XRF

A newsletter of the IAEA s Laboratories, Seibersdorf
Issue No. 17, July 2009 ISSN 1608 4632

X ray Fluorescence in the IAEA and its Member States

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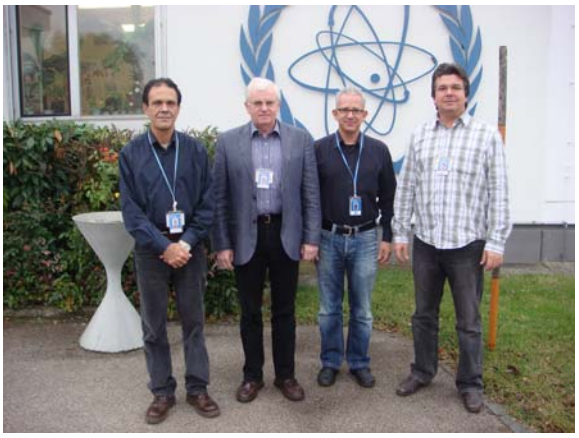
Activities in the IAEA XRF Laboratory

The XRF Newsletter is prepared by the Instrumentation Unit of the IAEA Laboratories at Seibersdorf. Current staff of the XRF Group in the Instrumentation Unit is on the photo.



From left: R. Padilla Alvarez, A. Markowicz (Head, Instrumentation Unit), A. Karydas (Leader, XRF Group) and E. Chinea-Cano

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

Coordinated Research Project (No.1576)

'Micro-analytical Techniques Based on Nuclear Spectrometry for Environmental Monitoring and Material Studies' (2009 – 2013)

1. Background

Considerable progress has been observed in recent years in the development and applications of micro-analytical techniques based on nuclear spectrometry. Major reasons for this include the possibility to use new excitation sources such as synchrotron radiation (SR) facilities, and low-power compact X ray tubes designed to offer optimum excitation geometry, combined with the availability of advanced new-generation thermoelectrically cooled semiconductor detectors and of miniaturized or large-scale X ray optics with improved performance (in particular for use with SR sources).

Consequently, the quality of characterization of various materials has improved considerably not only in large-scale laboratory facilities (ion-beam and SR sources) but also with in-house experimental set-ups, and new applications have become possible in support of applied research, teaching and education in nuclear science and technology in a wide variety of fields. 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), (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 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, mineralogy, study of corrosion processes, measurement of coating thickness, study of catalytic materials, waste characterization, characterization and quality assurance of thin-film solar cells.

• Production and quality assurance of materials for nuclear power generation

• Environmental and biomedical applications 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 in archaeology, art and conservation science including non-invasive characterization of raw materials and application techniques in cultural heritage objects, monuments and artworks, 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

• Food quality and agriculture studies

• Human health studies and pharmaceutical products characterization.

Taking into account the importance of the micro-analytical techniques based on nuclear spectrometry in different fields, the IAEA organised a technical meeting on current status, developments and trends in the relevant field, held in Vienna from 20-24 October 2008. The participants also reviewed the current and future role of the IAEA in promotion and effective use of micro-analytical techniques based on nuclear spectrometry. One of the recommendations of the technical meeting was to initiate a new Coordinated Research Project (CRP) on special configurations and new applications in order to coordinate and support the research efforts of the nuclear spectrometry laboratories. In response to this recommendation a new CRP has been proposed under the IAEA project 1.4.3.4. Nuclear Spectrometry for Analytical Applications. It is expected that the CRP will contribute effectively to meet the objectives of the Nuclear Spectrometry project, i.e. to enhance capability of interested Member States to effectively utilize nuclear spectrometries and analytical services in industry, human health, agriculture and environmental pollution monitoring.

2. Overall objectives:

The CRP will help Member States laboratories:

• to enhance their analytical capabilities to effectively utilize nuclear spectrometry techniques, and

• to provide improved analytical services in industry, environmental pollution monitoring, human health, agriculture etc. through new and extensive (broad-range) applications of micro-analytical techniques.

The results of the proposed CRP can be used both in small laboratories in the developing Member States and state-of-the-art synchrotron radiation facilities available in the developed countries. The results can also be transferred to other laboratories which will not participate in/contribute to the CRP directly.

