IAEA
International Atomic Energy Agency

XRF Newsletter

A newsletter of the IAEA's Laboratories, Seibersdorf
Issue No. 10, December 2005
ISSN 1608–4632

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.

(Trans)portable XRF spectrometer with polycapillary optics and vacuum chamber

In cooperation with the Atominstitut, Technical University, Vienna, a (trans)portable XRF spectrometer for the determination of the elements from Na upwards was designed and constructed (see Fig. 1). To avoid extensive absorption effects for the low energy characteristic X rays a vacuum chamber was attached. The spectrometer includes two options for excitation: a polycapillary with 20 µm spot size and a collimator with a 1 mm diameter that can be used alternatively. Major components of the spectrometer are a low power Pd-anode X ray tube, operated up to 50 kV and 1 mA with a focal size of 100 µm, and a Si drift detector. The excitation and detection parts of the spectrometer are integrated and placed inside the vacuum chamber. Special efforts were made to reduce as much as possible the distances between source (focal spot of the polycapillary), sample and detector.

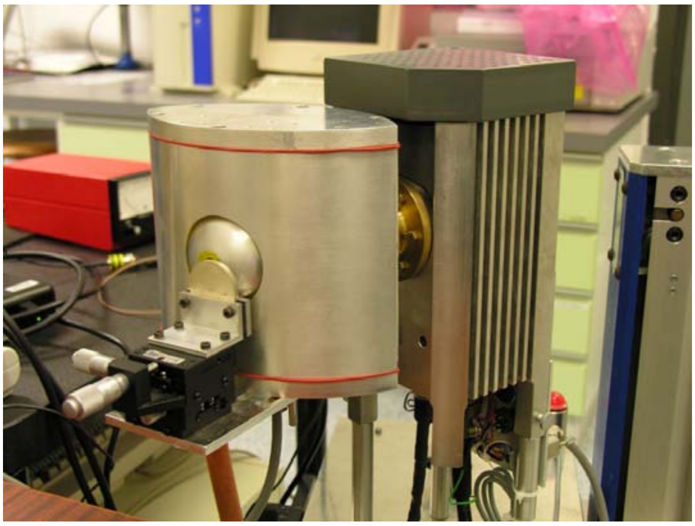

Fig. 1. Portable XRF spectrometer with vacuum chamber and polycapillary

The chamber is pumped by a small rotational pump down to the 10^{-1} mbar level. Kapton™ foil of 8 µm thickness was used for the window of the vacuum chamber which minimized the absorption losses for both the exciting and characteristic radiation.

The chamber can be placed at a very small distance (1 mm) from the object under investigation. Two adjustment lasers are used to define the spot of examination precisely. The performance of the spectrometer was assessed and preliminary results for the analysis of cultural heritage objects were obtained.

More information is available from Darek Wegrzynek (D.Wegrzynek@iaea.org).

Recent and forthcoming activities in ion beam accelerator methodology and applications

1. International Symposium

The International Symposium on Utilization of Accelerators was organized in Dubrovnik, Croatia, 5th–9th June 2005. The above Symposium was organized by the IAEA, in collaboration with the Government of Croatia. It provided a platform for experts in the field of particle accelerators to exchange information, to review the present status, and to discuss current trends and developments. There were about ninety participants from forty-one countries. Also present were representatives from some commercial companies who either contributed to the paper presentations or displayed some information about their areas of activity. The oral and poster presentations made at the conference addressed the following themes:

- Application of accelerators in materials and life sciences
- Application of accelerators in industry
- Application of accelerators for the safety and security of people
- Accelerator technology
- Key Issues.

1.1. Accelerator facilities

Different kinds of accelerators were described during the course of the presentations. These included Tandem, Tandetron and Pelletron linear accelerators, Cyclotron and Synchrotron accelerators, the Hadron Collider, and accelerator driven systems for sub-critical assemblies. Applications of these accelerators were in diverse areas of interest.

1.2. Industrial applications

- Presentations highlighted the use of electron accelerator beam systems for:

- Medical sterilization
- Food irradiation (spices and herbs)
- Polymer cross-linking, curing, grafting, and chain scission
- Wastewater treatment
- Flue gas treatment.

- The use of proton microbeam for writing of microstructures in silicon, and for fabrication of polymeric photonic structures, were some of the new developments presented.

- The use of proton micro beam for study of archaeological and art objects.

- The use of neutron generators (d+t reaction) for aviation security and detection of illicit materials in sea transportation system.

