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X ray Fluorescence in the IAEA and its Member States

In This Issue

Activities in the IAEA XRF Laboratory

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

Upgrade of QM documentation and QC tools in the Nuclear Spectrometry and Applications Laboratory (NSAL) at Seibersdorf

The NSAL (former Instrumentation Unit) is currently a part of the Physics Section, Division of Physical and Chemical Sciences, Department of Nuclear Sciences and Applications. In 2005 the XRF group developed a Quality Management Documentation (QMD) aimed to ensure the provision of high quality analytical support to the analytical laboratories in the IAEA Member States. Recently this set of documentation was thoroughly revised and upgraded as to comply with the latest developments in ISO quality management guidelines, as well as to reflect the changes that occurred after the realignment of the Instrumentation Unit in the IAEA organizational structure.

The QMD was enhanced with the addition of an operational procedure providing recommendations for method validation in the determination of elemental mass fractions by EDXRF. Recommendations for uncertainty estimation assessment of critical limits based on statistics distribution and on Bayesian approach were added to the existing SOP on estimation of uncertainty in EDXRF analysis. Some MS-Excel based tools were created for internal quality control activities, such as: 1) calculation of uncertainty based on Kragten approach, 2) acceptance of results based on combined assessment of trueness and precision, 3) a spreadsheet for internal quality control based on Shewhart charts.

The updated QM documentation and further information are available from R. Padilla Alvarez (R.Padilla-Alvarez@iaea.org).

Establishment of control site baseline data for erosion studies using radionuclides: a case study in eastern Slovenia

The XRF Group of the NSAL works in close cooperation with other units of the IAEA Laboratories at Seibersdorf. During 2009 a number of soil samples were analyzed as part of a research aimed to characterize a non-disturbed soil control site that might serve as reference for further studies on soil erosion. A total of 20 soil profiles from the agricultural region of Šalamenci (Goričko, Slovenia) that were collected at four 10 cm depth increments for evaluation of baseline level of ^{137}Cs inventory were analyzed to determine the mass fractions of major, minor and trace elements by using EDXRF technique.

Pellets from the samples were measured using an EDXRF spectrometer with a 400 watt Pd-anode X ray tube and several secondary fluorescent or scattering targets applied for effective excitation. The validity of the results was assessed by measuring three different certified reference materials: IAEA-Soil7 (soil sample), IAEA-433 (marine sediment) and IAEA-405 (sediment). For 31 elements the results were considered reliable to reveal differences in the soil depth profile, including major and minor constituents (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn and Fe) as well as trace elements (Cr, Ni, Cu, Zn. Ga, As, Br, Rb, Sr, Y, Zr, I, Cs, Ba, La, Ce, Pb, Th and U). However, the average values for each depth were calculated only for those elements for which the results had uncertainties better than 10 % (K, Ca, Ti, Mn, Fe, Cr, Ni, Cu, Zn, Ga, As, Rb, Sr, Zr, Ba, Ce, Pb and Th).

To reveal the differences in elemental mass fractions through the soil depth, several main steps for compositional analysis of archaeological ceramics recommended in a previous IAEA-TECDOC [1] were adopted.

Some tendencies in the variations of elemental mass fractions with soil depth were revealed by representing each sample (using its principal component scores) in the 3D space formed by the first extracted principal components. Detailed information on the results of this research is available on-line from the Journal of Environmental Radioactivity [2].

References:

[1] International Atomic Energy Agency. Nuclear Analytical Techniques in Archaeological Investigations. Technical Reports Series No. 416, IAEA, Vienna, 2003.

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Meetings and Conferences

First Research Co-ordination Meeting of the Co-ordinated Research Project on Micro-analytical Techniques Based on Nuclear Spectrometry for Environmental Monitoring and Material Studies

Vienna, Austria, 17-21 May 2010

Considerable progress has been observed in recent years in the development and applications of micro-analytical techniques based on nuclear spectrometry. The wide spectrum of the analytical features offered by advanced X ray excitation sources like the synchrotron radiation large scale facilities (SR), the development of compact low power X ray tubes designed with optimized excitation geometry for field applications, the utilization in many laboratories worldwide of charged particle beams and particularly of microprobes, the new generation thermoelectrically cooled semiconductor detectors for energy dispersive analysis and imaging, but also the advances in X ray optics have driven new developments in techniques and applications. The following nuclear spectrometry (and related) techniques can be used for microanalysis: (i) X ray fluorescence (XRF), (ii) total reflection X ray fluorescence (TXRF) (iii) neutron activation analysis (NAA), (iv) ion beam analysis based on applications of low-energy particle accelerators (including particle X ray emission – PIXE, particle induced gamma-ray emission – PIGE, Rutherford backscattering spectrometry – RBS, Nuclear Reaction Analysis - NRA), (v) extended X ray absorption fine structure spectroscopy (EXAFS) and X ray absorption near-edge spectroscopy (XANES), (vi) X ray fluorescence micro-tomography, (vii) scanning electron microscopy (SEM), etc. The techniques are usually used for elemental analysis, 2D and 3D microscopy imaging and sporadically chemical speciation.

The range of possible applications of micro-analytical techniques is very wide and covers, inter alia, the following fields:

- Industrial applications including microelectronics, study of corrosion and corrosion protection (measurement of the composition and thickness of coatings), study of catalytic materials, waste characterization, characterization and quality assurance of thin-film solar cells.
- Testing and quality assurance of materials for power generation (e.g. nuclear power, fusion).
- Environmental and biomedical investigations including individual aerosol particle elemental and structural analysis, biomonitoring, trace element mapping of tumour tissues and living plants, and study of waste disposal sites.
- Applications to archaeology, art and conservation science (e.g., non-invasive characterization of raw materials, authentication and provenance studies of museum objects, characterization of corrosion and alteration products of artefacts in support of their conservation, restoration and future preservation).
- Forensic applications.
- Mineralogy, geology and geochemistry.
- Food quality and agriculture studies.
- Biomedical and human health related studies (e.g. biocompatibility of implants, elemental deficiencies and/or anomalies in human tissues related to specific diseases, interactions and effectiveness of pharmaceutical products).

Taking into account the importance of the micro-analytical techniques based on nuclear spectrometry in the different fields, the IAEA initiated a new Coordinated Research Project (CRP) on Micro-analytical Techniques Based on Nuclear Spectrometry for Environmental Monitoring and Material Studies in order to coordinate and support the research efforts of the relevant laboratories. The objectives of the CRP are to develop improved instruments, analytical methodologies and standardized procedures for micro-analytical techniques based on nuclear spectrometry as well as applications of micro-analytical techniques to 2D and 3D microscopy imaging, element-specific compositional analysis, and limited chemical speciation.

The first Research Coordination Meeting (RCM) under the CRP was held in Vienna from 17-21 May 2010 with the following major objectives: (i) to review the current status of research activities in the field of micro-analytical techniques based on nuclear spectrometry in the participating laboratories, (ii) to collect information on the available instruments and facilities, (iii) to coordinate the research activities of the CRP and identify potential synergies among the participating groups, and (iv) to refine and define work program for the whole duration of the CRP and especially for the period until the next RCM planned in the second half of 2011.

Representatives of 15 laboratories from Argentina, Australia, Austria, Belgium, Croatia, Greece, Italy, Poland, Portugal, Slovenia, South Africa, Sri Lanka, Ukraine and United Arab Emirates attended the meeting (see photos below).

Session of the 1st RCM

Conclusions

Significant interactions have been identified among participants with common interests, particularly related to cultural heritage and environmental studies. This will also lead to more effective use of the available infrastructure and facilities to the benefit of the CRP. The success of these synergies will be reported in the next RCM. A work plan for each participating group for the whole duration of the CRP and especially for the next 15 months up to the next RCM meeting was proposed and agreed. The work progress will be followed by progress reports submitted by the participating laboratories and publications as well by presentations in the next two RCMs. Benefits and limitations of various methods used in the CRP were discussed and the optimum range of applications was defined. The results of research to be performed can be transferred to other laboratories which are not directly involved in the current CRP leading to a transfer of technology and know-how.

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Visit of the participants of the 1st RCM to the IAEA Laboratories at Seibersdorf

National Conference on X ray Fluorescence (XRF-2010), 12-15 January 2010, Kolkata, India

The Conference was organized by the Nuclear & Atomic Physics Division, Saha Institute of Nuclear Physics, Kolkata in collaboration with the Centre for Archaeological Studies and Training, Kolkata, UGC-DAE Consortium for Scientific Research, Kolkata and the West Bengal Pollution Control Board. Sixteen invited lectures were presented by the participants from Austria, Canada, Belgium, Brazil, Italy, India, Poland, and Republic of Korea supplemented by a poster session.

The participants reviewed the current status in methodology and applications of XRF techniques including in vivo applications, synchrotron-based XRF imaging and elemental mapping, biomedical applications, study and preventive conservation of cultural heritage objects (see photo).

