



A newsletter from the IAEA Laboratories, Seibersdorf
Issue No. 20, December 2010

ISSN 1608-4632

X ray Fluorescence in the IAEA and its Member States

Activities in the IAEA XFR Laboratories

A low cost digital spectrometer for XRF analysis

The Nuclear Spectrometry and Applications Laboratory (NSAL) at Seibersdorf in cooperation with Mr Mladen Bogovac, Croatia (currently a staff member of NSAL) has designed and constructed a low cost digital spectrometer for XRF. The spectrometer comprises the following components:

- (1) analog signal pre-conditioning board with power supply,
- (2) FPGA board with fast ADC,
- (3) stepper motor driver,
- (4) acquisition software running on the PC.

The spectrometer has a single input and can accept signal from standard spectroscopy preamplifier (TPR or RC feedback type). In addition it can drive existing sample changer on the XRF system. It is connected with PC via USB port. The system has been tested and compared with a standard fully analog-based processing system.

The rationale behind this development was to provide the laboratories in Member States with an affordable and cost effective way of modernizing existing XRF spectrometers. Thus, the system can be utilized with nearly all types of XRF detectors and is easily modifiable and adaptable to most of the typical needs in the field of XRF analysis.

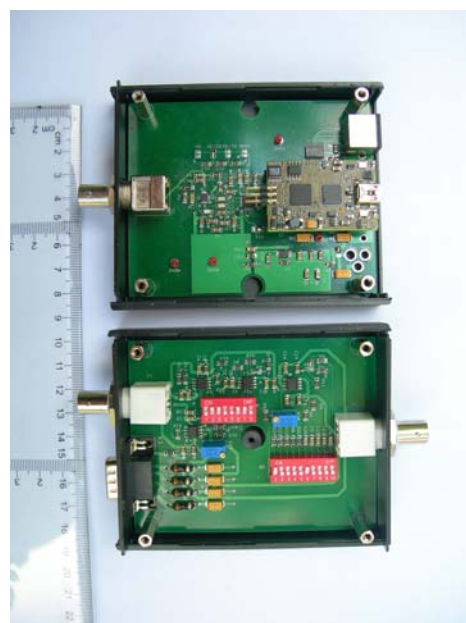


Fig.1. Image of the FPGA (top) and Prefilter (bottom) boards.

In This Issue

- Activities in the IAEA XRF Laboratories
- A low cost digital spectrometer for XRF analysis 1
- Meetings
- TM on In Situ Methods for Characterisation of Contaminated Sites 4
- TM on Instrumentation for Digital Spectroscopy 6
- An evaluation of Inter-Laboratory reproducibility for Quantitative XRF of Historic Copper Alloys 6
- Authentication Workshop for metal and stone antiques using scientific techniques, Egyptian Museum of Cairo, Egypt 8
- Support to Technical Cooperation Projects 10
- X ray Fluorescence in Member States
- Argentina 12
- Peru 14
- Spain 16
- Publications of potential interest to the XRF community 20

1. Prefilter board

The pulses coming from charge sensitive preamplifier usually have either a long tail or they are superposed to a saw-tooth ramp. The direct digitalization of long tailed-pulses, after being properly amplified, may lead to an inefficient usage of ADC in the case of the pile up. Also, the saw-tooth ramp should be removed due to the same reason. Therefore, a simple signal conditioning module, so called pre-filter has been designed and produced (see Fig.1).

2. FPGA board

The single ended output signal with 2VP-P nominal amplitude from the Prefilter board is digitized and processed using the FPGA board. The digitization is done by using 14 bit ADC (LTC2248) at sampling rate of 48 MSamples/s.

The ADC is coupled to Spartan-3E FPGA (XC3S500E-4CPG132C). The FPGA is placed on a separate small-sized board (48 × 22 mm, EFM01 produced by Cesium GmbH, www.cesium.com) providing two 34-pin connectors (see Fig. 1).

The board communicates with PC via USB port. Since the same port is used for powering both analog and digital part, no external power supply is needed but the board can operate only while it is connected to the running PC via USB cable.

In order to provide control signals for +5V TTL motor driver, a few FPGA I/O pins were allocated. Since the pins are not 5V tolerable, a corresponding level translator (74LVC4245) had to be used.

2a. MCA-DPP top level module

The MCA-DPP module contains a digital equivalent of a modern spectroscopy amplifier, peak detector and acquisition interface (to perform pulse-height analysis). It provides: pulse shaping, pile-up rejection, base line restoration, peak detection, live time correction, pulse sorting by amplitude and memory to store it. Implementation of these functions is a demanding task and may be additionally complicated by a pure VHDL coding. Therefore the Xilinx System Generator and Matlab/Simulink were used for developing the DPP module. It allows to use predefined and tested blocks (dual port memories, FIFO, math operations), script language for implementing control logic and finally to generate VHDL code. All these is done in a friendly graphical environment.

3. System performance

First the system performance was compared with analog one (Canberra Amplifier model 2020 and ADC 8715) using Fe^{55} source. Figure 2 shows that energy resolution of both system are similar at very low counting rate.

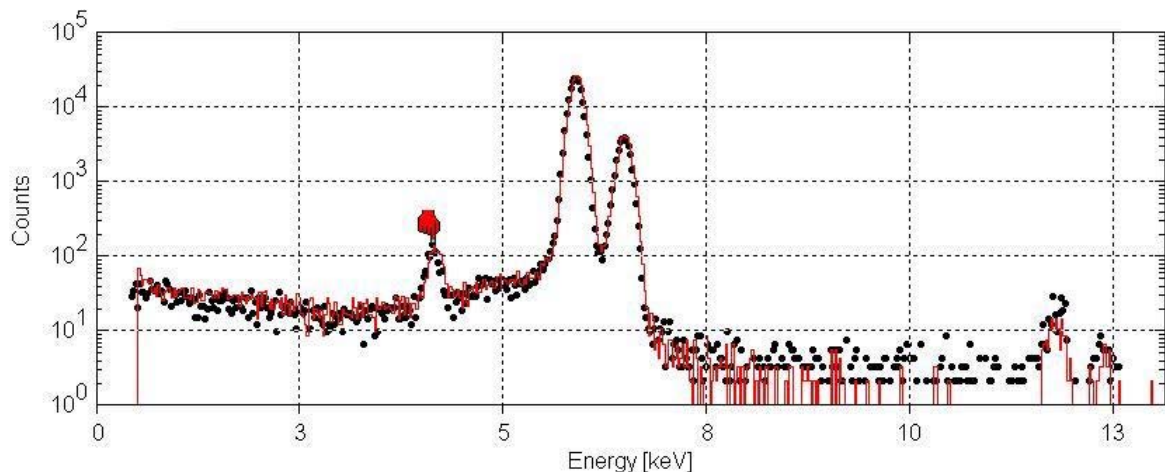


Fig. 2. Spectra of Fe^{55} source at low counting rate (200 counts/s) collected with state of the art analog (dots) and digital system (line) show similar performance. The resolution at Mn-Ka was 175 eV for both systems.

After that the system was tested using XRF spectrometer with Rh secondary target and Mo anode tube. The tube was running at 40 kV and two currents 5 mA and 40 mA. In the first case the counting rate was around 2000

counts/s and in the second 20,000 counts/s (see Fig.3). The systems were used with triangular shaping with several identical shaping constants.