1.3. Accelerator mass spectrometry (AMS)

Presentations were made on the application of AMS for radiocarbon dating, determination of ^{7}Be, ^{10}Be, ^{210}Pb for the study of atmospheric transport processes (including troposphere-stratosphere exchanges), and measurement of ^{244}Pu for detection of nuclear weapon tests and super-nova formation.

1.4. Accelerator driven systems (ADS)

A few but interesting presentations were also made on accelerator driven systems and their use in sub-critical assemblies, and applications for dealing with radiotoxicity of problematic elements like Pu, Am, Cm and Np through partitioning and transmutation of high level radioactive wastes.

2. GUPIXWIN School

The training school was organized by the developers of the GUPIX software, the PIXE group of Guelph University, Ontario, Canada. The school was hosted by the Physics Department of the University of Florence, from 12th–13th October 2005. The lectures, demonstrations, and discussions were facilitated by Prof. Iain Campbell of Guelph University. In total, there were twenty participants from Italy, Hungary, Poland, Ukraine, Germany, the Czech Republic, Slovakia, Croatia, Austria and Brazil. Participants were taken through the essential features, new additions and tips for the utilization of this updated software. User-producer interaction was done through discussions of observed bugs and areas of possible improvements in the next version.

3. IBMM 2006

The XV International Conference on Ion Beam Modification of Materials IBMM 2006 will be held in Taormina, Sicily (Italy) from the 18th–22nd September 2006. The conference will provide a forum for participants to present and discuss recent research results and future directions in the field of ion beam modification, synthesis and characterization of materials. Detailed information can be found on the website http://www.ibmm.it

4. CAARI 2006

The 19th International Conference on the Application of Accelerators in Research and Industry (CAARI-2006) will be held at the Renaissance Worthington Hotel in Fort Worth, Texas, 20th–25th August 2006. The CAARI conference can be considered a collection of symposia for the following topics:

- Nuclear Physics
- Atomic Physics
- Ion Solid Interactions
- Accelerator Physics
- Ion Beam Analysis
- Ion Beam Modification of Materials
- Medical Applications
- Homeland Security

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

Implementation of a Quality System in the IAEA X ray fluorescence laboratory.

The IAEA X ray Fluorescence Laboratory, fully committed to endorsing the IAEA quality policy, has implemented, with the assistance of Roman Padilla Alvarez, consultant from Cuba, a quality system aimed at ensuring the provision of reliable analytical support to the analytical laboratories of Member States. The provision of reliable analytical results to these laboratories shall serve to assess the quality of their results, to improve analytical performance and to extend the applicability of various XRS techniques. The created quality system documentation can be used as a basis to provide general recommendations to X ray Laboratories in Member States and to facilitate their efforts in adopting quality assurance policies.

The implemented quality system complies with the requirements of the ISO 17025 (2005) standard, and with the general procedures adopted in the Agency's Laboratories at Seibersdorf. The quality system includes a quality manual and a system for keeping documented and validated analytical instructions, a group of well documented operational procedures and records. The members of the XRF Laboratory have taken part in this implementation and are fully committed to observe the quality policy of the laboratory. The quality manual has been prepared so as to be consistent with further extension of the scope of the quality system.

The responsibilities of the laboratory personnel in regard to the functioning of the quality system have been defined to fulfill the quality system requirements with a limited number of staff members (3 in our case).

Specific procedures have been created in order to organize the analytical work to comply with the administrative clearance required by IAEA policy, and in a way that allows customers to trace the state of execution of a given work assignment. Records are prepared to easily demonstrate the technical competence and experience of the laboratory, as well as to prove the observance of the quality commitment in any of the actions taken by the laboratory.

In the implemented operational procedures, an effort has been made to provide a comprehensive interpretation of the concepts of traceability and internal quality control to be applied to the specifics of X ray fluorescence analytical practice.

The traceability of the XRF obtained results is ensured by using suitable reference materials for the purposes of calibrations of the spectrometers and for the assessment of analytical performance of the implemented methods. Traceability is also ensured by the implementation of both an internal quality control practice (which serves to assess the precision and trueness of the obtained results) and an external control practice, based on participation in inter-comparison and proficiency tests.

A procedure has been set to address general recommendations for the quantification of the uncertainty of the results in two alternative approaches. A detailed assessment of the uncertainty budget (top-bottom approach), based on inspection of the theoretical model used in a given analytical method, serves to obtain an expression allowing calculation of the uncertainty of the results for any mass fraction range and specific sample properties. This approach, although more laborious, reveals the weaknesses of a given analytical method by the estimation of the contribution to overall uncertainty of each particular operation or measurement. This is of special relevance to refine the implementation method and to minimize the uncertainty of the results.