Lecture of Prof. R. Van Grieken, Belgium, on X ray spectrometry for preventive conservation (credit: A. Markowicz)

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European Commission Frame Programme 7 (FP7) projects promoting nuclear based analytical techniques and technology

In 2009 two large European projects, SPIRIT (Support of Public and Industrial Research using Ion Beam Technology; http://www.spirit-ion.eu/Project.html) and CHARISMA (Cultural Heritage Advanced Research Infrastructures: Synergy for a Multidisciplinary Approach to Conservation/Restoration; http://www.charismaproject.eu/home-page.aspx) have been launched up to 2013 within the action: 'Research Infrastructures' of the 'Capacities' Frame Programme 7 (FP7). Both projects represent an Integrated Infrastructure Initiative (I3) that supports three basic activities, namely Networking, Joint Research (JRA) and TransNational Access (TNA). The later activity is of particular interest for researchers and academic personnel from eligible for transnational access European countries (Albania, Austria, Belgium, Bosnia & Herzegovina, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Israel, Italy, Latvia, Liechtenstein, Lithuania, Luxembourg, the Former Yugoslav Republic of Macedonia, Malta, Montenegro, Netherlands, Norway, Poland, Portugal, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey, and United Kingdom). Research proposals for TNA are accepted continuously without periodic deadlines by seven partners of the SPIRIT consortium (http://www.spirit-ion.eu/TNA/Information.html), whereas TNA within CHARISMA project (http://www.charismaproject.eu/calls-for-transnational-access.aspx) is modulated by three different and complementary groups of facilities (ARCHLAB, FIXLAB, MOLAB) continuously or at strict deadlines. The group users of chosen proposals, once criteria of eligibility are satisfied, obtain free access to the facility including infrastructure, logistical, scientific and technical support but also travel and accommodation grants.

SPIRIT consortium exclusively includes leading ion-beam facilities in Europe that support research in a wide range of analytical applications. CHARISMA large and medium scale facilities are dedicated to state of the art research in the cultural heritage field providing to users groups access to ion-beam facilities (AGLAE [1] in France and ATOMKI-HAS [2] in Debrecen, Hungary), synchrotron radiation in France (SOLEIL, IPANEMA [3]) and neutrons in Budapest, Hungary (Budapest, Neutron Centre [4]).

X ray based spectrometric techniques such as X Ray Fluorescence (XRF) analysis and X Ray Diffraction consist of the basic pillars of the mobile laboratory (MOLAB) that has been structured within CHARISMA to offer to the user groups access to in-situ non-invasive investigations of cultural heritage objects and artworks.

a) SPIRIT (**S**upport of **P**ublic and **I**ndustrial **R**esearch using **I**on **B**eam **T**echnology http://www.spirit-ion.eu/Project.html)

The SPIRIT consortium integrates eleven leading European ion beam facilities from six Member states (Belgium, France, Germany, Portugal, Slovenia and United Kingdom) and two associated states (Croatia and Switzerland). Ions in an energy range from ~10 keV to ~ 100 MeV are made available for the modification and analysis of solid surfaces, thin films and nanostructured systems. The main application areas are materials, biomedical and environmental research and technology. According the SPIRIT coordinator, Prof. Dr. Wolfhard Möller, Director of the Ion Beam Center Forschungszentrum Dresden-Rossendorf SPIRIT 'will increase user access and the quality of research by sharing best practice, balancing supply and demand, harmonizing procedures and extending the services into new emerging fields and to new users especially from the new Member States and industry. The networking activities include the development of common standards for quality assessment; training and consultancy for user researchers and foresight studies. Finally, the joint research activities promote emerging fields such as targeted single ion implantation for irradiation of living cells; ion-beam based analysis with ultrahigh depth resolution; ion-based 3-D tomography, and chemical and molecular imaging.

Transnational Access (TNA) within SPIRIT is provided throughout the duration of the project at seven infrastructures (see http://www.spirit-ion.eu/TNA/Information.html) in the following fields: materials science, biomedical studies and environmental investigations including cultural heritage, covering also the application of ion beams for irradiation/materials modification. A wide spectrum of specific devices, methods and processes is available within the consortium, which covers standard applications and novel developments and is in line with the international state-of-the art. The proposals are regularly evaluated by a SPIRIT-independent international user selection panel, reviewed by factors such as scientific and technical originality, feasibility and quality of the research group. SPIRIT encourages new users, users from new Member States, and participation of young researchers (e.g., Ph.D. students) and female scientists to apply for TNA.

b) CHARISMA (**C**ultural **H**eritage **A**dvanced **R**esearch **I**nfrastructures: **S**ynergy for a **M**ultidisciplinary **A**pproach to Conservation/ Restoration, http://www.charismaproject.eu/home-page.aspx)

CHARISMA provides transnational access to the most advanced scientific instrumentations and knowledge allowing scientists, conservators-restorers and curators to enhance their research at the cultural heritage forefront. Specialists from arts and sciences design and set-up new instrumentations and methodologies towards the development of the most promising technological applications that offer sustainable solutions and improve diagnostics and monitoring. New extended cooperation among European infrastructures, paves the way towards expanding the harmonisation of best practices in studies and conservation.

Concerning the transnational access, CHARISMA provides by means of three defined (sub)programs (ARCHLAB, FIXLAB and MOLAB) access to eleven most advanced European facilities centers used nowadays, from neutrons to synchrotrons and ion beams, from micro-focused spectroscopy to multispectral high-resolution imaging (see http://www.charismaproject.eu/transnational-access.aspx) .

In particular, the **MOLAB** access program provides mobile facilities for in situ non-invasive measurements on unmovable or low-mobility objects without any sampling or any contact with their surface. A collection of portable scientific equipment, suitable for in-situ non-invasive measurements, travels across Europe as an 'European Mobile Laboratory' (UNIPG-Centro SMAArt, IT, CNRS-LC2RMF, FR and CNR-INOA, IT), allowing scientists, conservators and curators to carry out imaging and/or analytical measurements directly on an open-air monument or on an artwork in a museum, a conservation studio or an archaeological site, thus avoiding all the risks and costs associated with the transportation of valuable art objects to a laboratory. (http://www.charismaproject.eu/transnational-access/molab/molab-welcome-desk.aspx).

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

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[1] http://www.umr171-cnrs.fr/spip.php?rubrique48
[2] http://iba.atomki.hu/charisma/index.html
[3] http://www.synchrotron-soleil.fr/ipanema/charisma
[4] http://www.bnc.hu/modules.php?name=News&file=article&sid=72

X ray fluorescence in Member States

Albania

Activities at the XRF laboratory of the Centre o f Applied Nuclear Physics, Faculty of Natural Sciences, University of Tirana, Albania

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The Center of Applied Nuclear Physics was created in 2008 as a research center of the Faculty of Natural Sciences of the University of Tirana, on the basis of the ex-Institute of Nuclear Physics of the Albanian Academy of Sciences.

Studies in the field of cultural heritage artifacts have been increased during the last years due to the increased awareness of the archaeologists, restorers and conservators about the importance that analytical data can have on their work. The new generation of specialists of this field educated abroad, their frequent contacts with the foreign teams, our previous work and the participation of some of them in the activities of the regional IAEA TC projects RER1006 and RER8015 dealing with the application of nuclear techniques for the study of cultural heritage artifacts, can be some of the reasons for this new trend.

Here we will briefly present two case studies in which we tried to come to some more sound conclusions by integrating the analytical information obtained by EDXRF with the information taken by other traditional methods.

Investigation of glazed ceramic objects from Durres, Albania

The archaeological museum in Durres has a big collection of glazed ceramic objects which have been discovered during the excavations performed in the area of Durres. The objects covering a wide period from 11 to 17 century belong to different periods and types. The group belonging to the Byzantine period is composed mainly of wares of different sizes, shapes and decorations. The archaeological studies support the thesis that most of the objects are imported from different foreign centers but there are also some indications for the existence of a local production activity. Although the glazed ceramic objects of Durres were widely studied from the archaeological point of view the present study represents the first attempt to investigate the materials used for their manufacture.

The objective of this study was the characterization of the materials used for the ceramic body, the glaze and the identification of the pigments used for the coloured decorations. Shreds from 22 glazed ceramic objects (Fig. 1) from the archaeological museum in Durres were collected. Most of the shreds (12 pieces) belong to the objects from the Byzantine period (12–14 century) with glazes of different colours and some of them decorated with the zgraphito technique. The other shreds represent protomajolica and majolica wares that according to the archaeologists belong to 13–17th centuries' imports from Italy. In the group were also included 14 pellets prepared from fired clays collected in the area of Durres.

Fig. 1. Glazed ceramic objects

The optical microscopy results indicate that most of the Byzantine objects were made of medium coarse clays and in some of them mineral inclusions were observed. The thickness of the glaze varies between 0.1 and 0.4 mm. In most of the cases the glaze is applied directly on the ceramic body but there are some shreds in which the glaze is applied on a white layer.

The elemental analysis of the glaze material and ceramic body were performed by energy-dispersive X ray fluorescence spectrometry (EDXRF). The results indicate lead as a major constituent of the glaze material (Pb - 26 ÷ 31%) and the presence of tin is observed in some objects. The increased presence of Fe in red, brown, yellow and black coloured glazes can be an indication that Fe compounds have been used as pigments while Cu compounds should have been used in green coloured glazes. The elemental analyses indicate that Ca rich clays were generally used for the preparation of the ceramic body.