3. Specific research objectives:

The specific results expected from the CRP are to develop:

• improved instruments for analytical methodologies and standardised procedures for micro-analytical techniques based on nuclear spectrometry

• applications of micro-analytical techniques to 2D and 3D microscopy imaging and element-specific analysis, chemical speciation in support of research and technological development in nuclear science and technology, industry, environmental pollution monitoring, production of reference materials etc.

4. Expected research outputs:

The expected research outputs of the CRP may include the following:

• Improvements in the analytical performance of micro-analytical techniques

• Standardized analytical procedures including optimised sample preparation techniques.

• Modern (upgraded) instruments and analytical methodologies including software packages for data acquisition and data evaluation

• New applications in support of research, innovation and technological development

• Publications including IAEA-TECDOCs and papers in national/international scientific journals.

5. Proposed action plan:

The activities under the CRP will include:

• Evaluation and award of research contracts and research agreement in line with the proposed objectives and expected outputs

• Establishment of coordinated research with active collaboration of all participants as soon as possible after the approval of the CRP and award of the contracts

• Hold a first Research Co-ordination Meeting (RCM) in the first half of 2010

• Conducting research and publishing the results (continuous)

• Submission of the annual reports to the IAEA, evaluation of requests for renewal of research contracts (mid 2011 and mid 2012)

• Hold a second RCM in the second half of 2011

• Hold a third (final) RCM in the first half of 2013

• Preparation and distribution of RCM reports (two months after RCM)

• Publication of an IAEA-TECDOC in 2013, publications in national/international scientific journals, conference contributions (continuous).

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Meetings and Conferences

Technical meeting on Quality Assurance for nuclear spectrometry techniques, Vienna, Austria, 12 – 16 October 2009

The objectives of the technical meeting (TM) held at the IAEA headquarters in Vienna were to review the current status in implementation and use of Quality Assurance in the nuclear spectrometry techniques; to assess/demonstrate the benefits and impacts of QA on improvement of reliability of chemical measurement results in order to further extend the applicability range of the analytical techniques, and to produce a meeting report (proceedings).

Participants representing 20 Member States and 21 organizations (see Photo 1) presented their approaches on quality assurance implementation and laboratory accreditation for alpha, beta and gamma ray spectroscopy and X ray fluorescence spectrometry, applied to a variety of fields such as environmental monitoring, food quality assessment and neutron activation analysis. The presentations resulted in technical discussions on sources of errors and uncertainties, interpretation of international requirements, pitfalls and developments in instrumentation, metrology and calculus.

The participants of the technical meeting (credit: Denis Glavic-Cindro)

The major conclusions of the TM are as follows:

• In several laboratories technical expertise is fading.

• Accreditation of management systems is never a mandatory issue, but quality assurance (including quality control) is indispensable. Accreditation for compliance with the ISO/IEC17025 may become a pre-requisite for nuclear spectroscopy laboratories if the laboratories provide test results, e.g. for environmental monitoring and global trade. The IAEA is playing an

important role in stimulating MS laboratories in implementing QA/QC, and reaching formal accreditation.

• Sensitization of executive management needs planned attention for the implementation of QA/QC practices and the final step towards accreditation.

• There is, to some extent, a need to consider harmonized guidelines for QA/QC practices as examples to laboratories for supporting the process leading to accreditation. Education in the principles and practices of QA/QC was identified as one of the important issues for successful implementation and sustainability.

• There is a need for assuring the sustainability of metrological competence in MS nuclear spectroscopy laboratories, given the retirement of experienced personnel as well as the existence of single-points-of-failure in small staffed groups, the developments in instrumentation and calculus, and the increasing requirements (and importance) to the quality of measurement data.

• New metrological approaches have been proposed for nuclear analytical techniques, including calibration of equipments, quantification of associated uncertainties, detection limits, etc. Development of materials for proficiency testing is needed to meet the newest metrological requirements.

• In-situ measurements have not yet reached a satisfactory level of implementation of QA/QC practices and field measurements may need to get adequate attention with respect to QA/QC.

These conclusions resulted in the following recommendations to the IAEA:

• To organize in 2010 a consultancy meeting to prepare the terms of reference of a new Coordinated Research Project on (some of) the above mentioned topics.