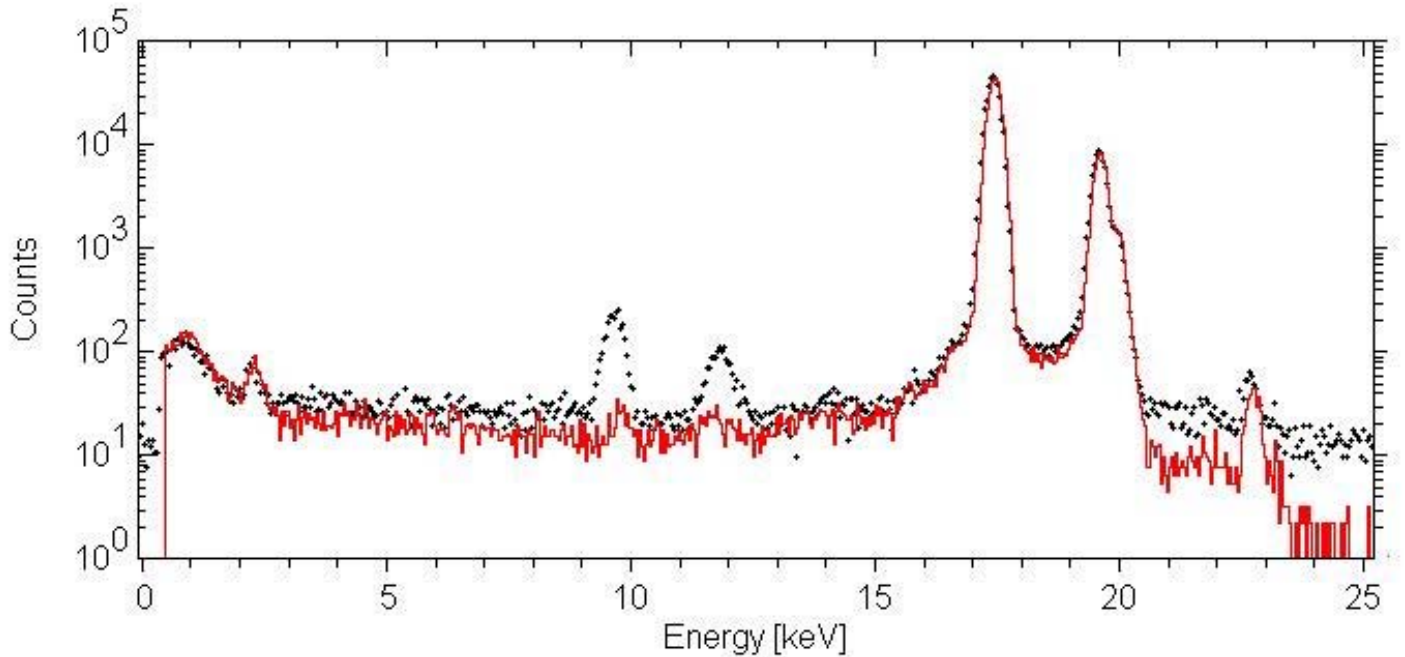


Fig. 3. Spectrum measured by using XRF changer with Rh secondary target and Mo anode tube at 20000 counts/s (40mA/40V) with analog (dots) and digital (lines).

Comparison of the digital and analog systems in terms of resolution and dead time for different counting rates and shaping times is given in the table below (the results for

resolution shown inside brackets are with BLR correction).

Input count rate[c/s]	Dead time[%]		Resolution [eV]		Peaking time [us] analog and digital
	analog	digital	analog	digital	
2000	4.5	3.6	328	326(335)	5
2000	7.3	7.0	297	295(307)	10
2000	10.4	10.3	287	288(303)	15
20,000	31.3	26.4	332	330(352)	5
20,000	55.3	46.5	301	296(314)	10
20,000	69.5	61.3	294	289(318)	15

4. Acquisition software

The acquisition software is written in C++ using Microsoft Visual Studio (see Fig. 4). It is capable of measuring several samples in a row. This is done in the so called 'job acquisition mode'. The user should define which sample positions are loaded and preset time (either live or real) for each sample. Each spectrum is shown in a

different window and saved automatically when preset is reached. Spectra are saved on QXAS (*.spe) format.

The technical details on the low cost digital spectrometer for XRF are available for the XRF laboratories in the IAEA Member States. For more information please contact: M. Bogovac (M.Bogovac@iaea.org) or E. Chinea-Cano (E.Chinea-Cano@iaea.org).

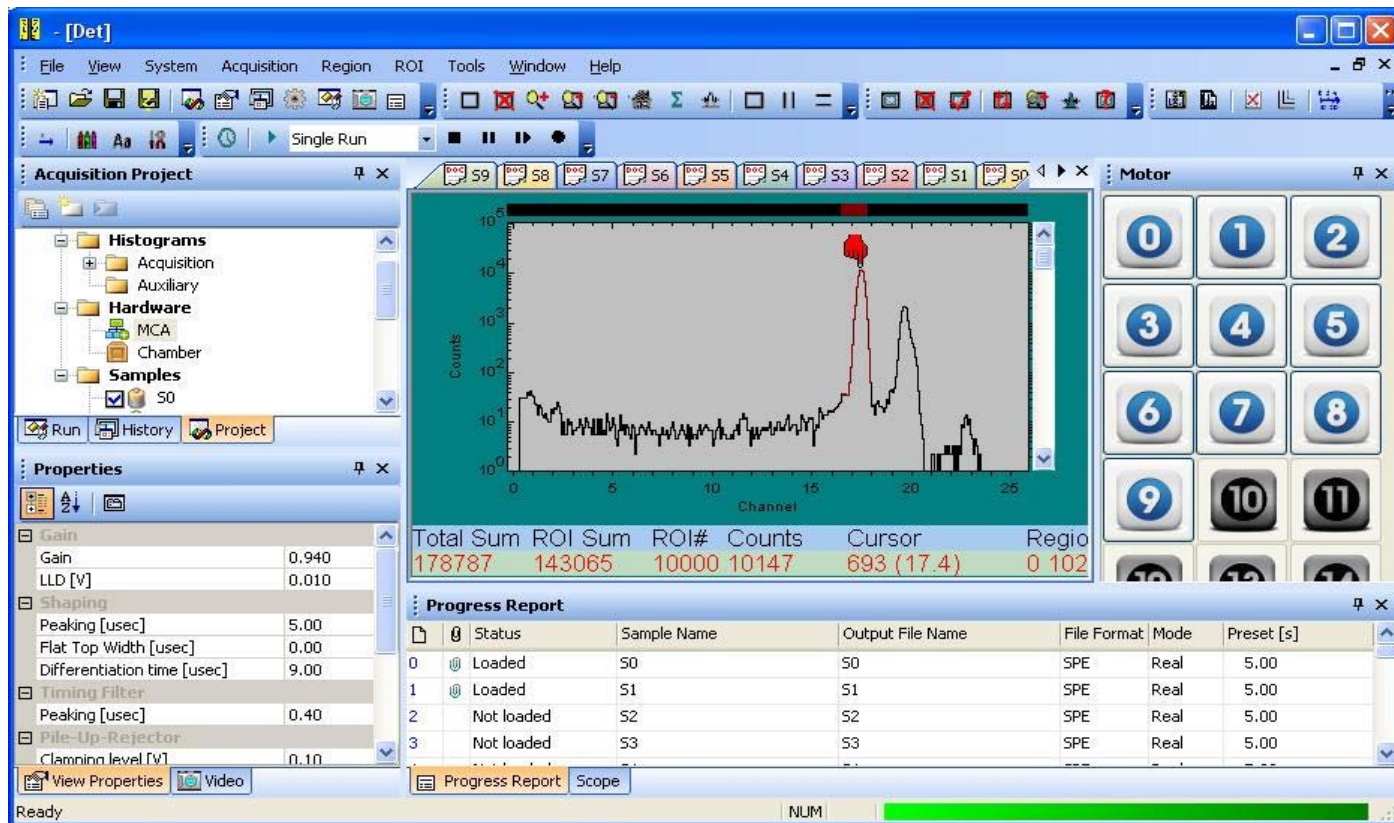


Fig. 4 Acquisition Software

Meetings

Technical Meeting on In Situ Methods for Characterization of Contaminated Sites, Vienna, Austria, 5–9 July 2010

In order to investigate, control and regulate a contaminated site, the direct in situ characterization of contaminated sites (meaning that the analytical instrument is taken to and placed over or in contact with the sampling area) is an important alternative or complement to procedures involving the laboratory analysis of samples collected in the field. Direct in situ characterization supports and improves the quality of the analytical data from a contaminated site. It is adopted by many national authorities as a tool in decision making policies through site-specific risk assessment. In this context, the in situ implementation of nuclear spectrometry techniques and of other complementary methods, have reached a high level of analytical performance and offer certain advantages over other more traditional characterization procedures of a contaminated site, including:

- Rapid determination of contaminant concentrations/activities in many spots/areas across the contami-

nated site without time-consuming sample collection and preparation.