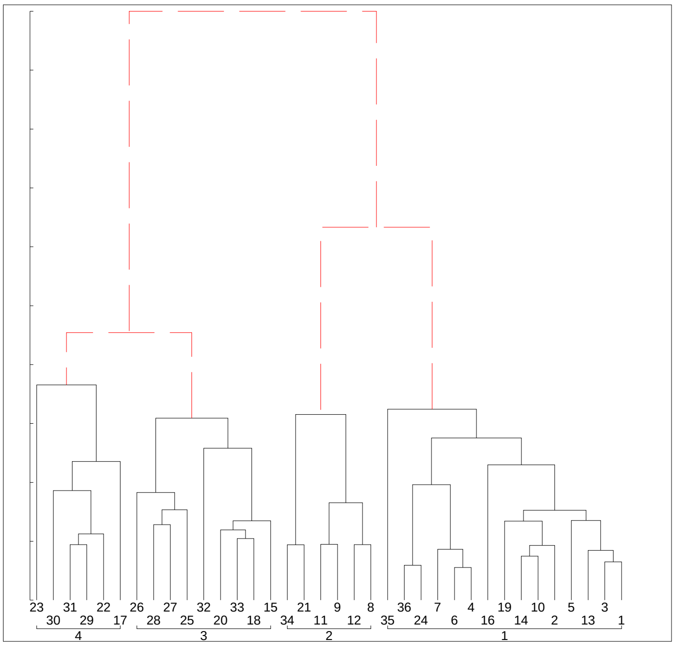

Fig. 2. Dendrograme of hierarchical cluster analysis

The application of hierarchical cluster analysis on the concentration data of the shreds (Figs. 2 and 3) shows the existence of two main different groups. The first includes mainly clays collected in the area of Durres while the shreds from the objects of Italian origin form the second group. The Byzantine glazed ceramics are distributed between these two main groups. On one side, these results can support the thesis for the existence of local production activity in Durres and on the other side they can indicate that the imports of glazed ceramic objects were coming mainly from Italy.

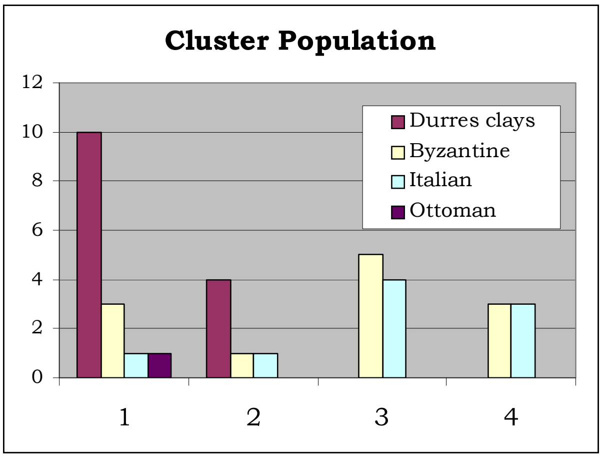

Fig. 3. Distribution of the objects among the clusters

In-situ, non-destructive examination of wall paintings in 16th century 'Saint Mary Blaherna' church in Berati Castle

The church of 'Saint Mary Blaherna' is one of the most important monuments situated inside of Berati Castle, which was inscribed in the World Heritage List in July 2008. The castle has been constructed by the Illyrians during the IVth century BC and there are clear signs of reconstructions during the Roman, Byzantine and Ottoman periods.

The church of 'Saint Mary Blaherna' represents one of the masterpieces of the Byzantine architecture and post Byzantine wall painting in Albania. The church dates from the 13th century and was decorated with wall paintings during the 16th century by Nikolla, the son of Albania's most famous medieval painter, Onufri. Despite previous restorations the church still presents serious conservation problems related with both the architecture and the internal decorations.

Part of the wall paintings of the church were examined in situ using portable non-destructive techniques as part of the attempts to adopt a standard procedure for the diagnostic examination of the conservation state of the wall paintings. This procedure aims to harmonize the information obtained by traditional methods used by restorers (visual examination and documentation, diagnostic survey, etc.) with those obtained by other nondestructive techniques like photography under sliding light, UV photography and application of EDXRF instruments for analyzing the wall painting's materials.

The examinations were performed by a common team composed of Albanian and Italian restorers and researchers, working together in the framework of a research project supported by the program of bilateral cooperation in the field of science and technology between Albania and Italy.

The first step of the work was the examination of wall paintings by the restorers during which they evaluated the conservation state of the different parts like the preparatory layer, the painted layer and the previous interventions. A new nomenclature for the electronic documentation of all this information, introduced in Italy by Instituto Centrale di Restauro in 1990, was used and proposed for future applications.

Additional information about the preparation and painted layers can be obtained by photography under ranking light and UV light (Fig. 4).

(a) (b) (c)

Fig. 4. Photos of a fragment, (a) front light, (b) sliding light, (c) UV light

The photography under ranking light informs us on how the artist used to work (distribution of the wet preparation layer, daily work, incisions for the drawings, etc.) while from the photography under UV light we can have information on the conservation state of the painted layer (depositions from deterioration, use of varnishes or other organic substances, etc.).

The final stage of the work included the application of portable EDXRF instruments for the identification of the materials used for the preparation of the wall paintings (Fig. 5). Two different EDXRF instruments assembled by the Albanian and Italian researchers (Table 1) were used.

Both instruments used direct excitation mode and were operated in two different conditions that enable the optimized identification of low Z elements (diagnostic measurement) and higher Z elements (archaeometric measurements).

TABLE 1. The characteristics of the parts of EDXRF instruments

Component	Parameters	Italian system	Albanian system
X ray tube	Type	Mini X	Eclipse IV
	Anode	Ag	Ag
	Max high voltage (kV)	40	30
	Max current (μA)	100	100
	Filter	Al, 3 mm	Ag, 0.3 mm
	Collimator (mm)	1.5	2
Detector	Type	SDD	Si PIN
	Area (mm^2)	7	7
	Thickness (mm)	0.3	0.3
	FWHM (eV)	150	195
	Cooling	Thermoelectric	Thermoelectric
Analyzer	Type	X-1-2-3	PX4

Fig. 5. In-situ examinations with the EDXRF instruments

The measurements allowed us to identify the materials used for the preparation layer and most of the pigments. The preparation layer was made of a thin layer of gypsum over calcite, while Calcium and Lead white, yellow ochre and Giallino (Fig. 6), Green Earth and Malachite, red ochre, minium, vermilion and azurite were identified in the examined areas with different colors.

During the diagnostic measurements S and Cl were identified. The presence of Cl was attributed to the chlorites being deposited on the painted layer as a result of materials' degradation or atmospheric deposition. The same can be true for the sulfur but we must be aware that at least part of it can come from the gypsum used in the preparation layer.

Both instruments were comparable in terms of their ability to identify the materials during these examinations. However, the overall performance of the instrument of the Italian team was better due to the higher HV of the X ray tube (Sn K lines could be excited and measured) and the better resolution and count rate performance of the SDD detector (Fig. 7).

Based on the collected information by all the different techniques we defined the conservation state of the wall paintings and we concluded that the painter has first painted the general scene working 'a fresco' with some of the identified pigments, and after that he has finished the work using the other part of the pigments by painting 'a secco'.

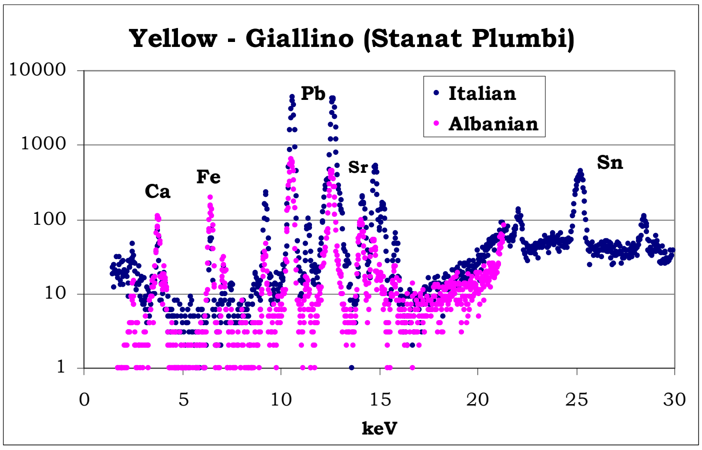

Fig. 6. XRF spectrum of a yellow color (high energy)

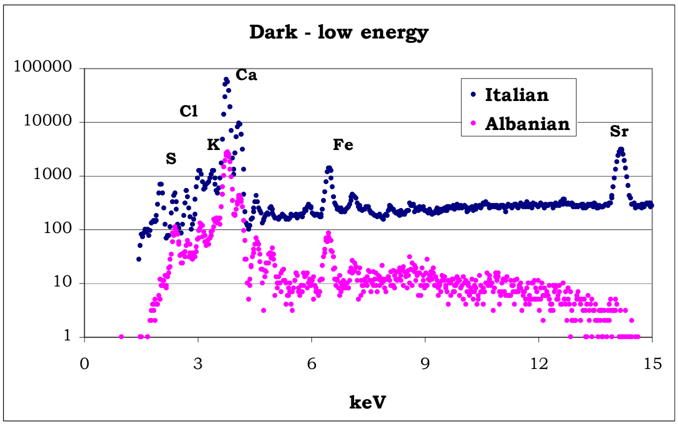

Fig. 7. XRF spectrum of a dark color (low energy)

Argentina

Combining X ray techniques, infrared spectroscopy and gas chromatography mass spectrometry for the characterization of a red paste in an archaeological shell

Contributors: Oscar M. Palacios[1], Blanca Gómez[2], Marta Maier[2] and Cristina Vázquez[1,3]

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Carriqueo rock shelter is situated in the Limay river basin, in a topographical environment of steppe plateaus, at Pilcaniyeu Department, Río Negro province. It lies on the West side bank of La Oficina creek, a tributary of the Limay river located at S40º37'27'' and W70º31'42'' (Fig. 1). This shelter - ENE oriented - could be one of several functional different sites (residential settlements, lithic worksite, pigment supply source) used simultaneously in a contemporary period. In spite of its small size, Carriqueo had intense settlements, considering the high density of archaeological artifacts found there, mostly lithic ones, bones and ceramic fragments. Also the site has an engraved northern wall in a footsteps style. This site has been known for several years: a sample of disperse charcoal found in exploratory pit was dated by ^{14}C analysis resulting 2620 + 110 years BP. Recently, during the 2006 excavation, some prepared hearths were found; three of them were dated, resulting: 940+40, 610+50 and 0-200 years BP.