In the event that information about the quantification model is not available in sufficient detail (such as in the case of use of some commercial spectrometer software) or when the model is too complex, recommendations are given to use the concept of group-effect estimation for uncertainty assessment. The possible causes affecting the uncertainty of several of the measured quantities can be grouped under a particular concept, and their contribution to uncertainty can be assessed by conducting specific experiments.

Further improvements in the quality system are expected by the adoption of several practices, such as the performance of periodic internal audits and management reviews, and by analyzing the opinions and suggestions requested from the customers.

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

In-situ applications of X ray fluorescence techniques

A final report of the Coordinated Research Project (CRP) on In situ Applications of XRF Techniques was published as IAEA-TECDOC-1456 (September 2005). The CRP covered a period of four years (2000-2003). Twelve laboratories from both developed and developing Member States and the IAEA's laboratories participated. The objectives of the CRP included:

- Development and optimization of sampling methodologies for in situ XRF measurements;
- Improvement in the analytical performance of FPXRF based on the study of mineralogical effects, surface irregularity effects, heterogeneity and the influence of moisture content;
- Development and validation of quantitative and/or semiquantitative procedures to be applied for in situ XRF analysis
- Development of complete operating procedures for selected in situ applications, including relevant quality assurance.

Improvements in quantification and correction procedures

The participants of the CRP have developed, adapted and improved several methods for quantitative analysis. The proposed methods and procedures led to improved precision and accuracy of in situ element determination by XRF techniques. 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 pigments and other objects of works of art;
4. Correction procedures for moisture/light matrix content, dilution effect and surface irregularity effects;
5. Compensation for differences in size between calibration standards and analyzed samples;
6. Method for estimating effective atomic number of analyzed samples in support of quantification;
7. Estimation of low-*Z* matrix composition by applying the emission-transmission method in support of quality control;
8. Applied corrections for surface roughness, mineralogy and preliminary work on 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.

Complete operating procedures and guidelines for selected in situ applications

During the course of the CRP sampling strategies and procedures as well as methods for in situ sample preparation and analysis have been elaborated. Based on the reports presented by the participants 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.

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

Proficiency test for XRF laboratories

A final report of the results of the worldwide proficiency test was published. This proficiency test was targeted at analytical laboratories applying X ray spectrometry techniques for determination of element concentration. The exercise was organized by the XRF Group, Instrumentation Unit, IAEA Laboratories Seibersdorf at no cost to the participating laboratories from the IAEA's Member States. This proficiency test coded as PTXRFIAEA/02 was carried out using a plant material, a lichen species. The well characterized material was distributed to 31 laboratories at the end of 2004 with a 3 month's deadline for reporting back the analytical data. 17 laboratories reported 259 analytical results for 30 elements. A subset of 120 results for 10 elements with well established property values (V, Mn, Fe, Cu, Zn, As, Sr, Cd, Ba, and Pb) was selected and evaluated. The results can be used by the participants to control and eventually improve the performance of the applied analytical techniques. Regular participation in proficiency tests should be "normal laboratory practice" for the laboratories performing routine analytical work

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

Database of reference materials for XRF laboratories

One of the most challenging tasks when validating XRF analytical methods is selection of suitable reference materials (RM). As is widely known, a suitable RM in the case of XRF analysis is not necessarily that one where the nature of the matrix is similar to the matrix of the samples to be analyzed. This is due to the fact that in XRF analysis the chemical form of elements is of no relevance. Thus, in many cases a soil could be an appropriate RM when validating an analytical method for sediments.

Another thing to consider is the so-called dark matrix. The elements present in the analyzed material but not present in the X ray fluorescence spectra, can often be described as one or two hypothetical elements with certain average atomic numbers having similar absorption properties to the real dark matrix. In this manner, very dissimilar materials may be considered to be suitable RMs, for example, a milk powder could be used as RM when validating methods for analysis of certain orchard leaves.

The next point to be addressed is related to spectral interferences. The analyst should select an RM where the ratio of concentrations of certain elements is within particular ranges, preferably matching the expected variability of those elements in the samples for which the analytical method is being validated. As illustration, the cases of arsenic and lead can be mentioned.