- A possibility to perform interactive characterization of contaminated sites with immediate real time identification of areas of interest ('hot-spot' areas), allowing further investigation of these areas with adequate spatial resolution.
- Cost reduction for the investigation of all the stages of an assessment, decommissioning and remediation process.

Major objectives of the Technical Meeting held in Vienna from 5-9 July 2010 were to highlight, review and discuss issues related to the current status and trends of various applications of in situ techniques for contaminated sites. The advantages and limitations of the techniques in various fields of application were assessed in order to support a development of new instruments and analytical methodologies.

The following applications of in situ techniques (including gamma- and X ray spectrometry) for study of the contaminated sites and various activities were addressed:

- Mineral exploration and mining (e.g. uranium mining) sites
- Nuclear power and nuclear processing facilities
- Industrial activities that produce naturally occurring radioactive materials (NORM)
- Industrial activities that produce metal contaminants (i.e. lead, zinc, copper, etc.)
- Military actions involving the utilization of nuclear material
- Accidents
- Terrorism actions.

The participants from Albania, Argentina, Australia, Brazil, China, Czech Republic, Egypt, France, Greece, Hungary, Italy, Jamaica, Lithuania, Montenegro, Spain, United States of America and Uruguay gave presentations on and discussed the following specific topics:

- Selected in situ applications at different kinds of contaminated sites
- Comparison of different techniques/methodologies for the characterization of contaminated sites
- Sampling approaches (i.e. choice of number and location of measurements)
- Mapping approaches of a contaminated site
- QC/QA of the in situ analytical techniques and interpretation of the results
- State of the art of the portable instrumentation for in situ characterization including current trends
- Possible role of the IAEA in the promotion and effective use of nuclear spectrometry instrumentation and of associated analytical methodologies for in situ applications in developing Member States.

Field Portable X ray Fluorescence analysis (FPXRF)

One of the techniques applied for in situ characterization of the contaminated sites is X ray fluorescence (XRF) spectrometry. The basic block configuration of XRF equipment includes an excitation X ray source, an energy dispersive detector, electronic modules, a CPU module, a display mechanism and various mechanical parts such as collimators, filters, positioning stage etc. The characteristics of these components have been considerably upgraded during the past decade offering nowadays the implementation of many analytical features of laboratory or desktop XRF spectrometers in compact, light weight hand-held devices (typically less than 2 kg) easily transported on-site.

Radioactive point-like excitation sources (like ^{55}Fe , ^{109}Cd , ^{241}Am) were very popular in field portable XRF analyzers up to very recently. Their small physical size (small cylinders of approximately 5 mm height and diameter), the zero power consumption and the almost monoenergetic nature of excitation supported their utilization in portable and compact devices. On the other hand, there are certain drawbacks like rather short half-lives of some isotopes (^{55}Fe -2.7 years, ^{109}Cd -453 days), in general low primary beam intensity (for the sources with activity in the range of 1-10 mCi) and the need – for most of the countries – to comply with specific regulatory requirements in transportation and field applications. However, still they are in use, and for specific XRF applications (e.g. for screening RoHS in electronic devices and components), the ^{57}Co , ^{241}Am and ^{109}Cd sources have been adopted by some manufacturers (in particular the first two that do not have an equivalent with other available portable X ray sources). Since approximately 2000-2002, miniaturized X ray tubes of low power consumption (<10 W), battery operated, air-cooled, with different anode materials (Cr, Mo, Rh, Ag and W), different electron spot sizes and X ray flux became available. They enabled a development of portable XRF spectrometers operated up to 50 kV that are now commercially available.

The IAEA through its Terrestrial Environmental Laboratory (TEL) and Nuclear Spectrometry and Applications Laboratory (NSAL) supports the applications of nuclear analytical techniques for in situ characterization of contaminated sites through different mechanisms including: (1) provision of training of the fellows from developing countries in gamma and X ray spectrometry at the IAEA Laboratories at Seibersdorf, (2) support to regional collaborating centres and preparation of ICT-based training and learning materials; (3) preparation of guidelines for good practices for nuclear and nuclear related analytical techniques; (4) support to QC/QA activities to improve the performance of nuclear and nuclear related analytical techniques including organization of world wide Proficiency Test exercises; (5) organization and support of research coordinated projects and technical meetings to address the relevant topics.

The participants of the Technical Meeting formulated a number of recommendations in order to strengthen and improve the IAEA support to Member States laboratories involved in *in situ* characterization of contaminated sites along the lines specified in points (1)–(5) above.

Further details are available at

<http://www-pub.iaea.org/MTCD/Meetings/Announcements.asp?ConfID=38924>

For more information please also contact: A.G. Karydas (A.Karydas@iaea.org) or A. Ceccatelli (A.Ceccatelli@iaea.org).

Technical Meeting on Instrumentation for Digital Spectroscopy Vienna, Austria, 11–15 October 2010

Digital pulse processing is a signal processing technique in which detector (preamplifier output) signals are directly digitized and processed to extract quantities of interest (pulse height, pulse shape, arrival time etc.). Such an approach has significant advantages compared to the traditional analogue signal shaping setup, including the following features: (i) extremely good stability, (ii) filtering capability exceeding analog systems, (iii) high resolution combined with a wide dynamic range, (iv) good linearity and timing information such as time of arrival information, (v) support of multiple acquisition modes and provision of very specialized functionality such as pulse shape, pulse timing discrimination loss free counting mode, (vi) multiple digital pulse processing can run with synchronized acquisition to allow for timing correlation of events from multiple signal sources such as separate detectors or detector segments, and (vii) facilitates networking of analysers.

During the last years, the analogue-to-digital converters (ADCs) as well as more complex digital-signal-processing (DSP) units are increasingly being used for nuclear spectroscopy applications. This is due to the fact that these systems are becoming fast enough for applications in the digital real time processing of nuclear radiation detection data. The recent R&D approach is to simply digitize the incoming pulse signal from a radiation detection system and deconvolve it into individual pulses on-line in real time. This might be accomplished by taking several deterministic approaches including fitting the intensity and delay time of individual convolved pulses by a linear–nonlinear least-squares method or by a sophisticated transform approach. It is expected that soon there will be a possibility to eliminate almost all pulse pile-up distortion associated with nuclear radiation spectroscopy with a dedicated PC combined with an ADC for an individual detector system.

The application of DSP systems leads to new possibilities in processing of measured data, development of automatic measurement setup, and offline data correction related to other measurement parameters like temperature or magnetic field influence. New software for processing of detector data can replace the task of analogue modules such as single channel analyzers, constant fraction discriminators, time-to-amplitude converters and/or multi-

channel analyzers. Another role is to add new possibilities such as an automatic measurement setup capability and offline data filtering. A significant advantage of DSP is the possibility to use different approximation methods without the need to repeat measurements as in analogue systems. For example, small changes in channel window or in other parameters of analogue systems require repetitive measurements, whereas in a digital system the same acquired data set can be used with the relevant software. From this point of view, the innovative DSP approach is much more efficient.