Apart from the high density of the above mentioned findings, it was evident that the use of pigments was intense, considering the several red and green fragments of mineral found, and also the large quantity of artifacts that have ochre on its surface.

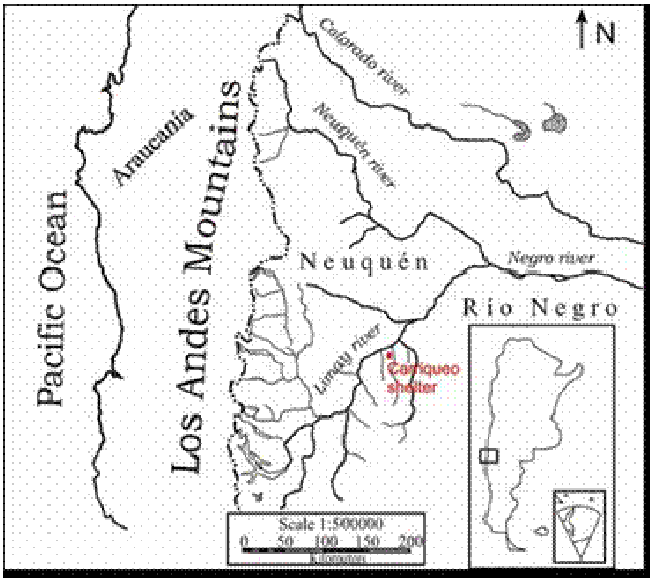

Fig. 1 Carriqueo rock shelter site

Among them, a shell, which is the subject of this study (Fig. 2), was found when the perturbed sediment by looting was cleaned. Considering that context, it was dated as modern, however, it might well be older than that. This was a remarkable finding because it suggested that it had been used as a container to prepare red paint. This research hypothesis was supported by the consistency and the large quantity of adhered unknown material. And also by the subsidiary presumption of the presence of a substance which worked as a vehicle in a nowadays hardened and maybe degraded matrix.

At least 85 lithic scrappers were found in the site, suggesting intense activity of leather processing. Thus, we must relate the leather pieces to their decoration, i.e., the painting. The practice of painting *quillangos* was common among the *tehuelches* and the *araucanos*.(inhabitants of the region). We also know that it was necessary to obtain certain fluidity in the paint mix, so we presume that fat or some animal marrow was used for this purpose. Besides, the high number of *guanaco* bones, arrowheads (100), scrappers and pigments encourage our presumption that this *camelidae* was the source of supply of meat, bones, leather and also fat, as an element for painting.

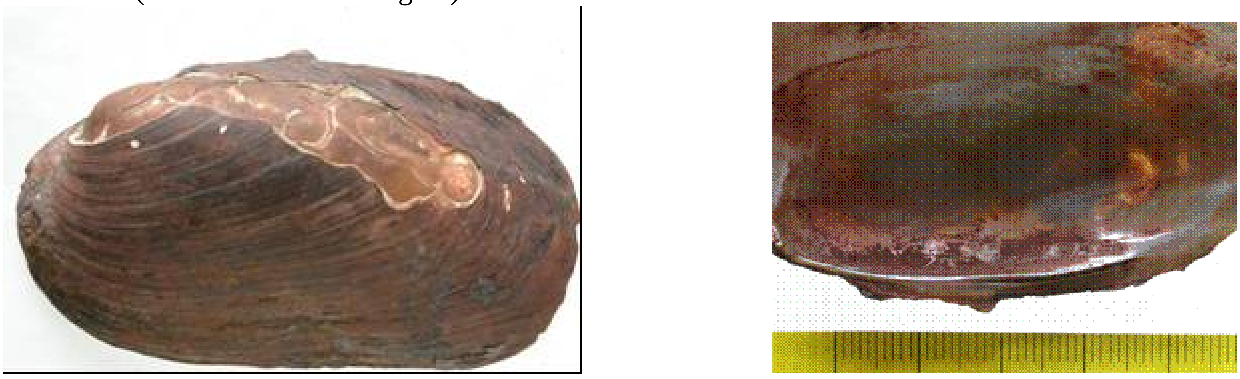

Fig. 2: Shell with a red paste inside

In order to elucidate the composition of the adhered material, a set of analytical techniques providing inorganic and organic information was employed: X ray diffraction (XRD) analysis showed phases attributable to hematite (Htt) and quartz (Q) (Fig. 3); Total reflection X ray fluorescence (TXRF) analysis showed peaks corresponding to iron, calcium as major elements among other minor elements; Fourier transform Infrared (FT-IR) spectrum of the paste showed characteristic bands for hematite, calcite and bands attributable to the presence of lipids.

Analysis by gas chromatography (GC) (Fig. 4) and GC mass spectrometry (GC-MS) of the fatty acid methyl esters obtained by saponification and methylation of the organic extract of the sample revealed the presence of palmitic (16:0) and stearic (18:0) acids as the main components together with minor amounts of myristic (14:0) and oleic (18:1) acids as well as azelaic acid, a product of the degradation of oleic acid.

Iron observed in TXRF spectrum confirms the presence of iron oxide in hematite form (see XRD diagram) which is responsible for the red colour.

The high calcium content is attributed to $CaCO_3$ that was confirmed by IR analysis. This component of the shell is unfailingly present in the paste sample. FT-IR data confirm the presence of hematite as the red pigment and suggest the mixture with a lipidic component. The fatty acid distribution, as determined by CG, with a greater abundance of palmitic acid than stearic acid is typical of degraded animal fats. There are several lines of evidence that allow the reconstruction of the ancient inhabitants' activities. The treatment of the pigments was an essential one in order to study their symbolic world. Pigments in rock wall paintings, bodies, burials and leathers had been part of their life in a way as important as were the hunting or feeding. The analytical characterization is the first step to study the social processes of the hunter-gatherers in Northern Patagonia.