In some other cases, when validating generic analytical procedures, the XRF laboratories face another problem. If it is needed to validate a method for determination of the concentrations of minor and trace elements in aluminous silicates (for predefined concentration ranges for Al, Si and maybe Ca and O), it is necessary to assess the validation ranges for the analytes in question. Depending on the existing set of RMs in the laboratory, an educated decision on the acquisition of additional materials should be made.

As part of the efforts of the IAEA XRF Laboratory to assist Member State laboratories in appropriate QA/QC, a database was put together to help the analytical laboratories find suitable RMs for method validation.

The particular set of materials compiled in this database was selected considering typical needs of X ray fluorescence analytical laboratories and contains information on over 5600 RMs and CRMs compiled from the existing sources available on the Internet (as of September 2005). The database consists of a fully searchable MS Excel workbook. The searches are designed to help analysts in facing the above-mentioned challenges. One can easily select, for example, the materials in powder form where both the concentration of Si and Al was 15% to 20%, Mn was 50 ppm to 500 ppm but Fe was not more than 10000 ppm. The database contains contact information of the producers and vendors of RMs and CRMs.

The database, together with detailed instructions for its use can be freely downloaded from the IAEA XRF Laboratory at http://www.iaea.org/OurWork/ST/NA/NAAL/pci/ins/xrf/pciXRFdown.php.

Further information is available from Ernesto Chinea-Cano (E.Chinea-Cano@iaea.org).

.

X ray fluorescence in Member States

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

Cuba

Center for Technolgical Applications & Nuclear Development, Havana, Cuba
Contributor: Roman Padilla-Alvarez (roman.padilla@infomed.sld.cu)

The Laboratory of Analytical Chemistry at the Centre for Technological Applications & Nuclear Development (CEADEN) has a two-fold mission: providing analytical services to the industry, health care and environmental control institutions and carrying out research projects aimed at introducing and applying nuclear and related analytic techniques in different types of investigations. The laboratory works on a self-sustained financial basis and has held accreditation by the Cuban QA/QC authority according to the ISO regulations since 1992.

In 2004 the laboratory fulfilled the requirements of the ISO 17025 standards. The laboratory has validated seven XRF analytical procedures, while three others are in the process of validation.

XRF is one of the most commonly used analytic techniques, due to the advantages of versatility, non-destructive character, low costs and relatively high productivity. The laboratory operates three XRF spectrometers, allowing the application of this analytical technique to samples of diverse nature:

- A spectrometer using ^{241}Am and ^{109}Cd annular radioisotope sources for excitation is employed for the analysis of metal alloys and raw materials, thus allowing determination of minor and major constituents in a prompt way.
- A TXRF spectrometer using a multilayer device to achieve monochromatic excitation and to reduce background continuum is applied to the analysis of different kinds of liquid samples.
- A third spectrometer is based on the principle of polarized excitation using X ray tube and secondary targets (EDPXRF). X ray production is maximized by using a homemade compact design for sample-secondary target positioning (X-PRISM), and its combination with a digital signal processing spectrometer (DSP) allows achieving of a significant improvement in the instrumental sensitivity. The enlarged counting statistics, allowing significant reduction of the measuring times and of lowering the uncertainty due counting statistics results of great relevance to improve the productivity in the analysis of trace elements in samples of diverse origin.

Main analytical services include the following:

- Composition of metal alloys (stainless steel, ferrous, copper, aluminum, magnesium, nickel, zinc, lead);
- Natural radioactive elements by gamma spectrometry;
- Water quality analysis (injection quality, drinking, swimming pools, wastewater):
    - Organoleptic parameters
    - Alkalinity, hardness, turbidity, pH, total solids, dissolved total solid
    - Cl^- , NO^{3-}, NO^{2-} , SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}, Si, y Fe^2 (standard methods)
    - Trace and heavy metals (TXRF, APDC-EDXRS, ASV, FAAS)
    - OBD_5, OCD, dissolved oxygen, total N;
- Heavy metals and other micro and trace elements in environmental samples (soils, fertilizers, sediments, lichens, algae, fish and shellfish tissues);
- Essential and toxic trace elements in food and pharmaceutical products;
- Composition of industrial raw materials, residues and concentrates.