• To create a database of nuclear analytical laboratories to provide information on accredited laboratories, current status of nuclear spectrometry, etc; serving as a platform for creating a network of nuclear spectroscopy laboratories.

• To continue the development and revision of guidelines and IAEA-TECDOCs concerning QA/QC as well as the metrology of NATs to foster laboratory accreditation.

• To assist MS laboratories by provision of harmonized guidelines for QA/QC practices to facilitate comparability and internal audits.

• To continue organizing workshops and technical meetings on QA/QC in specialized fields of nuclear spectroscopy to monitor the progress of implementation, to share experiences and to identify the areas of innovation and recent developments.

• To strengthen support of nuclear analytical techniques to improve and sustain metrological competence by supporting implementation of a mechanism to assure and strengthen the metrological competence in methodologies for determining alpha, beta and gamma ray emitting radionuclides. The mechanism should also strengthen the collaboration between research and university laboratories, as well as laboratories involved in the Agency's ALMERA network with national metrology institutions for measurement of radiation.

• To direct attention for QA/QC and metrology of (semi-quantitative) in-situ measurements of radionuclides and hazardous elements.

At large, it was recommended that the IAEA should continue the organization of coordinated research projects on subjects related to quality and metrology of nuclear spectroscopy, to organize proficiency testing schemes for nuclear spectroscopy as well as to support Member States' requests for Technical Cooperation projects and fellowship training.

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Technical meeting to review and modify training programme for nuclear instrumentation to develop first line maintenance capacity in developing Member States, Vienna, Austria, 31 August – 4 September 2009

Any application of the nuclear sciences, including X ray spectrometry techniques, requires a measuring instrument which needs to be properly operated, calibrated and maintained. Maintenance is very often a major problem for developing Member States (MS) due to the lack of support from manufacturers; local markets are small and local representatives are usually unavailable. In order to alleviate the problem the IAEA

has provided support to MS in their efforts to improve the local manpower and infrastructure. This includes the provision of training for electronics technicians and engineers in topics related to nuclear instrumentation which are often not covered by the engineering courses and university curricula. With the advent/development of new technologies like microcontrollers, field programmable arrays (FPGA) etc., maintenance of modern equipment became increasingly dependent on the manufacturers. Therefore nowadays it is essential to involve the manufacturers as partners in provision of the relevant training. Manufacturers are able to provide a 'specialized training' on their equipment but they are neither interested nor prepared to provide a basic training which is often needed prior to a 'specialized training' and requires substantial time, dedicated training facilities and financial resources. With support of the IAEA, some laboratories in MS have acquired satisfactory knowledge and practical skills, and established adequate infrastructure as Region Resource Centers (RRCs), which are expected to transfer basic knowledge in the field of nuclear instrumentation to other countries in the region. In order to homogenize/standardize the training on nuclear instrumentation, and to improve its effectiveness and quality, it was necessary to review the existing training programs from the point of view of the changing needs of MS and also to include the training on emerging technologies. This technical meeting (TM) was organized to review and update the training programs for nuclear instrumentation in order to develop a first line maintenance capacity in developing MS. 17 participants from Algeria, Brazil, Cuba, Germany, Indonesia, Malaysia, Mexico, Slovenia, South Africa, Sri Lanka, Syrian Arab Republic, Tunisia, United Republic of Tanzania and Zambia attended the meeting.

Major conclusions of the TM:

In order to assure the effectiveness of the past investment in the field of nuclear sciences and applications (including equipment and manpower development) and sustainability of established projects, first line maintenance services are critical in order to assure functioning and effective utilization of the nuclear instrumentation (NI) in Member States' laboratories. The first line maintenance is based on technical staff with appropriate theoretical knowledge and practical skills required to cope with modern nuclear instrumentation.

Specific conclusions of the TM are as follows:

- The first line maintenance personnel are heavily involved in solving practical problems associated with NI. Practical training to solve such problems is not provided during regular courses at universities and technical schools, therefore additional specialized courses are needed to support the activity of the first line maintenance staff.

- The proposed program for the training covers a broad range of topics to transfer the knowledge and skills required to develop the first line maintenance capabilities.

- The already developed teaching materials based on Information Communication Technology provide a solid base in the education of the first line maintenance staff.

