *SAGVNTVM* (P.L.A.V.), 38, 2006: 49 - 60.

- "Análisis elemental del fragmento cerámico con cérvidos incisos de la Cova de l'Or (Beniarrés, Alacant, Spain)". Accepted for publication in Trabajos de Prehistoria, 2007.

b) *Comparison of the performance of laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS) and portable X ray fluorescence spectrometry (PXRF) for the characterization of Co pigments found in traditional Valencian ceramics*, in collaboration with the Museo Nacional de Cerámica y Artes Suntuarias González Martí (MNCAS-GM, Dr. J. Coll), the Zaragoza University (Dra. J. Pérez Arantegui, Dr. M. Resano, Dr. E. García-Ruiz) and the Analytical Chemistry Laboratory of the Ghent University (Dr. F. Vanhaecke).

The use of PXRF and LA-ICPMS techniques has enabled to characterize the blue pigments of some selected Valencian ceramic fragments from the *MNCAS-GM* (Valencia, Spain). Qualitative data for the elemental composition of the blue pigments obtained by using both techniques show a good agreement and similar conclusions can be extracted from the measurements. Elements, like arsenic, manganese, copper and zinc, allow characteristic blue pigments from several periods to be distinguished from one another, proving that potters used different kinds of cobalt materials in several centuries and suggesting changes in pigment-supply or technological changes in the extraction of Co from the ore(s). Both analytical techniques seem fit-for-purpose in this case, although they show different advantages and limitations which have to be taken into account in further applications. PXRF spectrometry is a less expensive and totally non-destructive technique, capable of providing fast and reliable results at the mg g^{-1} level. LA-ICPMS, on the other hand, offers a much higher detection power and better spatial resolution, but its use results in some sample damage (sample consumption at the µg level), while it is more expensive and non-portable technique. More details are available from: "Characterization of Co pigments found in traditional Valencian ceramics by means of Laser ablation-inductively coupled plasma mass spectrometry and portable X ray fluorescence spectrometry". Submitted to Talanta in May 2007.

c) *Evaluation of a soft cleaning method for historical stained glass windows by TXRF spectrometry,* in collaboration with the Centro Interdisciplinare di Scienza e Tecnica per la Conservazione del Patrimonio Storico Architettonico (CISTeC, Dª P.Foglia, Dra. M.L. Santarelli).

Historical stained glass has a clear tendency to form a crusted layer on the surface. One of the most delicate aspects to be faced during the restoration of historic glass windows is the cleaning of the different dirt depositions and thick corrosion crusts. For several centuries, stained glass was cleaned using mechanical methods and also with acidic or alkaline solutions. Today's understanding of the cleaning process embraces two complementary aims - firstly improving the readability of the glass, and secondly slowing the ageing process of the historical glass itself. The act of removing deposits and encrustations resulting from corrosion should not endanger the artwork itself.

There have been few scientific studies of potentially suitable cleaning processes. In this study we examine a soft cleaning method that can be employed to remove encrustations without damaging the glass surface. Extremely effective mechanical methods and the use of cleaning solutions are being developed. Because corrosion crusts are difficult to dissolve in pure water, we propose an optimized neutral solution to solve calcium and lead sulphates and carbonates. The solution's parameters such as pH, temperature, conductivity and concentration of Na and Ca are controlled on line which allows monitoring of the cleaning process. In particular, Ca concentration in cleaning solution is controlled by two methods using Ca ion selective analyzer and Total Refection X ray Fluorescence (TXRF) measurements. Results of on line Ca analysis are compared with Ca concentrations in cleaning water evaluated by TXRF.

Publications of potential interest to the XRF community

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F. Ulberth, Certified reference materials for inorganic and organic contaminants in environmental matrices, Anal. Bioanal. Chem., 386, 1121-1136, 2006.

P.J. Potts, A.T. Ellis, P. Kregsamer, C. Streli, C. Vanhoof, M. West, P. Wobrauschek, Atomic spectrometry update – X ray fluorescence spectrometry, Journal of Analytical Atomic Spectrometry, 21, 1076-1107, 2006.

Analytical Methods Committee, The Royal Society of Chemistry, Evaluation of analytical instrumentation. Part XX - Instrumentation for energy dispersive X ray fluorescence spectrometry, Accreditation and Quality Assurance, 11, 610-624, 2006.

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