Research projects involving XRF studies during the last 15 years:

- Determination of REE in phosphate rocks by EDXRF (IAEA Research Contract 5464/RB, 1988-1990).
- Determination of heavy metals in marine sediments from Moa Bay (IAEA Research Agreement No. 6729/CF, 1993-1994).
- Multi-element analysis of Cuban marine sediments by EDXRF (CEADEN Project, 1993-1994).
- Identification of probable causes of epidemic neuropathy in Cuba (IAEA Technical Assistance Project CUB/2/008, 1994-1997).
- Analysis by EDXRF of marine sediments and biological species in environmental studies in Cienfuegos Bay (National Program for Environmental Care, 1995-1997).
- Determination of the heavy metal contents in Cuban mangroves by EDXRF, FAAS, and ASV (National Program for Environmental Care, 1996-1998).
- Heavy metal analysis in rainwater and seawater (National Program for Environmental Care, 1996-1997).
- Archaeological pottery INAA composition analysis (IAEA Research Contract CUB/9397, 1997-2000).
- Heavy metal pollution in mean agricultural cultivars in Cuba (National Program for Improving Food Production PN 00-2042, 1998-2000)
- Identification of pigments in mural and easel paintings (PRN/7-2/6, 2002-2003).
- EDXRS fundamentals in several applications (PRN/7-2/5, 2002-2003).
- Cu and Zn analysis in blood serum from patients undergoing dialysis (PRN/7-1/2, 2001-2003).
- Alarm system for accidental toxic chemical spills into Cauto River (IAEA Technical Co-operation project CUB/8/017, 2002-2004).
- Bio-monitoring studies based on lichen analysis (IAEA ARCAL LX, 2002-2004).
- Analysis of the heavy metal contents in saline waters and dolphins' food and blood serum from National Aquarium by Nuclear and Related Techniques (PRMA, 2002-2005)
- Metal speciation in environmental studies in coastal ecosystems (as part of IAEA CUB/7/006, 2004-2006).

- Non-destructive EDXRF archaeological pottery composition analysis (IAEA Research Contract CUB/13051, 2005-2007)

Notes on funding programs: PRN - Program of Cuban Nuclear Energy Agency; PRMA – Program of the Cuban Environmental Care Agency

Main papers published during the last 10 years:

ESTÉVEZ ÁLVAREZ, J.R., PADILLA ÁLVAREZ, R., AGUIAR LAMBERT, D., CHINEA CANO, E., PUPO GONZÁLEZ, I., GONZÁLEZ GARCÍA, H., Feasibility of several EDXRF methods in environmental studies in Cienfuegos Bay, Proceedings of an International Symposium on Harmonization of Health Related Environmental Measurements using Nuclear and Isotopic Techniques, Hyderabad, India, STI/PUB/1006 IAEA, 1997, 609-613.

PADILLA ALVAREZ, R., CHINEA CANO, E., ESTÉVEZ ALVAREZ, J.R., GREAVES, E.D., Instrumental detection limits in TXRF: Comparison of cut-off and monochromatic excitation devices, J. Radioanal. Nucl. Ch. **240**, 2 (1999) 517-522.

MONTERO ALVAREZ, A., ESTEVEZ ALVAREZ, J.R., PADILLA ALVAREZ, R., Heavy metal analysis by nuclear related techniques. Application of APDC precipitation and energy dispersive X ray fluorescence, J. Radioanal. Nucl. Ch., **245**, 3 (2000) 485-489.

ESTÉVEZ ALVAREZ, J.R., MONTERO, A.A., JIMÉNEZ, N.H., MUÑIZ, U.O., PADILLA, A.R., MOLINA, R.J., QUINCUTE DE VERA, S., Nuclear and related analytical methods applied to the determination of Cr, Ni, Cu, Zn, Cd and Pb in a red ferralitic soil and Shorgum samples, J. Radioanal. Nucl. Ch. **247**, 3 (2001) 479-486.

LARTIGUE, J., PADILLA, R., MARTÍNEZ, T., ORTA, M., EDXRF determination of Pb in aerosol samples from Mexico City Valley, Radiat. Phys. Chem. **61** (2001) 681-682.

ALVAREZ, R., VAN ESPEN, P.J.M., PLA, R.R., ROSSI, E.M., DELGADO, R.A., GODO TORRES, P.P., GONZALEZ, M.C., Compositional classification of archaeological pottery based on NAA and SEM-EDS, J. Trace Microprobe T. **21**, 4 (2003) 677-695.

PADILLA ALVAREZ, R., VAN ESPEN, P., ABRAHANTES QUINTANA, A., Assessing scattering effects in annular radioisotope excited XRF, X ray Spectrom. **33**, V1 (2004) 74-82.