- The training program for the first line maintenance staff should be systematically reviewed and updated by the external experts in order to follow the current status of the instruments available in Member States' laboratories and respond effectively to the changes. This also includes continuous update of the knowledge of the teachers and a need for periodical assessment.

- The IAEA, in particular the Instrumentation Unit of Seibersdorf Laboratories, has been very efficient in training specialists in the field of nuclear electronics. The current training program was reviewed by the meeting participants, and was considered as a good starting point for the proposed training for the first line maintenance staff based on the train-the-trainer approach.

- The Seibersdorf Laboratories have the adequate infrastructure and equipment required to upgrade the knowledge and to carry out courses on modern NI.

- Courses provided by Member States can be used to complement the activities of the IAEA in establishing a successful first line maintenance services. For most courses support from the IAEA is still needed.

- The involvement of NI manufacturers in maintenance of complex NI is currently very important, and it will become even more important in the future with the development of highly specialized electronic components and increased use of software in instrumentation.

It was emphasized that the performance and the reliability of nuclear instrumentation including X ray spectrometers are inevitable for significant advances in nuclear science and technology.

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Advanced School on in-situ XRF and gamma ray spectrometry, The Abdus Salam International Centre for Theoretical Physics (ICTP), Trieste, Italy, 26-30 October 2009

The Advanced School on in-situ X ray fluorescence and gamma ray spectrometry was organized jointly by the Abdus Salam International Centre for Theoretical Physics (ICTP) and the International Atomic Energy Agency (IAEA). X ray fluorescence (XRF) and gamma ray spectrometry techniques have successfully been applied in the field and in industrial environments for in-situ analysis, which covers the analysis of artefacts and materials that have not been moved from their original place of deposition/storage. Examples of applications include soil screening for metals, indoor and outdoor air pollution monitoring, screening of contaminated areas in emergency situations, investigation of cultural heritage objects (paintings, sculptures, etc), radioactive mapping of the terrestrial environment, monitoring of building materials, investigation of the radiation field in the vicinity of sunken objects, and decontamination assessment etc. A modern portable analyser based on XRF or gamma ray spectrometry brings to the field site unsurpassed savings in time and labour as well as an excellent performance often matching that of the laboratory instrument.

Major advantages of portable (or transportable/movable) analysers include simplicity, speed of operation and flexible requirements for sample preparation. XRF and gamma ray spectrometry methods applied for in-situ analysis provide immediate analytical results in a truly non-destructive way which is of prime importance in the fields of environmental, archaeological and industrial applications.

The purpose of the School was to present recent advances in this area as well as the benefits of applying these techniques. It also created an opportunity for scientists from developing countries to initiate collaboration with more advanced laboratories on use of portable XRF and gamma ray spectrometry and associated in-situ analytical methodologies.

The School was attended by more that 40 participants from Argentina, Brazil, Bulgaria, Cameroon, Canada, China, Cuba, Egypt, Germany, Ghana, Greece, Hungary, India, Indonesia, Italy, Jordan, Nigeria, Philippines, Republic of Korea, Romania, Spain, Sudan, and Zambia. The programme of the School included the following topics:

a) Current status of portable instruments based on XRF and gamma ray spectrometry for in-situ measurements

b) Calibration of spectrometers

c) Spectra evaluation and analytical methodologies for in-situ analysis

d) Data interpretation and Quality Control procedures

e) Advantages and limitations of XRF and gamma ray spectrometry techniques for in-situ measurements

f) X ray microanalytical techniques

g) Selected in-situ applications

h) Practical experience in in-situ measurements by using X ray fluorescence (XRF) and gamma ray spectrometry techniques.

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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 events related to TC projects were supported in 2009.

Progress Review Meeting of the IAEA/RCA project RAS/7/015 on 'Characterization and Source Identification of Particulate Air Pollution in the Asian Region', Kuta, Bali, Indonesia, 10 – 14 August 2009

The meeting was organised by the Centre for Nuclear Technology of Materials and Radiometry, National Nuclear Energy Agency (BATAN). Major objectives of the meeting were as follows:

• to assess the current status and progress achieved under RAS/7/015 with an emphasis on the linkages of air particulate matter pollution to visibility and air quality management, as well as the status of the regional database

• to review and fine-tune the proposed future activities to ensure successful completion of the project and ensure its sustainability.