The Technical Meeting held in Vienna from 11-15 October 2010 was attended by the representatives of Algeria, Bangladesh, Canada, Croatia, Egypt, Germany, Russian Federation, Slovakia, Tunisia and United States of America. The overall objective of the TM was to present and discuss the best practices, design aspects and practical experiences including maintenance. Moreover, the TM helped in building a communication bridge between various research groups from both developed and developing countries as well as various industrial partners involved in development of nuclear spectroscopy for peaceful applications of nuclear technology. The outputs of the TM include:

- An overview of state-of-the-art in the field of DSP including current trends,
- Review of DSP techniques, applications and implementations including their advantages and limitations with an emphasis on nuclear spectroscopy,
- Identification of the needs of the Member States laboratories for implementation of DSP systems in support of nuclear sciences and applications,
- Strengthening international and regional cooperation and networking between scientists from developing and developed countries with a special emphasis on the transfer of knowledge and possible role of the IAEA.

For more information please contact A. Zeman (A.Zeman@iaea.org) or A. Markowicz (A.Markowicz@iaea.org).

An evaluation of Inter-Laboratory reproducibility for Quantitative XRF of Historic Copper alloys

The recent widespread introduction and adoption of relatively low-cost, portable XRF spectrometers will soon result in the rapid proliferation and publication of XRF data from various fields of analytical research. Increasingly,

questions are being raised within the scientific community concerning the accuracy and inter-laboratory comparability and reproducibility of published XRF data. Generally, the comparison of data between laboratories,

or even between different instruments within a laboratory, is not a simple task. A recent study aimed to address the inter-laboratory comparability and reproducibility has been carried out in the particular case of quantitative XRF analysis of historic copper alloys⁽¹⁾. The study was coordinated by Arlen Heginbotham, Associate Conservator of Decorative Arts and Sculpture at the J. Paul Getty Museum, Los Angeles, USA. Fourteen institutions, from the art and archaeology community, primarily in the USA, but also from Europe, whose interests include a focus on historic copper alloys, participated in the study, producing 19 data sets. The XRF instruments incorporated different hardware components, e.g. tube anode materials, X ray detectors (Si(Li), silicon drift detector, Si-PIN), offering variable incident beam spatial resolution (from μm to mm spot area irradiation), operated at different experimental conditions (high voltage, filtered/unfiltered excitation) and supported by a variety of quantification procedures and software. The objective of the study was to quantify the extent of inter-laboratory reproducibility by determining correlations between the accuracy of results and the experimental methods and procedures followed. In this way, recommendations regarding best practice in applying XRF quantitative analysis in metals could be proposed to practitioners working in the conservation field.

The design of the study was based largely on ASTM standard E1601, *Standard Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method*, following Test Plan A. Each participating laboratory was asked to analyze a set of 12 samples of metal. The same sample set was circulated to each participant via a traceable shipper over the course of eight months. The test samples consisted of three types: 1) cuttings obtained from reference materials (RMs) n=4; 2) pieces of historic metal, n=6; and 3) small ingots prepared by Arlen Heginbotham, n=2. The range of elemental compositions included in these samples was tailored to imitate the broad range found in historic copper alloy artefacts from the Bronze Age through the 19th century.

The results of the present study showed a relatively poor overall inter-laboratory reproducibility. In general, the average percent relative reproducibility is greater than 50% (an upper threshold that according the ASTM guideline, the method reproducibility must be considered unacceptable) for all elements (except Cu, Zn, and Sn) including Fe, Ni, As, Sb and Pb⁽¹⁾. The authors of the study have thus reached the consensus that the current reproducibility of XRF analysis of historic copper alloys within the art and archaeology community is, in general, not sufficient. The reproducibility results reported should evoke a strong sense of caution in those who might wish to publish data, compare their own data with that generated by other laboratories, or pursue meta-studies based on the work of multiple laboratories.

Another significant result of the study was the fact that the higher-performing laboratories all appear to have one

common characteristic, i.e. they use Fundamental Parameters (FP) software, calibrated with standards. In comparison, all other factors examined in this study appear to be relatively poorly correlated with laboratory accuracy. Thus, the authors suggest that the wider adoption of quantification methods utilizing FP with standards offers the possibility of significant improvements in inter-laboratory reproducibility, whereas the use of a common, open source FP software package used in conjunction with a common and readily available set of reference materials could further improve the reproducibility of quantitative XRF analysis. The laboratories that have produced the most meaningful and reliable error values relative to true values did so by analyzing multiple reference materials and conducting a regression analysis of certified vs. calculated values. These laboratories used the 'standard error' associated with the regression to define meaningful confidence intervals relative to the estimated true value. Another recommendation suggested is that the publication of XRF results should include the ones produced for one or two control samples that have not been included in the calibration procedure.

The model of the work conducted with respect to the evaluation of the inter-laboratory reproducibility of quantitative XRF analysis of historic copper alloys should also be used as a basis to evaluate and assess similar questions associated to different types of materials (e.g. ceramics, obsidians etc.), not necessarily related with conservation science or archaeometrical research, but also of interest to other fields (for example in the XRF analysis of air particulate matter). Recently, another study focused in the assessment of the comparability of TXRF systems at different laboratories in analyzing spin coated silicon wafers where a point-like contamination has been deposited⁽²⁾. The Nuclear Spectrometry and Applications Laboratory (NSAL) of the IAEA laboratories conducts, almost on an annual basis, inter-comparison tests of analytical XRF data produced in various Members States laboratories. These efforts should further be enhanced by the scientific community towards the harmonization of analytical procedures and improvement in the precision and accuracy of quantitative XRF analysis performed by the newly developed portable XRF spectrometers.

⁽¹⁾Arlen Heginbotham, Aniko Bezur, Michel Bouchard, Jeffrey M. Davis, Katherine Eremin, James H. Frantz⁶, Lisha Glinsman, Lee-Ann Hayek, Duncan Hook, Vicky Kantarelou, Andreas-Germanos Karydas, Lynn Lee, Jennifer Mass, Catherine Matsen, Blythe McCarthy, Molly McGath, Aaron Shugar, Jane Sirois, Dylan Smith, Robert J. Speakman, *An Evaluation of Inter-Laboratory Reproducibility for Quantitative XRF of Historic Copper Alloys*, Proceedings of the International Conference on Metal Conservation, Edited by Paul Mardikian, Claudia Chemello, Cristopher Watters and Peter Hull, 11-15 October 2010, Charleston, South Carolina, USA

This paper and supporting material are available at:

<http://www.getty.edu/museum/conservation/papers.html>

Relevant links associated with the International Conference on Metal Conservation are:

http://www.clemson.edu/clemson_conservation_center/metalindex.html and

<http://www.icom-cc.org/52/event/?id=69>

⁽²⁾A. Nutsch, B. Beckhoff, R. Altmanna, M. L. Polignano, E. Cazzini, D. Codegoni, G. Borionetti, M. Kolbe, M. Müller, C. Mantler, C. Strel, P. Kregsamer, Comparability of TXRF Systems at Different Laboratories, ECS Transactions, 25 (3) 325-335 (2009)

For more information please contact A.G. Karydas (A.Karydas@iaea.org)

Authentication workshop for metal and stone antiquities using scientific techniques, Egyptian Museum of Cairo, Egypt, October 26-27, 2010

'Witness the Past' is a two year EC funded project under the Culture Programme (2007-2013) coordinated by Dr. Vasilike Argyropoulou from the Technological Educational Institution of Athens where the main objective is to carry out a public awareness campaign in the Egyptian Museum in Cairo and its Children's Museum, and implement a didactic children's program in museums in Egypt, Greece, Cyprus, and Germany on the importance of proper excavation of archaeological sites (www.witnessthepast.gr). The main thrust of the project will be to have an impact on the prevention of looting of antiquities through the pillaging of sites, as well as to educate Cultural Heritage (CH) professionals on the

scientific tools to help authenticate and fingerprint looted antiquity. Finally, it will produce best practice guidelines or a 'Museum theft response plan' aimed at law enforcement and museum professionals for stolen goods.