PADILLA, R., PÉREZ OLIVA, J. F., PUPO, I., TXRF analysis of Cu and Zn in blood serum from haemodialysis patients, Nucleus **35** (2004) 5-10.

PADILLA, R., VAN ESPEN, P., ABRAHANTES, A., JANSSENS, K., Semi empirical approach for standard less calibration in µ-XRF spectrometry using capillary lenses, X ray Spectrom. **34**, 1 (2005) 19-27

PADILLA, R., SCHALM, O., VAN ESPEN, P., JANSSENS, K., ARRAZCAETA, R., Microanalytical characterization of surface decoration in Majolica pottery, Anal. Chim. Acta **535** (2005) 201-211.

PADILLA, R., VAN ESPEN, P., ESTÉVEZ, J.R., Improving instrumental sensitivities in polarized X ray fluorescence analysis. Submitted to J Anal. Atom. Spectrom. in June 2005.

PADILLA, R., VAN ESPEN, P., GODO, P.P., The suitability of EDPXRF analysis for non-destructive compositional classification of pottery: a comparison with results of a previous INAA study. Submitted to Anal. Chim. Acta in June 2005.

Contact information:

CEADEN, Laboratorio de Análisis Químico
Calle 30 # 502, Playa, Ciudad Habana, Cuba
http://www.ceaden.cu
Tel./Fax: (+537) 2066110
email addresses:
Juan R. Estévez Alvarez: jestevez@ceaden.edu.cu
Román Padilla Alvarez: padilla@ceaden.edu.cu , roman.padilla@infomed.sld.cu
Alfredo montero Alvarez: amontero@ceaden.edu.cu

Peru

Instituto Peruano de Energia Nuclear, Lab. de Fluorescencia de Rayos X, Lima, Peru
Contributors: Paula Olivera (polivera@ipen.gob.pe)

Work applied to the archaeology in Peru using the X ray fluorescence technique

The application of the XRF technique performed in our laboratories in the field of archaeology began in 1994. It started with the analysis of different samples, as an incisive tooth, a fragment of occipital, a rib fragment, a segment of dorsal vertebra and small glasses found in the internal surface of a Nazca Culture mummy. In the paleopathological study performed by Dr. Guido Lombardi a ^{109}Cd excitation source and an X ray spectrometry system were used. The elemental concentrations of Ca, Fe, Zn, and Sr were determined for the paleonutrición studies by using the relationships of Zn/Ca and Sr/Ca. The XRF technique also contributed to the mycobacterium tuberculosis detection in a mummy, supplementing other non destructive tests carried out previously[1].

Reconstruction of diets

In recent years, 29 right clavicles belonging to mature individuals were analyzed out of 143 found in the Villa El Salvador area (identified by sex and approximate age). Sr and Zn concentrations were used to determine the relative proportion of vegetable and animal foods in the population's diet under study. Bony remains and silts of the place were analyzed using the energy dispersive X ray fluorescence technique. Sr, Zn, Ca and other elements such as Fe, Cu, Br, Mn, Ni, Rb, Zr and Pb were determined in the samples. The evaluation of spectra was carried out with AXIL-QXAS software. A regression model was developed using the logarithmic relationships of the Sr and Zn concentrations. It was concluded that the old residents of Villa El Salvador manifested an omnivorous feeding with carnivorous tendency, due to consumption of products of marine origin[2].

Analysis of ceramic (fragments and whole pieces)

Ceramics have also been analyzed to determine the chemical composition of the paste which was used in the production process. For example, 39 fragments of ceramic from the place called Lomo de Corvina of Villa El Salvador, low valley in Lurin town were analyzed. The analysis of these samples was focused on quantitative determination of Ti, Fe, Rb, Sr, Y, Zr and Nb, to complement the results obtained by neutron activation analysis.

Pigment identification

Identification of the pigments used for production of art objects is of great importance for its characterization, authentication and/or restoration. This is possible because the types of pigments are often specific for a time and place where the art objects were produced; therefore they can be used as fingerprints to identify the origin, confirm/reject authenticity or even to reveal the presence of later restoration works after their creation. For this reason, we are currently working on identification of pigments used in the decoration of archaeological ceramics.

This work started from construction of a portable XRF spectrometer based on a small size, low-power X ray tube and a thermoelectrically cooled semiconductor detector, similar to the one developed and constructed in the Instrumentation Unit, IAEA Laboratories, Seibersdorf, Austria, and presented to us during our visit at the beginning of this year. The system consists of an air-cooled low-power (50 W) Pd-anode X ray tube. The X ray spectra were acquired with a Si-PIN detector and MCA 8000A multichannel analyzer. All measurements were carried out in air under direct excitation geometry. A palladium filter was inserted between the tube window and the sample. The tube was operated at 40 kV high voltage and 0.998 mA current. The measurement time was 1000 s per point and per sample (Fig. 1).