The meeting was attended by the National Project Counterparts (NPCs) from the following twelve countries participating in the project: Australia, China, India, Indonesia, Malaysia,

Myanmar, Pakistan, Philippines, Republic of Korea, Sri Lanka, Thailand and Vietnam (see photos below).

Participants of the meeting (credit: A.Markowicz)

Session of the meeting (credit: A. Markowicz)

Major conclusions:

Based on the country presentations and discussion sessions the following major conclusions were drawn:

• Most of the countries continue sampling and have more than five years data for fine and coarse air particulate matter

• Most of the countries have performed Positive Matrix Factorisation (PMF) source apportionment on their analytical data

• Most countries have identified significant smoke and soil transboundary events

• The IAEA/ RCA database now contains data from 14 of the 15 Member States together with the concentration uncertainties and MDL worksheets

• The regional database has been extensively scanned for quality assurance and potential problems by all participants under guidance of the regional data coordinator

• Successful technical meetings and workshops run in 2009 in Mongolia, Philippines and the Republic of Korea considerably improved data interpretation together with the quality of the database

• The project and its participants are now contributing significantly to information dissemination, journal publications, conference presentations, and national seminars

• The country presentations showed a high level of end-user involvement in the project. The end-users are contributing to the project in-kind or cash. In many countries, the data generated under the project is used by the end-users for air quality management

• The presentations given at this project review meeting have shown that all of 15 participating Member States are using the long-term database on fine and coarse air particulate matter for the identification of anthropogenic and natural pollution sources. Typical anthropogenic sources identified include biomass burning, fossil fuel combustion, motor vehicle emissions, bunker oil combustion, brick kiln and other industry emissions. Natural sources identified include transboundary wind blown soil smoke and sea spray.

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Planning and Coordination Meeting of the regional TC project RER/2/005 on 'Characterizing Seasonal Variations in Elemental Particulate Matter Concentrations in European Urban and Rural Areas under Different Climatic Conditions', Cracow, Poland, 17 – 19 June 2009

The meeting was organized by the Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Cracow, Poland. Major objectives of the meeting were as follows:

• to initiate the activities of the IAEA TC project RER/2/005,

• to get acquainted with the objectives, overall strategy, expected outcomes and outputs of the project,

• to define current status of techniques, methods and tools used for air particulate matter (APM) monitoring and characterization in the individual countries and participating institutions,

• to discuss the technical and managerial aspects related to the project,

• to review, revise and agree on the work plan and timing of the events,

• to help in development of interpersonal and inter institutional links among the project participants in order to facilitate implementation of the joint activities.

The meeting was attended by the representatives of the following nine countries: Albania, Bosnia and Herzegovina, Croatia, Greece, Hungary, Montenegro, Poland, Portugal and Serbia (see photos below). During a technical visit to the Faculty of Physics and Applied Computer Science the participants made a tour through the analytical laboratories involved in the development and applications of nuclear analytical methods.

The participants of the meeting (credit: A. Markowicz)

Session of the meeting (credit: A. Markowicz)

Major conclusions:

The Planning and Coordination Meeting confirmed the importance of the air pollution monitoring and established a solid baseline for the project which will be used for monitoring implementation and progress. The participants defined urgent needs of the individual countries, agreed on the work plan and regional events as well as on the importance of systematic sampling, analysis and data interpretation. The current status of the activities and technical infrastructure for APM monitoring are diversified and the actions to help the countries to achieve the objectives of the project were identified and included in the project work plan. An extensive expertise exists in some participating countries in the field of air pollution monitoring, and can be used for the benefit of the whole region (a first example of using the expertise was a regional training course on data evaluation and source apportionment held in Lisbon, Portugal in October 2009).

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Regional training course on evaluation of analytical data, source identification and source apportionment (RER/2/005), Lisbon, Portugal, 19 – 24 October 2009

The Regional training course (RTC) was organised by the Institute of Nuclear Technology (ITN), Lisbon, Portugal in cooperation with the IAEA under TC project RER/2/005 on 'Characterizing Seasonal Variations in Elemental Particulate Matter Concentrations in European Urban and Rural Areas under Different Climatic Conditions'.