In this framework, a workshop was co-organized at the Egyptian Museum of Cairo by its Director Dr. Wafaa El Saddik and by the Rathgen Research Laboratory and its director, Prof. Dr. Stefan Simon, National Museums Berlin, with a focused audience of museum conservators and curators.



Fig.1. Participants of the Workshop

The aim of the workshop was to provide education on the application of scientific tools to help authenticate and fingerprint looted and stolen antiquity and to disseminate

non-destructive characterization techniques such as the X ray Fluorescence (XRF) analysis. The program of the first day included plenary presentations that described

and disseminated the international experiences and state of the art analytical methodologies for authentication. A comprehensive summary of analytical methods for authentication and recent developments was given by Stefan Roehrs, Rathgen Research Laboratory, Germany, whereas Maria Luisa Vitobello, EJTN Belgium, explained how technical and chemical studies on metals can give answers to questions of authentication. More specific, this presentation included the results of an EU project 'AUTHENTICO' that developed methodologies and technologies for authentication of metal artefacts based on material composition and manufacturing techniques. Despoina Desponia Kotzamani, Head of Metals Conservation, Benaki Museum, Greece, tackled the interesting topic of the provenance of metal artefacts by means of non-invasive analytical techniques such as the XRF analysis, whereas Josef Riederer, former Director, Rathgen Research Laboratory, Germany explained with didactic examples the contribution of electron microscopy and the associated energy dispersive X ray analysis in authentication studies. Andreas Karydas, from the Nuclear Spectrometry and Applications Laboratory of the International Atomic Energy Agency explained and highlighted the contribution of XRF analysis in revealing materials and painting/gilding techniques used to create the polychromy of late Hellenistic marble statues. The second day of the workshop was focused on practical demonstration activities and hands on practices in optical microscopy (Josef Riederer, Maria Luisa Vitobello) and handheld XRF analysis (Andreas Karydas, Stefan Roehrs) per-

formed at the conservation laboratory of the Egyptian Museum.

Almost twenty museum professionals and younger trainees were engaged with enthusiasm, interest and many questions in the practical training. In the case of XRF analysis, focus was given to explain the type of analytical information that can be gained depending on the type or/and preservation state (e.g. corroded/altered surface) of the analyzed artefact and how the XRF results should be interpreted to avoid misleading conclusions. Best practices in XRF analysis were suggested and discussed regarding the selection of operational parameters, measurement methodologies and the need to develop and establish data bases of materials and techniques used in authentication of artefacts. It was concluded and evidenced by specific applications on artefacts undergoing conservation treatment that the handheld XRF analysis is a very useful analytical tool that can provide fast, non-invasive identification of the elemental composition, whereas it can offer also crucial support in authentication analytical methodologies. By the end of the workshop, certificates were awarded to the participants by Prof. V. Argyropoulos, coordinator of the Witness the Past Culture program, Dr. Wafaa El Saddik, Director of the Egyptian Museum and Prof. Dr. Stefan Simon, Director of the Rathgen Research Laboratory, Berlin.

For more information please contact A.G. Karydas (A.Karydas@iaea.org)



Fig.2. Demonstration of a portable XRF analyser

Support to Technical Cooperation Projects

The XRF Group at Seibersdorf provides assistance to a number of IAEA regional and national Technical Cooperation (TC) projects where XRF is used as one of the analytical techniques. The following selected events related to TC projects were supported in 2010.

Second Planning and Coordination Meeting of the IAEA Regional TC project RER/8/015 on ‘Using Nuclear Techniques for Characterization and Preservation of Cultural Heritage Artefacts in the European Region’, St. Julian’s, Malta, 6-9 September 2010

The meeting was organised by the Heritage Malta, Kalkara and held at the InterContinental Hotel in St. Julian’s. Major objectives of the meeting were to review and assess the current status of the project including major achievements, technical problems and lessons learned, to review and update the work plan for 2010-2011 as well as to discuss a regional project concept for 2012-2013.

The meeting was inaugurated by the Hon. Dr Mario de Marco - Parliamentary Secretary for Tourism, the Environment and Culture, Office of the Prime Minister, Mr Frank Mifsud – Board Secretary and Acting CEO Heritage Malta, Dr Claire Baluci – Manager Diagnostic Science Laboratories, Heritage Malta and the IAEA



Session of the Meeting

staff (Programme Management Officer and Technical Officers) of RER/8/015. The meeting was attended by 33 representatives from Albania, Azerbaijan, Bulgaria,

Croatia, Cyprus, France, Greece, Hungary, Malta, Montenegro, Poland, Portugal, Romania, Serbia, Slovenia, The Former Yugoslav Republic of Macedonia, Turkey,

Ukraine, and an invited expert from France. The IAEA staff gave a joint presentation entitled 'The IAEA Technical Cooperation Programme and Project RER/8/015: Introductory Notes'. The presentation defined a broader context of the present project, the role the IAEA, the resources available, the responsibilities of the key players in the IAEA and Member States as well as the objectives and expected outputs and outcomes of RER/8/015. The

first two days were dedicated to the individual country reports. The institutes participating in the project have a wide range of facilities and equipment applied for the implementation of the project activities. A final version of the Regional Project Concept was prepared and agreed upon by the participants. Two visits to the archaeological site and cultural heritage areas were included in the meeting programme.



Visit to the Conservation Division of the Heritage Malta

Conclusion

Extensive cooperation between nuclear research and cultural heritage institutions exists in many countries. Nuclear techniques are successfully applied for characterization and preservation of cultural heritage objects. The advantages and success stories of preservation by using irradiation have been demonstrated and promoted through brochure and video. One of the strengths of the

project is numerous examples of bilateral cooperation and extension of the application to the countries which do not have adequate nuclear techniques and facilities (by using the facilities available elsewhere). A consensus was reached regarding necessity to continue the activities under new regional and interregional TC projects.

For more information please contact A. Markowicz (A.Markowicz@iaea.org).

National Workshop on X ray Fluorescence Techniques in Heritage and Archaeology, Sharjah, United Arab Emirates, 17–18 March 2010

The Workshop was organised by and held at the University of Sharjah in cooperation with the Ministry of Energy. Around 25 participants from the University of Sharjah, American University of Sharjah, UAE University, Sharjah Museums Department, Directorate of Heritage (Government of Sharjah), Umm Al Qwain Museum, Sharjah Archaeology Museum, Department of Culture, Applied Physics Department, Department of Tourism and Commerce, and UAE National Council of Tourism and Antiquities attended the event. The lectures delivered by two external lecturers covered fundamentals of XRF, qualitative and quantitative XRF analysis, X ray micro-analytical techniques, X ray micro-tomography and various aspects of applications of XRF for study and characterization of cultural heritage (CH) objects including preventive conservation.

The IAEA staff presented a talk on the role of the IAEA in promotion and applications of nuclear analytical techniques with an emphasis on Technical Cooperation projects and advantages of XRF techniques. Major objectives of the Workshop included: (i) introduction of the fundamentals of XRF technique, (ii) review of applica-

tions and advantages of XRF in support of CH studies, (iii) demonstration of the XRF equipment available in the National X ray Fluorescence Laboratory, and (iv) identification of partners and their needs in the relevant field. Selected examples of practical applications of micro-XRF spectrometers and portable XRF spectrometers (provided by commercial companies) were also presented. The Workshop was the first opportunity to present the advantages and potentials of XRF technique to the cultural heritage (CH) community in the United Arab Emirates. The event attracted attention of many participants from potential end-user institutions. Successful applications of XRF technique for characterization of CH objects requires the close cooperation of scientists from the nuclear field and restorers, conservators and art historians from the CH community. In the future specialised practical training courses will be organised to demonstrate full analytical procedures for selected CH objects and well defined target groups.