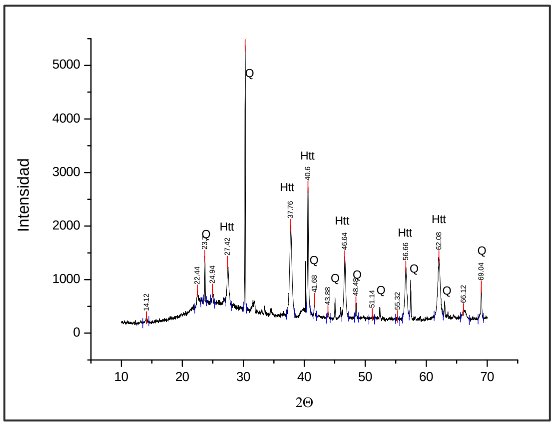

Fig.3. XRD diffractogram of the paste

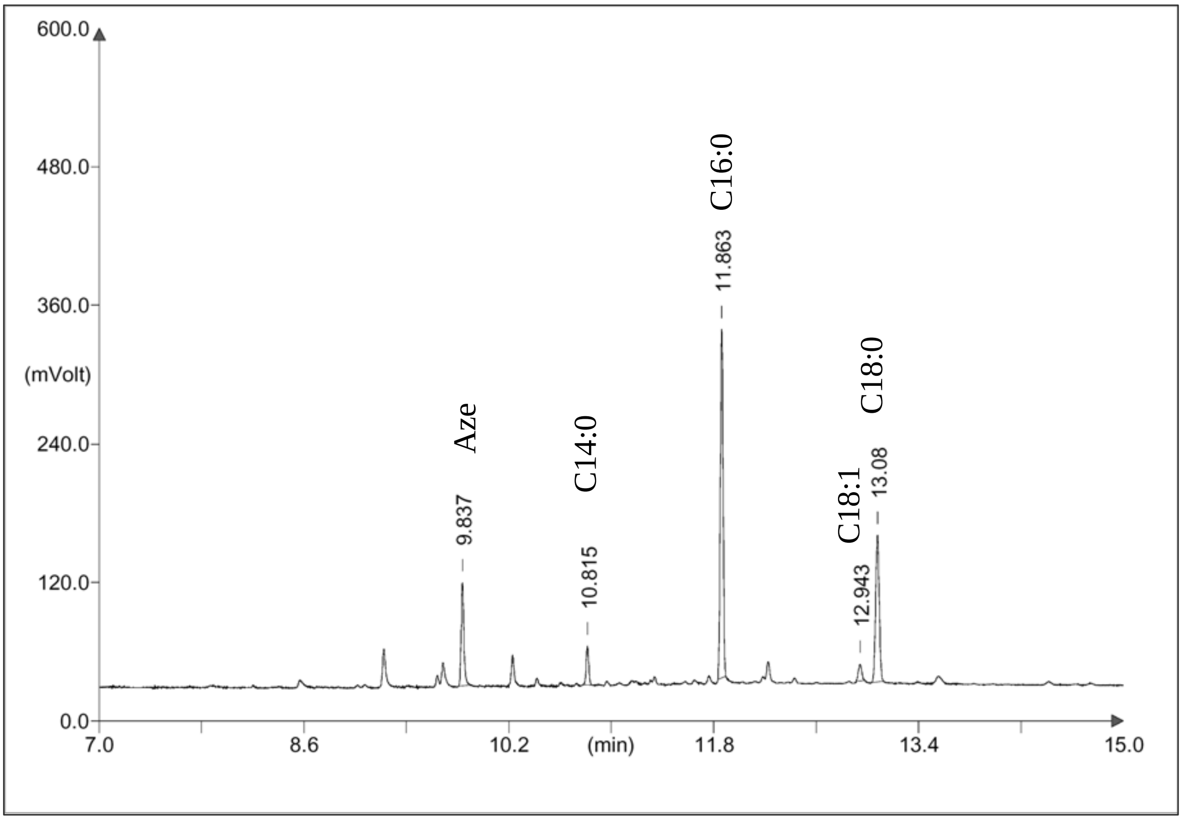

Fig. 4. GC analysis of the fatty acid methyl esters.

Peru

Recent activities in X ray fluorescence laboratory of the Peruvian Institute of Nuclear Energy – Peru

Some results presented at the II Latin-American Congress of Archaeometry held in Lima, Peru, 19-21 October 2009, are summarized below.

Multielemental X ray fluorescence non-destructive analysis of the bony remainders attributed to the conqueror Mr. Francisco Pizarro for a study of contamination post-mortem, kind of diet and paleopathologies

Contributors: Paula Olivera[1] (polivera@ipen.gob.pe), Raúl Greenwich[2,3,4]

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[2]*Proyecto Académico de Investigación Bioarqueológico e Historiográfico Francisco Pizarro-PAIBHFP*
[3]*E.A.P. Arqueología – Fac. Ciencias Sociales – Universidad Nacional Mayor San Marcos*
[4]*Equipo Peruano de Antropología Forense*

The elementary chemical analysis of bones provides very important information that allows studying topics like post mortem contamination, diet and diverse paleopathologies that are observed based on the concentration of the elements identified. The bony remains of the conqueror Don Francisco Pizarro were analyzed by using an energy dispersive X ray fluorescence system with a Cd-109 source of 25 mCi. The spectra were analyzed by IAEA-AXIL-QXAS software. The quantification was carried out with the option of simple quantitative analysis, with the method of elemental sensitivity. The presence of the elements: Ca, Fe, Cu, Zn, Sr and Pb was mainly observed confirming a vegetarian diet and the presence of the surrounding materials.

Preliminary conclusions

- Due to that a high proportion of Sr against Zn observed, the diet tends to be vegetarian.
- The head has apparently been conserved in an environment of lead or in contact with materials containing this element (Fig. 1).
- The presence of Cu in the bones of the foot was observed that would indicate contamination by contact with this metal.
- The materials of environment have a strong influence on the composition of the archaeological material due to the processes of diffusion, ionic exchange and of chemical equilibrium in the time.

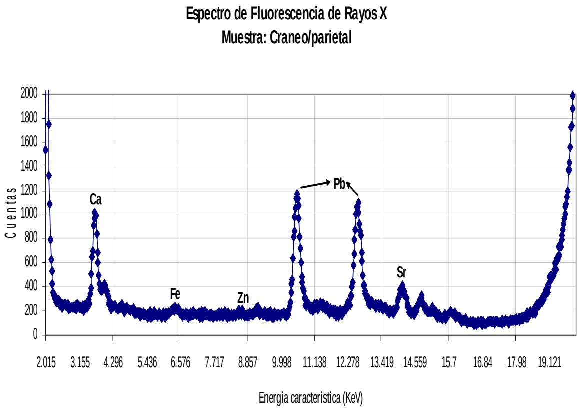

Fig. 1. Irradiation of the skull and XRF spectrum

Archaeometric study of metallic pieces from Museo Inka – Universidad Nacional San Antonio Abad from Cusco, Peru

Contributors: Paula Olivera[1], Alcides López[1,2], José Solis[1,2] , Carmen Gutiérrez[3], Julio Santiago[1,4]

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[2]*Facultad de Ciencias, Universidad Nacional de Ingeniería, Av. Túpac Amaru S/N, Lima 25, Perú*
[3]*Facultad de Ciencias Químicas, Físicas y Matemáticas, Universidad Nacional San Antonio Abad del Cusco, Av. de la Cultura 733, Cusco, Perú*
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An archaeometric study of metallic pieces, pins (tupus), has been presented. These pieces were found in excavation of Sacsayhuaman strength, Cusco - Peru, from the Inca culture. Metallographic, X ray diffraction and X ray fluorescence analysis of these pieces reveal that pins presents neither the same technology of preparation nor the same elemental composition. All the pieces include copper, as major element, combined with As or Pb. Some of them have a superficial layer of gold and/or silver.

The piece N° 1 principally consists of copper and arsenic; it is rare to find this type of alloy in metallic pieces of this region. Even, the 'tupus' originating in Machu Picchu did not include arsenic in their composition [1]. These alloys were utilized by the Sicans (900-1100 AC). For example, in the excavations of the pre-colombian tomb of the Town Batan Grande instruments of copper arsenical were found [2-4].

Piece N° 3 basically consists of copper, while piece N° 6 shows copper, gold, lead and silver in the first analysis (Fig. 2). In the second analysis, after a deep cleaning of the surface, the same elements were found as in the first analysis, except silver. This would indicate that the piece has a silver layer, which was removed by the cleaning process. In conclusion, the metallographic, XRD and XRF analyses of Inca objects revealed various technologies of preparation and various elemental compositions.

Photo: Courtesy Dr. A. López

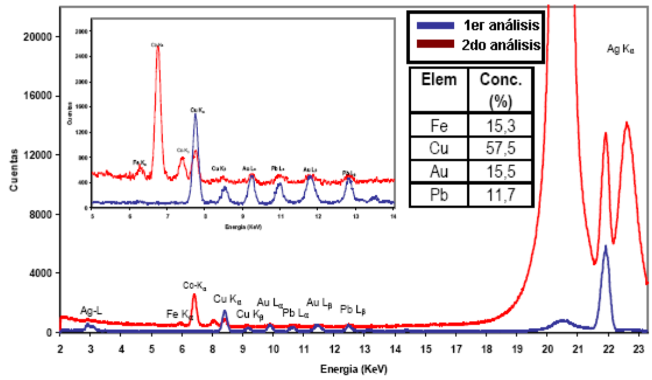

Fig. 2. XRF spectrum of the piece No. 6

Ornamental Nasca ceramics pigments identification by X ray diffraction and X ray fluorescence analysis

Contributors: Paula Olivera[1], Luisa Vetter[2], Susanna Petrick[3]

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[2]*Museo Nacional Sicán, Av. Batán Grande Cdra. 9, s/n, Carretera a Pítipo, Ferreñafe, Lambayeque, Perú*
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The Nasca culture was developed in the southern coast of Peru (100 BC to 650 AD), during the Early Intermediate Period. The most significant remain of the Nasca Culture is the fine polychrome pottery. The goal of this work is to identify the pigments used in 54 pottery fragments recovered nearby Palpa and Cahuachi (Fig. 3) by using XRF and XRD analysis. The XRD was performed using synchrotron radiation at the Spanish Line in the ESRF, Grenoble, France. The XRF spectra were taken at the IPEN. The non destructive XRF analyses of the pottery surfaces coloured of brown, orange and yellow show a high content of iron, as well as calcium and manganese. The high proportion of iron is the result of the intensive use of iron oxides, especially hematite (Fe_2O_3), observed also by XRD analysis, almost pure in the red pigments and mixed with other minerals to obtain different shades and colours.

Twelfe fragments of ceramic from Palpa (PAP 733 and PAP 73), 20 fragments of ceramic of Wari (PAP 180) obtained during excavations carried out under the project Nasca-Palpa and 20 ceramic of Cahuachi collected from surface were analyzed. The fragments were washed with bi-distilled water and dried at room temperature. The measurements were done with an annular source of Cd-109 individually for different colours during 3000 seconds in the areas of 5 mm in diameter (Fig. 4). The data acquisition was carried out with an X ray spectrometry system consisting of a Si(Li) detector (resolution of 190 eV for 5.89 keV) and a multichannel analyzer PCAII Nucleus.