Practical exercises to use software packages for data interpretation (credit: A.Markowicz)

The training course was attended by the participants from Albania, Bosnia and Herzegovina, Croatia, Greece, Hungary, Montenegro, Poland, Portugal and Serbia. The participants represented nuclear research institutions, universities, and environmental/health related institutions. The lectures were delivered by Prof. Gurdal Tuncel, Middle East Technical University, Ankara, Turkey, and the demonstration of software packages including experiments with computers performed individually by the participants were supervised by Dr. Maria do Carmo Freitas and Dr. Susana Marta Almeida, both from the Institute Nuclear Technology, Lisbon (see photo). During the training a visit to the research reactor and NAA Laboratory was organised.

Major conclusions:

The regional training course was of high professional standard due to a proper training programme, high level of lecturers, well prepared demonstrations and experiments, good training facilities and strong involvement/interest of the participants. Substantial time was dedicated to develop practical skills in using software packages for source identification and source apportionment. Based on the information received, most of the project participants are currently selecting sampling sites and plan to start sample collection immediately after receiving and installation of the samplers and meteorological stations. The first progress report from the participants of RER/2/005 is expected at the IAEA before the end of 2009. Based on the received information the dates of the progress review meeting should be fixed in 2010.

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X ray fluorescence in Member States

Belgium

Integration of analysis techniques of different scales using x ray induced and electron induced x ray spectrometry for applications in preventive conservation and environmental monitoring

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(i) Abstract

In the past years we have used a combination of several nuclear and non-nuclear techniques in fundamental research and especially in various applications. Most work has been done with energy-dispersive X ray fluorescence in combination with electron probe X ray microanalysis, but several other more common analysis techniques have been used as well. The applications have included mostly preventive conservation (e.g. characterisation of damaging

atmospheric particles in many museums) and environmental monitoring (e.g. for atmospheric particles in relation to their health effects in outdoor and especially indoor environments). Fundamental aspects have been in the optimising of interfaced electron microprobe and Raman microprobe analysis and the evaluation of the potential of such an instrument for atmospheric aerosols; quite a few unexpected and unpredicted problems have appeared in the latter study.

(ii) Introduction

X ray spectrometry (XRS), in its various forms, has been very useful for broad analytical applications, for decades. Electron probe X ray microanalysis (EPXMA) is well known for analysis with microscopic spatial resolution, albeit with local detection limits in the 1000-ppm range; it is a very common technique and available in many institutes in the Member States, although it is not often used or well known by the direct beneficiaries of IAEA funding. Our EPXMA units have been upgraded to include low-Z element detection and quantification (using thin-window detectors and Monte Carlo simulations) for chemical speciation at the single micro-particle level, analyses at liquid nitrogen cooling conditions to assess also more volatile particles, and analyses of surface and in-depth layers of single particles (using variable energy electron excitation followed again by quantification calculations). X ray fluorescence (XRF), and especially the more nuclear-related energy-dispersive version (EDXRF), allows bulk analysis at the sub-ppm level. Unifying, e.g. for atmospheric aerosol studies (and for environmental particles in general), bulk XRF with single particle EPXMA allows to identify much more straightforwardly the sources of such particles and to predict their fate. The chemical composition and size of single particles are important for assessing the potential of these particles to penetrate deep into the lungs and to be deposited on works of art, but bulk analysis with much better sensitivity allows obtaining information about e.g. heavy metals.

Recently, the added value of combining the application of various nuclear spectrometries to samples ranging from bulk to the micro- or nano-scale, was probed. The aim was to demonstrate the added advantages of using various nuclear and non-nuclear techniques for application in the fields of preventive conservation and environmental research, with the main emphasis on atmospheric particles.

(iii) Overview of the research performed and the results obtained

Instrumentation used. The instrumentation included as ‘nuclear techniques’: for bulk-EDXRF: Epsilon-5 of PANalytical, a high-energy polarized-beam secondary-target system; for single-particle EPXMA: a JEOL-733 electron microprobe and a JEOL-6300 scanning electron microscope (SEM) with energy-dispersive X ray (EDX) attachment. For supplementary ‘non-nuclear’ bulk analysis, we applied a Varian ion chromatograph (for ion determinations), passive diffusion tubes for the accumulation of gaseous pollutants to be analysed later by ion chromatography or UV/Vis spectrophotometry, an on-line Magee soot monitor, gravimetry for aerosol mass determinations, and for additional micro analyses, we used a Renishaw InVia micro-Raman spectrometer (MRS). All these instruments are located in and belong to the Micro and Trace Analysis Centre at the University of Antwerp.