For more information please contact A. Markowicz (A.Markowicz@iaea.org).

X ray fluorescence in Member States

Argentina

Mapping Chromium (VI) bioaccumulation in Lemna minor using SR- μ XRF

Contributors: Susana Boeykens¹, Laura Carignano¹, Cristina Vázquez^{1,2}

¹ Chemistry Laboratory of Heterogeneous Systems, Engineer Faculty, Buenos Aires University

² Atomic Energy Commission, Chemistry Department, Buenos Aires, Argentina

Trivalent chromium, Cr(III), is essential for animal and human health, whereas hexavalent Cr, Cr(VI), is a potential carcinogen and extremely toxic for animals, plants and humans. Thus, the accumulated Chromium in food plants may represent a potential health hazard for animals and humans if the element is accumulated as hexavalent form or in high concentrations. The aim of this study was to determine the accumulation of Cr(VI) by *Lemna minor* from aqueous solutions. *Lemna minor* belongs to a vascular plants group and is considered within the floating macrophytes ecotype.

Particularly, the species have a high capacity to remove heavy metals from liquid media with a wide tolerance to extremes of pH, salinity and temperature. Both absorption and adsorption mechanisms, and evidence of differences in the bioaccumulation between fronds and roots, were observed.

Mesocosms were formed by using twelve 250 mL plastic containers with chromium solutions and 2 g of *Lemna minor* sp. We tested three increasing concentrations of chromium: 2, 10 and 50 $\mu\text{g l}^{-1}$, in triplicate, from aqueous solutions of K_2CrO_4 ; and corresponding controls for a fortnight (Fig. 1).



Fig.1. Plastic containers with chromium solutions and 2 g of *Lemna minor* sp

Standardized laboratory conditions were: 12 h light, 12 h darkness, 40 W power light, 60% relative humidity and 25° C temperature. The conductivity and the pH of aqueous medium were recorded from the beginning to the end of the experiment. Then, the macrophytes were fixed in formalin and dehydrated gradually with alcohol in order to be placed individually in liquid vaseline for further quantitative analysis of Cr accumulation using X ray microfluorescence beam line at Synchrotron Radiation Laboratory, Campinas, Brazil. The experimental setup at the D09B-XRF line is shown in Fig. 2.

Results show the presence of formed adsorption Chromium nodules between 0.5 to 1 mm diameter at the bottom of the roots as is shown in Fig. 3. Microfluorescence spectra were analyzed to perform a pattern of accumulation by adsorption in the tissue of the fronds. Significant concentrations of Cr were observed at the center and lower concentration at the edges. Bioaccumulation of Cr in roots was 100-times higher than in fronds. In conclusion, these macrophytes showed a differential bioaccumulation between fronds and roots which suggests that adsorption mechanism is more efficient. Further investigation of the mechanism used by *Lemna minor* for removing heavy metals from aqueous solutions is required.

This work has been supported by the Brazilian Synchrotron Light Laboratory (LNLS) under proposal D09B - XRF 8168.



Fig.2. The experimental setup of the D09B-XRF beamline at Synchrotron Radiation Laboratory, Campinas, Brazil.

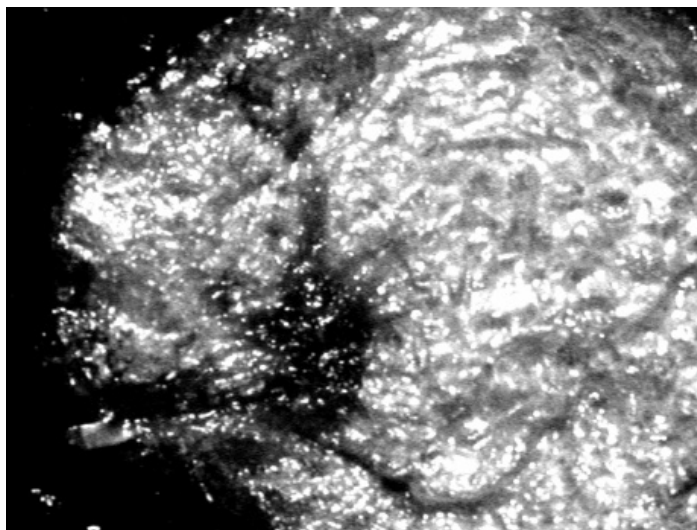


Fig. 3. *Lemna minor* Chromium nodules at the bottom of the roots.

Peru

Archaeometric Study of gold pieces form Morro de Eten, Peru

Contributors: Luisa Vetter Parodi¹, Susana Petrick², Paula Olivera³

¹ Museo Nacional Sicán, Instituto Riva Agüero-PUCP

² Facultad de Ciencias, Universidad Nacional de Ingeniería,

³ Direccion de Investigación y Desarrollo. - Instituto Peruano de Energía Nuclear

In the archaeological place of Morro de Éten, Elera located during his excavations between 1979 and 1988, small pieces of gold were collected and analyzed revealing presence of platinum. At a first study some samples seemed to be partly covered by dust or red pigment initially identified by Elera as hematite.

The objective of this work has been to check/clarify the presence of platinum in the pieces in order to understand its role and influence on the technology of the old goldsmiths. Besides, we tried to clarify if the pigment found in the gold pieces of Morro de Éten is hematite or cinnabar. For this purpose different analytical techniques were used including Optical Microscopy, Electronic Microscopy of Sweeping (SEM), Spectrographic Atomic Emission, Energy Dispersive X ray Fluorescence (EDXRF), Neutron Activation (NAA) and Energy Dispersive X ray Microanalysis (EDAX).

The results of the multielemental chemical analysis carried out for the same sample (described as E) by using NAA and XRF techniques are shown in Table 1.

Table 1. - Results of piece E: 10 analysis by NAA and XRF

Element	NAA (%)	XRF (%)
Cu	2.50 ± 0.02	2.5 ± 0.1
Ag	30.5 ± 0.7	31 ± 2
Pt	ND	< 0.25
Au	66.5 ± 1	66 ± 2

ND: Not detected

The Platinum was not detected by either of the two techniques, although the results obtained by EDAX showed 0.3% of Pt.

Conclusions

The analysis of the pieces that contain Pt in small quantities, between 0.6 and 1%, suggests that the gold utilized in the production stage was contaminated and Pt came in small quantities in the form of accumulation or dust.

The presence of Pt in the pieces could not be utilized in this case as an indicator of the provenience of the gold (north / south - Sclosser et al. 2008), since according to the available information, the Pt would be found in several localities in the center and east of Peru (personal communication of Atilio Mendoza, September 2009), where in some cases the inclusions of pure Pt reach the sizes greater than 250 microns.

In the case of the ring, microprobe analysis revealed that the Pt distribution is not uniform which confirmed a hypothesis that Pt has not been mixed with the matrix but dispersed in very small inclusions which may even go unnoticed in a metallographic examination.

From the analysis performed for the pendant we found that this piece has the highest Au content (93%) and low content of Ag and Cu. This suggests that gold has a different geological origin of the other pieces or have been treated differently for refining.

The analysis of the powder adhered to the surface of the ring shows cinnabar, while iron oxide identified by electron diffraction pattern in the TEM does not appear to be intentionally added as suggested by Elera (1986).