The main objective of this initial work was to identify the inorganic pigments present in the paintings of the Nazca region, and to confirm (or to reject) the hypothesis that they worked basically with a product called cinnabar.

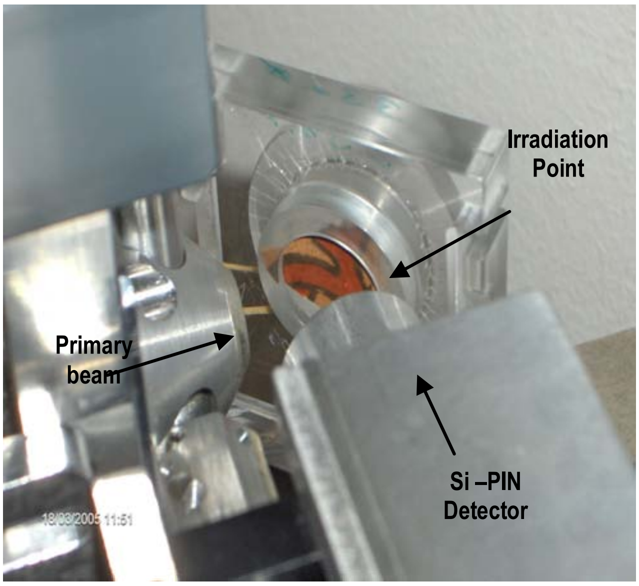

Fig. 1. Irradiation geometry used for point analysis of paintings.

In fact, the presence of S, Fe and Hg in the sample were determined (see Fig. 2); additionally this pigment was analyzed by transmission electron microscopy (TEM) showing the presence of crystal with the HgS structure (cinnabar)[3].

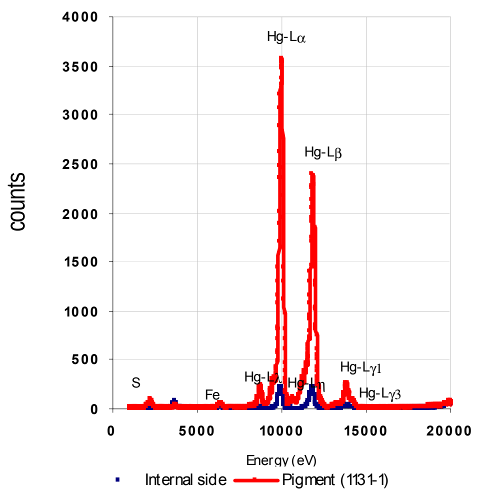

Fig. 2. Spectrum of red archaeological pigment (1131-1)

At present, we are working on characterization of fragments of archaeological and recent pottery in order to check whether the artists of our time use the same pigments.

Acknowledgements

We express our gratitude to the XRF Group of the IAEA Laboratories at Seiberdorf for support and fruitful discussion.

References

[1] LOMBARDI, G., Detección de Myco-bacterium Tuberculosis en una momia, 1994.

[2] MONTALVO, a., Análisis Multielemental de restos óseos por Fluorescencia de Rayos X para la reconstrucción de dietas del Periodo Temprano en la Cultura Lima, Thesis, 1997.

[3] LOPEZ, A., Informe de análisis de muestra arqueologica, código TM 1131 por TEM, 2005.

Spain

Instituto de Ciencia de los Materials, Universidad de Valencia, Valancia, Spain

Contributors: C.C. Roldán, S. Murcia-Mascarós, J.L. Ferrero* (clodoaldo.roldan@uv.es)

Instrumental facilities of the ICMUV include: a total reflection X ray fluorescence (TXRF) spectrometer, and laboratory and portable energy-dispersive X ray fluorescence (EDXRF) spectrometer. These instruments are applied in the field of art and archaeometry.

Current projects in collaboration with the Department of Prehistory and Archaeology (University of Valencia), the Valltorta Museum and Vetraria Muñoz de Pablos S.L, are:

In situ analysis of rock art painting by portable EDXRF spectrometry in the Valltorta Valley, East of Spain

A purpose of the research was to investigate the elemental composition of the prehistoric cave paintings located in the Valltorta Valley in Coves de Vinromá (Castellón, Spain) and to demonstrate the usefulness of portable EDXRF spectroscopy for in situ elemental analysis. Analysis of the red and black pigments by portable EDXRF showed the presence of iron and manganese compounds, respectively; in the future it will facilitate sampling decisions prior to use of other analytical methods to obtain additional information about chemical composition, structure and preparation techniques.