Conclusions

The brown and red pigments consist of iron oxides, mainly hematite. In the dark brown pigmented samples goethite was also identified. In the brown colour applied for the samples from Wari, Mn was detected by XRF technique.

The white base consisted of quartz, carbonates and clay, possibly kaolin.

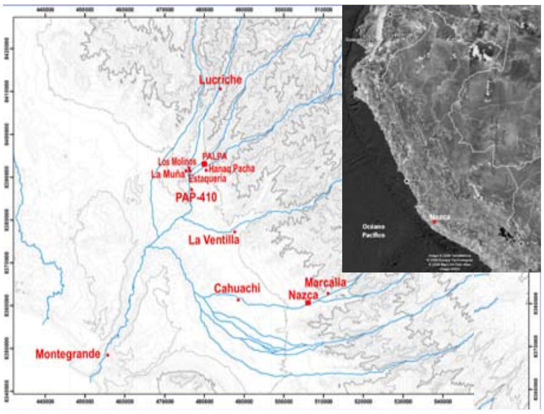

Fig. 3. Map of the archaeological places studied

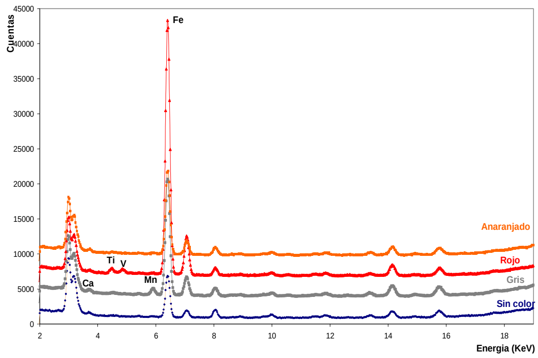

Fig. 4. *Ornamental Nasca ceramics pigments*

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[1] GORDON, R., KNOPF, R., Late horizon silver, copper, and tin from Machu Picchu, Peru. Journal of archaeological science, 34, 38-47 (2007)

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Spain

XRF activities in the ICMUV (Spain)

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

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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 related to the prehistoric pigment characterization.

Analysis of Neandertal pigments from 'Cueva Antón' and 'Cueva Los Aviones' (Murcia, Spain)

Experts in Paleoanthropology and Archaeology have long debated just how similar was Neanderthal cognition to our own. Prof. João Zilhão and others specialists argue that Neanderthals invented some symbolic traditions on their own (body paint, jewellery, etc.), before anatomically modern humans arrived in Europe around 40,000 years ago. Critics, however, believe the items originated with moderns. Past January (2010), in a paper published in the Proceedings of the National Academy of Sciences USA, Prof. João Zilhão and an international team, reported on the findings that could settle the dispute: yielded perforated and pigment-stained marine shells from two Neandertal sites (Cueva de los Aviones and Cueva Antón) in Spain dated to nearly 50,000 years ago. At Cueva de los Aviones, three umbo-perforated valves of Acanthocardia and Glycymeris were found alongside lumps of yellow and red colorants, and residues preserved inside a Spondylus shell consist of a red lepidocrocite base mixed with ground, dark red-to-black fragments of hematite and pyrite. A perforated Pecten shell (Fig. 1), painted on its external, white side with an orange mix of goethite and hematite, was abandoned after breakage at Cueva Antón, 60 km inland. Comparable early modern human-associated material from Africa and the Near East is widely accepted as evidence for body ornamentation, implying behavioral modernity.

The ICMUV has participated in this research and has analyzed pigment's remains found in a Pecten shell 'Cueva Antón (Murcia, Spain)'. The Pecten found in the level I-k of Cueva Antón presents a red pigment that is ubiquitously preserved but on the shell's external, discoloured side only, suggesting that it may have been deliberately painted, either to regain the original appearance or to make it the same color as the internal side, which remained its natural red. The ephemeral nature of the occupation of level I-k argues against on-site tool production or tool maintenance tasks and strengthens the case for the interpretation of this shell as an item of body decoration.

In order to identify the red pigment, analyses using X ray fluorescence and micro-Raman spectroscopy were carried out at the Institute of Materials Science, University of Valencia. We used a portable XRF and a μ-Raman Jobin Yvon T64000 triple spectrometer using the 514.5 nm line. Measurements were carried out directly on the sample with no previous preparation of any kind.

The internal face of the shell presents a reddish coloration, for which observation under binocular microscope suggested a biogenic origin. The external face presents a whitish coloration and features red/yellow terrigenous deposits that, under the binocular microscope, overlie the surface of the shell. We carried out XRF analysis of one of these accretions and compared the results with those obtained by XRF analysis of the shell's body in areas where it presents both a whitish and a reddish coloration. The spectra of the calcareous matrix are practically identical in both the whitish and the reddish areas, indicating that the coloration is biogenic (Fig. 2). The spectrum of the red/yellow accretion presents an iron fluorescence peak significantly more intense than that of the calcareous matrix. This indicates the presence of an iron oxide compound with an iron concentration higher than that of the shells.

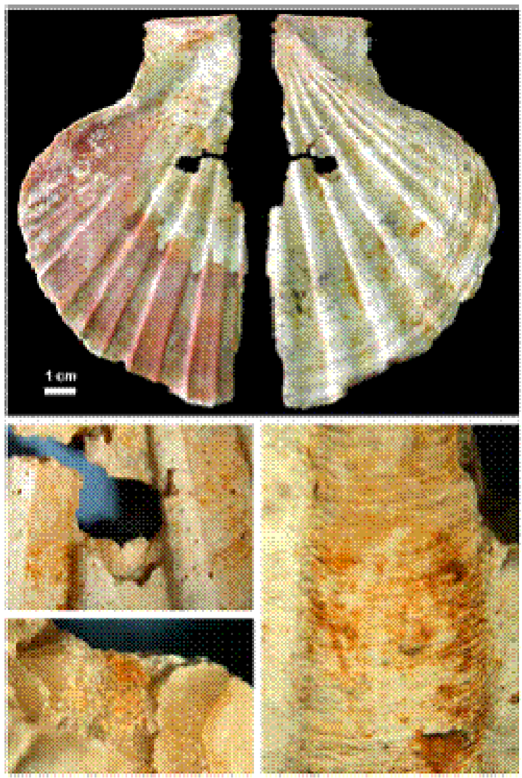


Fig. 1. Details of the performated upper half-valve of Pecten maximus from Ceuva Aton [1]

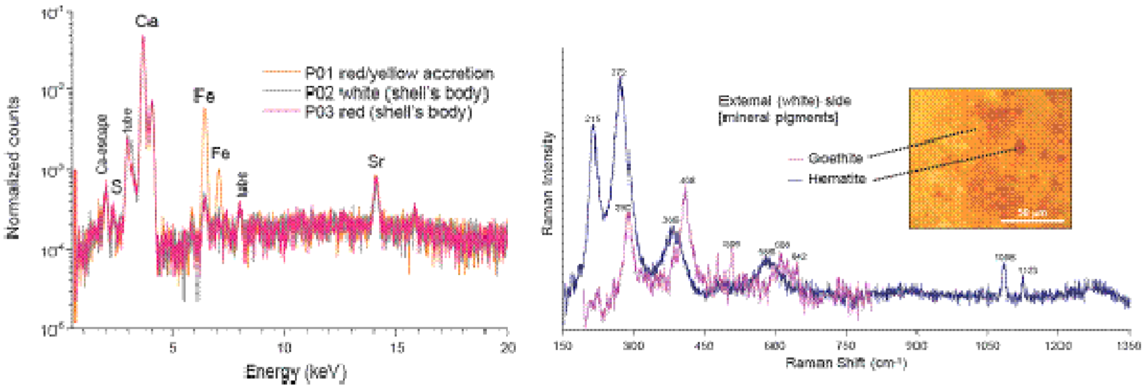


Fig. 2. Left: XRF study of the Cueva Antón Pecten. Right: μ-Raman for the external (whitish) side and microphoto (at 100x) of pigment residue

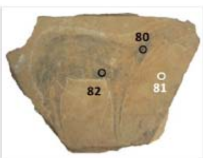
The Raman spectrum of the internal (reddish) side shows calcite attenuated by the presence of bands related to the pigments of the shell itself, which are carotenoids (Fig. 2). No anthropogenic mineral pigments were detected on this side of the shell. The different spectra obtained in the three areas with red/yellow pigment that were analyzed show very clearly the presence of bands that correspond to two iron oxides: hematite (α-Fe_2O_3), responsible for the red colour, and goethite (α-FeOOH), responsible for the yellow colour. The final result is a mixture of both pigments, yielding an overall orange hue.

The analyses of the remains from these two sites in the Murcia province of southeast Spain, report secure evidence that, approximately 50,000 years ago, 10 millennia before modern humans are first recorded in Europe, the behaviour of Neandertals was symbolically organized and continued to be so until the very end of their evolutionary trajectory.

Characterization of the mobiliar rock art black pigments from the 'Parpalló' Cave (Gandía, Valencia, Spain) by XRF.