Pieces studied
Courtesy: Mg. Luisa Vetter

In the specimens analyzed, platinum appears as an associated element, and to date, doesn't work as a metal in any piece of Morro de Eten, or any other pre-Columbian Peruvian piece, as if it happened in Ecuador. It is premature to conclude that the goldsmiths who manufactured the pieces of Morro de Eten were aware that they were working with a different alloy. There are also other open questions, e.g. regarding color of the alloy. Still it is unknown if Pt was introduced intentionally or accidentally.

Study of Metal Pieces from the Collection Versteylen by Using Nuclear Analytic Techniques

Contributors: Paula Olivera¹, Pilar Portocarrero²

¹ Dirección de Investigación y Desarrollo, Instituto Peruano de Energía Nuclear, Av. Canadá 1470, Lima 41, Perú

² Museo de 'Arqueología Josefina Ramos de Cox', Instituto Riva-Agüero, Pontificia Universidad Católica del Perú, Lima 1, Perú

A collection Versteylen presently in custody of the Museum of Archeology 'Josefina Ramos de Cox' of the Instituto Riva-Agüero of the Pontificia Universidad Católica del Peru has a number of specimens like tumis, agricultural tools, pincers which requires extensive study in order to identify a place of provenance, period of manufacturing, and materials associated to them. Energy dispersive X ray fluorescence technique was used for determination of the elemental concentrations of the metal pieces (see Table 1) in order to characterize raw materials and to identify production process.

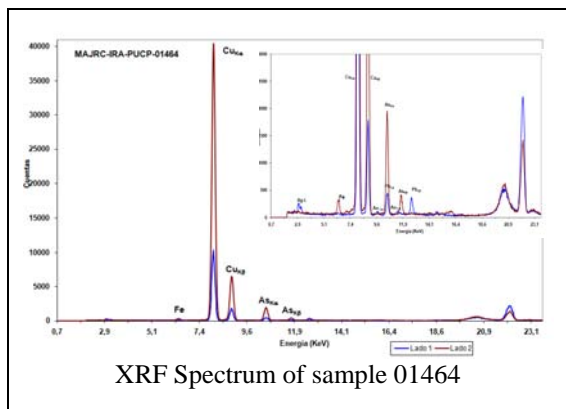
Table 1: Elemental concentrations for some metal pieces obtained by energy dispersive X ray Fluorescence non-destructive method.

Sample\Elem	Fe (%)	Cu (%)	As (%)	Ag (mg/cm ²)	Au (µg/cm ²)	Pb (µg/cm ²)
01464*	0.8	93.6	3.9	1.6	5.6	30
01469	0.5	96.6	3.0	ND	ND	ND
01470	ND	96.6	3.4	ND	ND	ND
01471	ND	96.8	3.2	ND	ND	ND
01476**	0.2	97.1	2.7	ND	ND	ND
01479		97.8	2.2	ND	ND	ND
01480***	ND	98	2	0.4	ND	ND
01485	0.3	92.9	5.7	ND	ND	ND

* This piece has on one of the faces a surface layer of Silver and Gold, Figure 6.

** On one of the faces of the piece 01476 a greater content of Iron found as Fe₂O₃ was identified

*** This piece has a surface layer of Silver for both sides.



Analysis of results and conclusions:

All the pieces have Cu as major element and As as minor element. This composition is characteristic for the objects of copper arsenical from north of Peru [7]. The presence of Fe used as flux was also observed.

The sample 01464 apparently would be a golden copper obtained by plating technique, with presence of silver, possibly added in an intentional way. In the case of the samples 01464, 01469, 01470, 01471, and 01485 we cannot determine with certainty their function. However, a high concentration of arsenic in the alloy indicates that it would be a material of the objects of sumptuous use, since when the concentration of As is greater than 3% the hardness diminishes and the material becomes malleable

[8] and not suitable for production of compact utilitarian objects.

Bibliography

- [2] Gordon R, Knopf R. Late horizon silver, copper, and tin from Machu Picchu, Peru. *Journal of archaeological science*. 2007; 34: 38-47.
- [3] Hocquenghem A, Vetter L. Las puntas y rejas prehispánicas de metal en los Andes y su continuidad hasta el presente. *Bulletin de l'Institut Francais d'Etudes Andines*. 2005; 34 (2): 141-159.
- [4] Shimada I, Montenegro J. El Poder y la Naturaleza de la Élite Sicán: Una mirada a la Tumba de Huaca Loro, Batán Grande. *Boletín de Lima*. 2003; 15(90): 67-96.
- [5] Cornell, R.M. y U. Schwertmann, 1996. *The Iron Oxides. Structure, properties, Reactions, Occurrence and Uses*. VCH.
- [6]. Huaypar, Yezeña; Trujillo, Alejandro; Mejía, Mirian; Fabián, Julio; Torres, Eusebio y Bravo, Jorge. *Caracterización Mineralógica y Determinación de la Temperatura de Cocción Original de Cerámicas Nasca – Comunicación interna*. 2008.
- [7] Letchman, Heather 1978 *Temas de Metalurgia Andina*. En Ravines, Roger (ed.) *Tecnología Andina*. Lima. Páginas: 489-520.
- [8] Vetter Parodi, Luisa 2008 *Plateros Indígenas en el Virreinato del Perú: Siglos XVI y XVII*. 1ra Edición Fondo Editorial UNMSM. Lima. Páginas: 59 -64

Spain

XRF activities in the ICMUV (Spain)

Contributors: Clodoaldo Roldán, Sonia Murcia-Mascarós, José Ferrero, Isabel Ródenas

Instituto de Ciencia de los Materiales-Universidad de Valencia (ICMUV)
P.O. Box 22085, E-46071-Valencia (SPAIN)
Email: clodoaldo.rolدان@uv.es; jose.ferrero@uv.es; sonia.mascaros@uv.es

The Material Science Institute of the Valencia University (ICMUV) has been involved during past years in the development, evaluation and analytical applications of XRF spectrometry in the field of the cultural heritage analyses. Here, we present some examples applied for characterization of the prehistoric pigments and Spanish glasses.



Portable EDXRF spectrometer. Red archer and black deer.



Application of field portable EDXRF spectrometry to analysis of pigments of Levantine rock art.

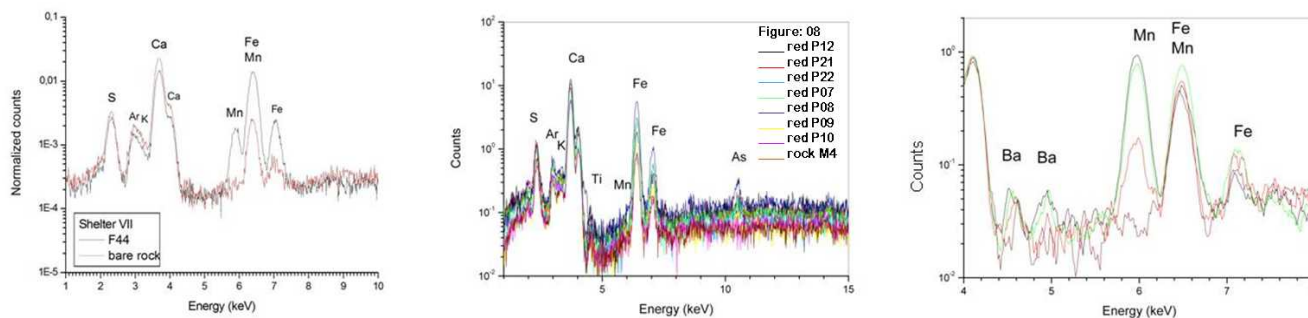
Levantine rock art is one of the main Postpaleolithic rock art traditions located in the Mediterranean slope of the Iberian Peninsula. Superimpositions and variations in forms, themes and techniques reveal a complex and lasting tradition, whose internal variations reflect the changing identities of the authors in space and time. Actually, it is widely accepted that their origins could be related with the Neolithisation process (5400-5200 B.C.).