Application of portable EDXRF system to the study of ancient glasses

Since there is no method available to determine directly the age of glass objects, it is necessary to compare the material composition of questionable pieces with genuine pieces. Therefore, a non-destructive and sensitive analytical technique was needed with a capability to perform in-situ measurements in order to avoid transportation of precious and fragile objects to the analytical laboratory. A portable EDXRF system meets these requirements more than adequately. The application of a portable XRF spectrometer for solving authenticity-related problems in the field of ancient glasses has demonstrated its capability for revealing essential information for study of the Stained Glass Windows of Avila Cathedral. During the restoration work, clear differences in the composition of glasses from the Renaissance and 20th century were found by the EDXRF analysis.

The measurements provided a large comparable set of reference data for glass research. Because of a small information depth for the light element fluorescence lines (especially Na and Mg), alternative methods are required. The quantification procedure included deconvolution of the peak areas with measured peak profiles determined by using standard glass materials provided by Verrerie Saint-Just or by comparison with well known glasses. The same procedure was applied to the study of buried glasses from the Morella excavation. In the last case, enamelled pieces of glass were studied. The results were compared with different pieces coming from the same area.

References:

[1] ROLDÁN, C., MURCIA-MASCARÓS, C., FERRERO, J., VILLAVERDE, V., MARTÍNEZ, R., GUILLEM, P., LÓPEZ, E., In situ analysis of Mediterranean cave paintings by EDXRF. Presented in the VI Congreso Ibérico de Arqueometría. Girona (Spain), 15-19 November, 2005.

[2] MURCIA-MASCARÓS, S., ROLDAN, C., FALOMIR, C., IBÁÑEZ, R;. SAPIÑA, F., MARTÍNEZ-TAMAYO, F., FERRERO, J., Análisis no destructivo de una pieza singular de vidrio esmaltado. Presented in the VI Congreso Ibérico de Arqueometría. Girona (Spain), 15-19 November, 2005.

[3] MURCIA-MASCARÓS, S., DOMINGO, C., SÁNCHEZ, S., GARCÍA, J.V., ROLDÁN, C., MUÑOZ, A., Composition and distribution of crusts in weathered stained glass windows through mapping and confocal micro-Raman spectroscopy. Proceedings 8th International Conference on “Non destructive Investigations and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage. ISBN 88-89758-00-7 (2005).

*Correspondence to: C. Roldán, Unidad de Arqueometría. Instituto de Ciencia de los Materiales de la Universitat de València (ICMUV). P.O. Box 22085, E-46071 Valencia (Spain). Telf.: +34 96 354 3619. Fax: +34 96 354 3633. E-mail: clodoaldo.roldan@uv.es

.

Publications of potential interest to the XRF community

In Situ Applications of X ray fluorescence Techniques – Final Report of a Coordinated Research Project 2000-2003, IAEA-TECDOC-1456, 2005.

WEGRZYNEK, D., MARKOWICZ, A., BAMFORD, S., CHINEA-CANO, E., BOGOVAC, M., Micro-beam X ray fluorescence and absorption imaging techniques at the IAEA Laboratories, Nucl.Instrum. Methods in Phys. Res. **B231** (2005) 176-182.

BAMFORD, S.A., WEGRZYNEK, D., CHINEA-CANO, E., MARKOWICZ, A., Application of X ray fluorescence techniques for the determination of hazardous and essential trace elements in environmental and biological materials, NUKLEONIKA **49**(3), (2004) 87-95.

IAEA
International Atomic Energy Agency

XRF Newsletter No. 10
December 2005

The XRF Newsletter is prepared twice per year by the IAEA Laboratories in Seibersdorf. Correspondence and materials to be considered for publishing should be sent to:

Dr. A. Markowicz
IAEA Laboratories
A-2444 Seibersdorf, Austria

Fax: (+43 1) 2600-28222 or (+43 1) 26007
E-mail: A.Markowicz@iaea.org

International Atomic Energy Agency
Wagramer Strasse 5, P.O. Box 100,
A-1400 Wien, Austria

Printed by the IAEA in Austria,
December 2005

05-48131