The Parpalló cave is located near the Monduver mountain chain (Gandía, Valencia, Spain) at 450 m above sea level. The site has a complete sequence of levels spanning the Gravettian, Lower, Middle, and Upper Solutrean, Solutreo-Gravettian, and early-Magdalenian periods. The most spectacular aspect of the Parpalló site is the presence of large quantities of small engraved and painted limestone slabs in all levels, but especially in the Solutrean and Solutreo-Gravettian ones. On the surface of the slabs we can find geometrics drawings and zoomorphic representations (Table 1). The Parpalló collection consists of 5.034 lime slabs with 6.245 engraved and/or painted surfaces. Parpalló is the only Palaeolithic site in the Mediterranean Spain with a complete sequence of levels spanning from 26.000 to 11.000 BP. No other site has such enormous quantities of mobiliar art. Furthermore, other peculiarity of the Parpalló cave is the presence of about 2.000 painted slabs. These slabs were considered substitutes for parietal art in the central sector of the Iberian Mediterranean region.

TABLE 1. Parpalló slab with black pigment. The circles on the figures are the analyzed points. Chronology, size and description are shown

SLAB	DATE BP	SIZE (mm) width, height, thickness	DESCRIPTION
 16061A	21.500 - 20.500	191, 129, 42	Zoomorphic representation, probably a deer. The outline of the figure was initially realized by engraving and then the internal part was painted by means of a black pigment.

The Parpalló's collection represents an important key to understand Palaeolithic art of east Spain and it is a clear example of the existence of a regional artistic tradition in this area. In this first work we studied, by means of portable EDXRF spectrometry (Fig. 1), a total of 21 slabs with black pigments conserved in the Prehistoric Museum of Valencia. We have analyzed in total 42 points with black pigments that are compared with points without pigments on the surface slabs. This work is a preliminary study to characterize the black pigments through a qualitative analysis of the coloured areas and the support ones. The comparison between the spectra from the coloured points and spectra from the rock surface gave us some information about the elemental composition of the pigmented layer and allowed us to understand the process used to create the painting.

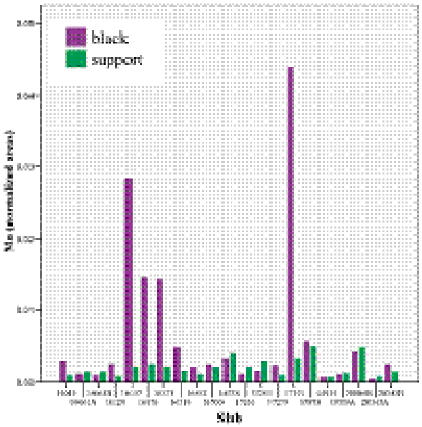


Fig. 1. Normalized areas of the Mn-Kα line in black pigments and supports

Comparing the normalized areas of the Mn XRF lines from the black points and from the support next to them, it was possible to classify the black pigments in two groups [2]: (a) pigments containing high concentration of Mn that brought us to a conclusion that black manganese oxide based pigment was used; (b) pigments without Mn or with traces of Mn that suggests that carbon black based compounds were used.

References:

[1] J. ZILHÃO, J., et al., Symbolic Use of Marine Shells and Mineral Pigments by Iberian Neandertals, in:Proceedings of the National Academy of Sciences USA, Vol. 107, No. 3, pages 1023–1028; January 19, 2010.

[2] F NOVELLI, 'Physical characterization of red, black and yellow prehistoric rock art pigments from the Mediterranean central region of Spain'. Tesi di Laurea Specialistica in Scienze Applicate ai Beni Culturalli. Facolta di Scienze Matematiche Fisiche e Naturali. Universitá degli Studi di Roma 'La Sapienza'. Relatore: Prof. Clodoaldo Roldán. Relatore interno: Prof. Givanni Gigante. Relatore esterno

Venezuela

X ray Fluorescence in Venezuela at the Agronomy Faculty, Laboratory Unidad de Análisis Instrumental, Universidad Centroccidental Lisandro Alvarado, Venezuela

Contributor: Lué-Merú Marcó

Parra, Universidad Centroccidental Lisandro Alvarado, Decanato de Agronomía, Tarabana-Cabudare, Venezuela. mparra@ucla.edu.ve

The research in the field of XRF was devoted to the development of methods for arsenic determination and the application of the TXRF technique in bioremediation studies and archeometry. X ray techniques and chemometrics were used for the determination of composition as well as for classification and provenance studies of archeological samples.

The projects were conducted in collaboration with the Laboratory of Nuclear Physics at Universidad Simón Bolívar, Venezuela, the University of Concepción and the University of Arica, Chile, the University of Buenos Aires, the CNEA (Comisión Nacional de Energía Atómica de Argentina), and the Instituto de Radioproteção e Dosimetria of Brasil.

Method development for As determination by TXRF

TXRF technique allows the arsenic determination but a prior separation and pre-concentration procedure are necessary. Alumina is a suitable substrate for the selective separation of the analytes. A method for separation and pre-concentration in alumina, followed by direct analysis of the alumina was evaluated [1]. Quantification was performed using the Al-Kα and Co-Kα lines as internal standard for samples prepared in an alumina matrix, and compared to a calibration with aqueous standards (see Fig. 1). Artificial water samples of As (III) and As (V) were analyzed after the treatment. Fifty millilitres of the sample at ppb concentration levels were mixed with 10 mg of alumina. The pH, time and temperature were controlled. The alumina was separated from the slurry by centrifugation, washed with de-ionized water and analyzed directly on the sample holder. A pre-concentration factor of 100 was found, with detection limit of 0.7 μgL^{-1}. The percentage of recovery was 98% for As (III) and 95% for As (V) demonstrating the suitability of the procedure.

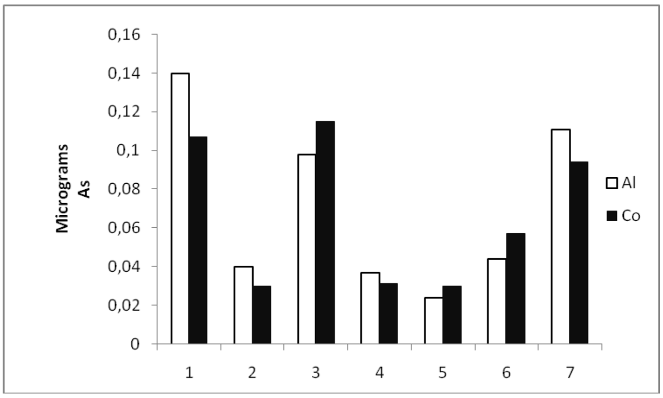


Fig 1. Micrograms of arsenic in water samples determined by using Aluminum or Cobalt as internal standard.

Applications in bioremediation studies

The TXRF was applied in the study of absorption, transport and translocation of arsenic in onion plants and compared with the hydride generation atomic absorption technique [2].

The onion (*Allium cepa L*) is one of the most important cultivars in the world and its production level occupies the second place in Venezuela. It becomes important to develop analytical procedures for arsenic determination and to study the effect of this element on the cultures, as well the absorption, transport and translocation processes.

A TXRF method for As determination in onions was developed. Two treatments were applied to the onion plants, As contaminated and control. Fifteen replicates were performed for each treatment. After a careful selection of the onion plantlets (hybrid Seminis 438), they were transplanted to dark polyethylene pots filled with prepared sand weighed in each case. A modified Hoogland solution was added to the plants for the growing in hydroponic conditions. The contaminant was added to the plants to an amount of 100 micrograms, in a single time three weeks after the transplantation. Then the non-contaminated Hoogland solution was added till the end of the experiments, after a period of 45 days. The green leaves, bulbs, and roots together with the stems were separated with a plastic knife. Next the different parts were dried at 70°C and wet ash digested for total arsenic determination by TXRF and HG-AAS. A good agreement was found between these two techniques, demonstrating a good accuracy of the TXRF procedure (see Fig. 2). It was found that the highest concentration corresponded to the root and stems (37±31 μgg-1), followed by the bulbs (11±7 μgg-1), and the green leaves (4±3 μgg-1). The growth parameters were not affected by the arsenic levels, as shown in Table 1.

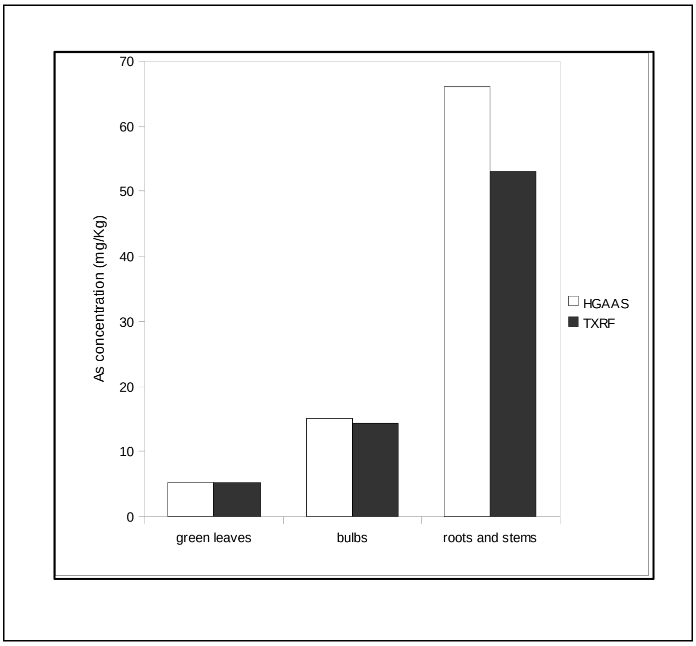


Fig. 2. comparison of the results obtained by TXRF and HG-AAS techniques (n=15)

TABLE 1. Growth parameters and P in onion plants cultured in As contaminated substrate. Values in parenthesis are standard deviations.