Our goal in this study is the characterization of the elemental composition of Levantine rock art pigments located at the 'Saltadora' rock shelters (Castellón, Spain) and to show the usefulness of the field portable EDXRF spectrometry for in situ, non-destructive analyses on hard to get archaeological sites. The EDXRF analysis of these red and black pigments provides interesting data that help to identify the materials used in their execution, to determine their state of conservation and test the existence of

connections between different figures and discriminating different raw materials and execution phases.

Additionally, in situ characterization of these pigments by EDXRF will determine future sampling decisions in use with other analytical techniques to obtain additional information about structure and chemical composition of pigments.

EDXRF spectra were acquired by using a portable spectrometer directly on pigments with no contact, preparation or cleaning. The whole spectrometer (including X ray tube, detector, electronic modules, personal computer, and mechanical positioning system on a tripod) has a weight of 15 kg and can easily be brought to the archaeological sites on arranged suitcases. Analyses were carried out with a 600 W generator and inverter for current control that allows working in places with no power source available.



Left: XRF spectra from a red pigment showing traces of Mn. Center: XRF spectra from different points of a figure showing red pigments with and without traces of As. Right: XRF spectra of the pigments from black figures (X ray Spectrom. 2010, 39, 243–250)

The detected elements indicate the use of red earth or ochre for the red pigments and manganese oxides for the black pigments. Presence of manganese was detected in some red pigments showing the use of iron oxides from different sources, as well as a possible intentional addition in one of the figures. The detection of traces of arsenic in part of a red deer is in agreement with the utilization of two kinds of red pigments and different phases of execution. Analysis of black pigments shows the presence of barium that correlates with manganese, therefore, the use of raw materials of manganese oxides or hydroxides with traces of barium may be assumed.

Field portable EDXRF spectrometry proved to be a useful technique to detect the chemical elements present in prehistoric rock art pigments and to identify different raw materials used in their production process.

C. Roldán, S. Murcia-Mascarós, J. Ferrero, V. Villaverde, E. López, I. Domingo, R. Martínez, P. Guillem. **Application of field portable EDXRF spectrometry to analysis of pigments of Levantine rock art**, in *X ray Spectrom.* 2010, 39, 243–250.

Characterization of Mediterranean Spanish glasses

In the excavations carried out inside the Collegiate Church of Gandia in 2001, some pieces of glass from funeral burials were found. Amount of several grave goods as chalices and mass wine jug, stands out above all two of which that are blue and decorated with white

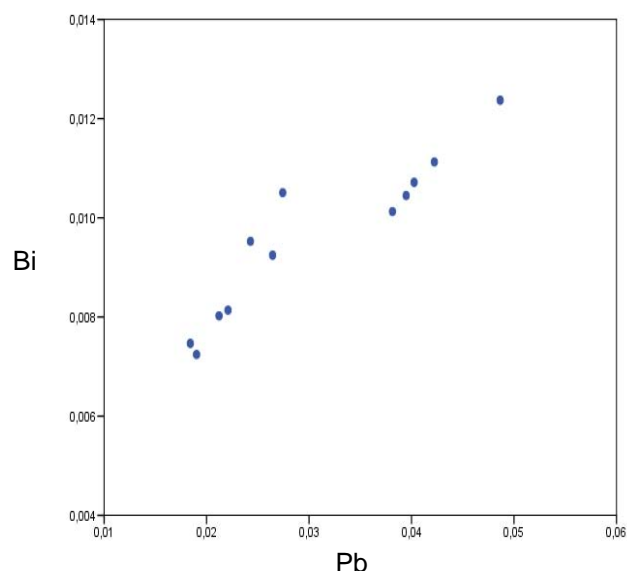
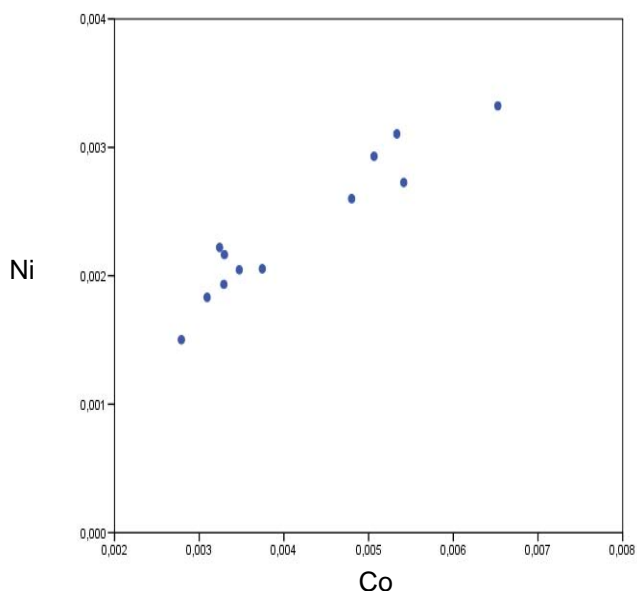
enamel. The pieces are similar to other Mediterranean Spanish glasses dated to the sixteenth century and with shapes and decoration as the Venetian fashion but with local stylistic characteristics.



Gandia Collegiate Church glasses from the burial 2 on the Chapel 2

The analysis of the materials composition of these pieces were performed by portable energy dispersive X ray fluorescence (EDXRF). The technique has already been used successfully for the characterization of other Spanish 'façon de Venise' glasses (1). These analyses make it possi-

ble to relate the composition of Gandia glasses with already analyzed objects. The measurements do not require sampling and no alteration of the pieces is observed. Linear correlation has been established between Co and Ni, and Pb and Bi.



Ni versus Co and Bi versus Pb normalized areas from blue Gandia glasses

No correlation was found between As and Co. Probably, Ni was incorporated as part of Co mineral. Also Bi is a part of Pb mineral. The results reveal the particularity of the pieces because in addition to cobalt responsible for blue glass colour, considerable amount of lead, bismuth, nickel and arsenic are present. This composition is compatible with chronologies covering the fifteenth to seven-

teenth centuries. Since gold was detected over the glass one can conclude that these pieces were completely covered at source.

- S. Murcia-Mascarós, C. Roldan, C. Falomir, I. Domenech, J. Carreras, R. Ibáñez. **A Non Destructive Analysis of Enamelled Glass in The Façon De**

Venise Discovered in Morella (Castelló, Spain).

Proceeding of the international congress of Association Internationale pour l'Histoire du Verre Conference. Ed. K. Janssens. Publisher: VUB University Press, Belgium 2009. ISBN-10: 9054876182. p 493-499.

- S. Murcia-Mascarós, C. Roldán, I. Rodenas, C. Vidal. **Non-destructive Analysis of Christian funerary glass from Gandia Collegiate Church (Valencia)**. Proceeding of the VIII Congreso Ibérico de Arqueometría, 2010. in press.
- ‘

Publications of potential interest to the XRF community

A Practical guide to scientific data analysis, D. Livingstone, Wiley, November 2009

P. Wobrauschek, C. Strelt, E. Selin Lindgren, Energy Dispersive, X ray Fluorescence Analysis, in Encyclopedia of Analytical Chemistry, John Wiley & Sons, Ltd. 2000 (published online, June 2010)

Impressum

XRF Newsletter, No. 20, December 2010

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

A. Markowicz
IAEA Laboratories
A-2444 Seibersdorf, Austria
Fax: (+43 1) 2600-28222 or (+43 1) 26007
Email: A.Markowicz@iaea.org

International Atomic Energy Agency
Vienna International Centre, PO Box 100, 1400 Vienna, Austria
Printed by the IAEA in Austria, December 2010