Treatment	% Humidity n=15	Foliar P (μgg^{-1}) n=15	Root length (cm). n=15	Leaf size (cm) n=15	Bulb diameter (cm) n=15
As(III)	89 (4)	55 (15)	4 (1)	23 (3)	1.6 (0.3)
Control	90 (3)	64 (17)	3.0 (0.4)	21 (4)	1.6 (0.5)

Applications of X ray techniques in archeometry

The XRD and XRF were applied for the composition, classification and provenance studies of archeological samples.

The synchrotron radiation X ray diffraction technique was successfully applied for the analyses of pigments found in excavation at Carriqueo rock shelter, Neuquén, Argentina [3]. The pigments samples of orange, red and brown shades were collected from different levels of this archaeological site and compared with a suspected source of provenance (La Oficina creek). Several yellowish, reddish and red pigments demonstrated X ray diffractograms corresponding to haematite, goethite, kaolinite and quartz. The majority of the samples collected at Carriqueo belong to the same group of the suspected source, having haematite and quartz as main crystalline phases. The results indicate that the raw material from La Oficina is the source of most of the pigments found at Carriqueo. The present work helped to understand the strategy of supplying of raw material by human groups in Northpatagonia region. Data obtained are of interest to the archaeologists and archaeometrists who will continue studies in this region or surrounding areas.

On-going projects

Applications in bioremediation

- Remediation and biominning of uranium in a mine sediment from Poco da Caldas, Brazil, using Eisenia fetida. Authors: Alí Timaure, Lué-Merú Marcó P. from Universidad Centroccidental Lisandro Alvarado, Venezuela and Dejanira Da Costa Lauría from Instituto de Radioproteção e Dosimetria, Brasil. Research in the frame of the ARCAL project RLA 010.

- Remediation of arsenic from a contaminated sludge from north Chile using Eisenia fetida. Authors: Juan Sebastián Villabona, Lué-Merú Marcó Parra, Haydn Barros (Laboratory of Nuclear Physics, Universidad Simón Bolívar, Venezuela) and Lorena Cornejo (Universidad de Arica, Chile). Research in the frame of the ARCAL project RLA 010.

Applications in Archeometry

A study is conducted in order to assess the impact of compositional data processing by means of conventional standardization and row-centered log-ratio transformations on principal component analysis discrimination capability of Obsidian samples from Patagonia. Authors: Cristina Vázquez[1,2], Oscar Martín Palacios[3], Edwin Hernández[5], Lué-Merú Marcó P[5]. [1]Comisión Nacional de Energía Atómica - Buenos Aires. Argentina. [2]Universidad de Buenos Aires - Buenos Aires, Argentina. [3]CIAFIC Group, Buenos Aires University, Argentina. [4]UIA, Chemistry Department, Belgium. [5]Universidad Centroccidental Lisandro Alvarado, Dpto. Química y Suelos, Decanato de Agronomía, Venezuela.

A data base was developed and used, including the concentrations of major oxides (Na_2O, K_2O, MgO, CaO, TiO_2, MnO, Fe_2O_3, Al_2O_3, SiO_2), and of some minor elements (B, Cl, Sm, and Gd), determined by XRF in 76 samples from different places of the region (see Fig. 3).

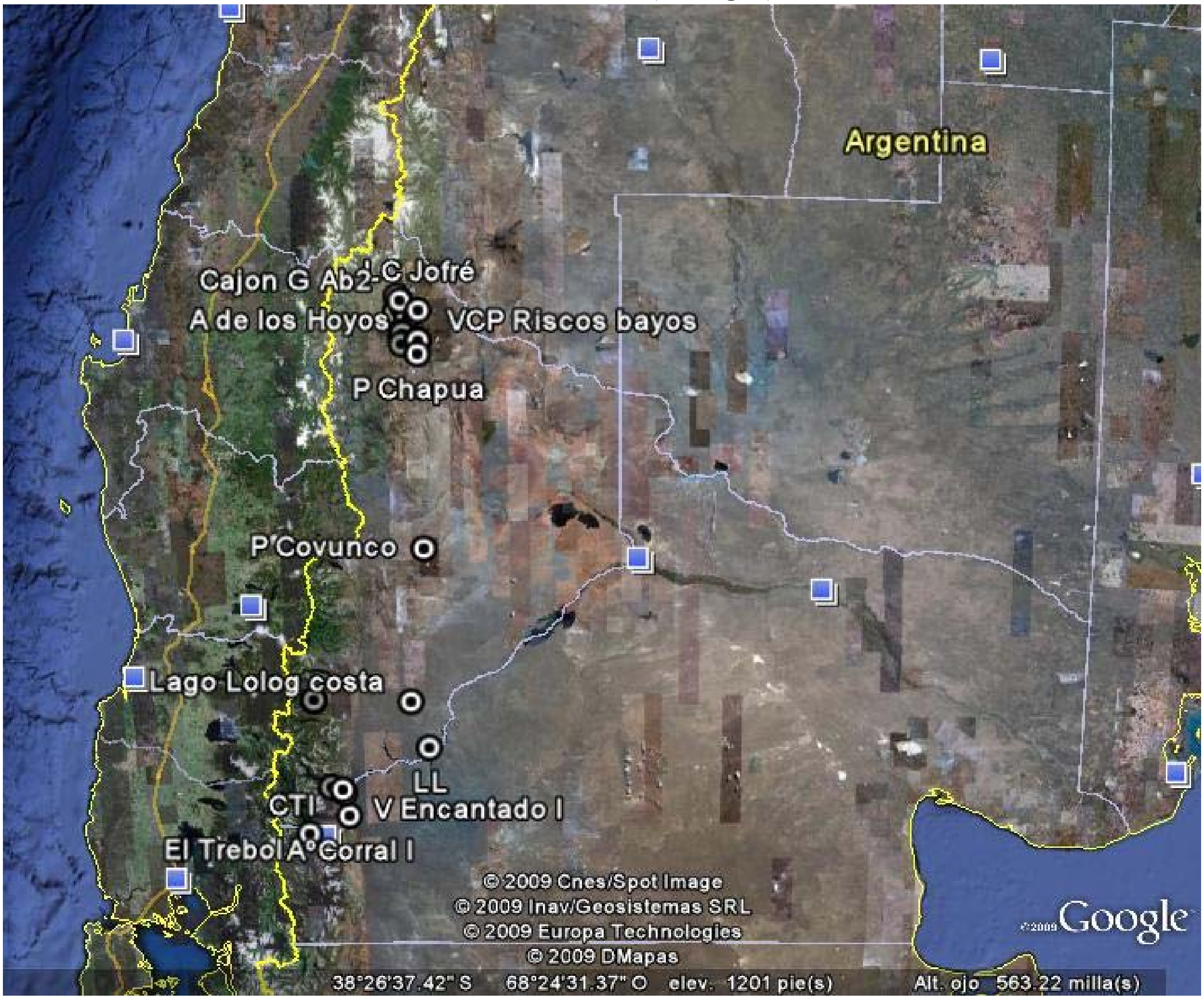


Fig. 3. Sampling sites for Obsidiane at Patagonia, Argentina.

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[2] MARCÓ PARRA, L.-M, MATUTE, S., TXRF analysis of total As in onion plants growing in contaminated substrates; 13th International Conference on total X ray Fluorescence (TXRF), Göteborg, Sweden, 15-19 June 2009.

[3] Compositional study of prehistoric pigments (carriqueo rock shelter, Argentina) by synchrotron radiation induced X ray diffraction; carried out under the Brazilian Synchrotron Light Laboratory (LNLS) proposal D12A XRD1 6558/08m U/aea 13864 and the Argentinean Projects PIP 5344, UBACYT F059 y 1809 and PICT14171.

Publications of potential interest to the XRF community

Analytical Techniques in Art, Archaeology and Conservation Science, D. Anglos and A.-G. Karydas, eds., Analytical & Bioanalytical Chemistry, Vol.395, No. 7, 1947 – 2262, December 2009

G. Buzanich, P. Wobrauschek, C. Streli, A. Markowicz, D. Wegrzynek, E. Chinea-Cano, M. Griesser, K. Uhlir, PART II (Portable ART analyzer) – development of a XRF spectrometer adapted for the study of artworks in the Kunsthistorisches Museum, Vienna, X ray Spectrom. 39, 98-102, 2010

Physical fundamentals of X ray physics, G.W. Pawlinskii, ed., Cambridge International Science Publishing Ltd, Cambridge, UK, 2008

Analytical Applications of Synchrotron Radiation, R. Abela, D. Grolimund and E. Pretsch, eds., Trends in Analytical Chemistry, special issue, Vol. 29(6), June 2010.

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