Additionally, specific interfaced EPXMA-MRS instruments were used, in the Department of Industrial Chemistry, University of Bologna, Italy, namely a Renishaw SEMSCA unit interfaced with an EVO Zeiss SEM, and a Renishaw SEMSCA unit interfaced with an advanced JEOL SEM-EDX within Renishaw plc in Wotton-on-Edge, UK. Of late, use was also made of a state-of-the-art JAMP 9500F JEOL instrument, of IntellectAnalytics in Kiev, Ukraine, which combines EPXMA with both micro-XRF and Auger electron spectrometry.

Applications in preventive conservation. Preventive corrosion refers to any study on or in the surroundings of objects of cultural heritage importance, that has the intention to predict better conservation conditions. Such studies include: air quality measurements, micro-chemical reactions at the interfaces, atmospheric corrosion, and many more. We have used a combination of instruments, always including XRF and/or EPXMA, mostly in combination with other techniques, in preventive conservation studies of: the Royal Wawel Castle Museum in Cracow, Poland (see Figs. 1 and 2), the Metropolitan Museum of Arts in New York, the Alhambra in Granada, the Cultural History Museum in Vienna, the Correr Museum in Venice, the Musical Instrument Museum in Brussels, the Rubens’ House Museum, Royal Museum of Fine Arts and the Plantijn-Moretus Printing Museum in Antwerp and other museums in Belgium, the Netherlands and Japan, mountain churches with valuable art work in Rocca Pietore, Italy and Szalowa, South-eastern Poland, the Altamira caves with prehistoric rock art in Spain, and (in the context of the effect of protective glazing in front of medieval stained glass windows): the Basilica St. Urban in Troyes, France, the Dom in Cologne, Germany, and the Sainte-Chapelle church, Paris, France, etc.

Fig.1. Some of our aerosols sampling equipment in the Senator room in the Wawel Castle museum in Cracow, Poland. Note some of the wall carpets in the museum, which constitute one of the finest collections in the world; the indoor air quality study is intended to suggest possible improvements in air quality, to improve the conservation of the wall carpets (= preventive conservation).

In the more general field of cultural heritage research, some Argentinean artefacts, rock paintings, ancient bones and other archaeological finding were studied by a combination of EDXRF, EPXMA and MRS in collaboration with Prof. C. Vazquez from CNEA and the University of Buenos Aires.

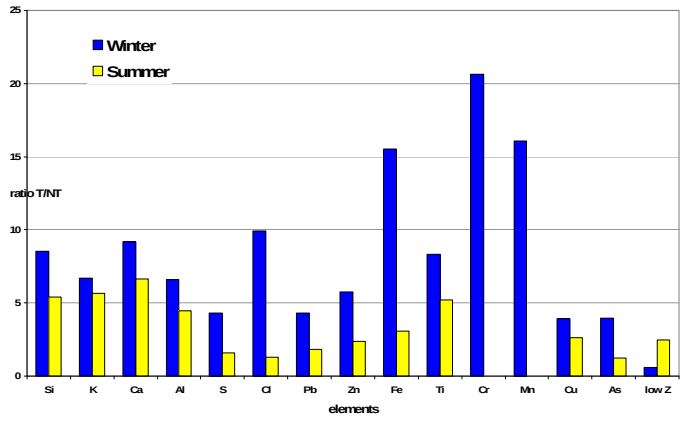

Fig.2. Some results of the XRF aerosol analyses in the Wawel Castle: given are the concentration ratios for days with visitors and without visitors in the museum; if the visitors do not have any influence, these ratios will be close to unity. For some elements, however, the ratio (especially in winter when there is more coal burning.

Other environmental applications, which have been finalised and studied, using a combination or integration of analysis techniques are: particulate atmospheric matter in schools, old-age homes and offices in Belgium and in private residences in Antwerp, Amsterdam and Helsinki, North Sea air aerosols, Hungarian Tisza river sediments, heavy mineral sands from South Africa (see Fig.3), welding aerosols, Amazon Basin aerosols, lime industry air pollutants, air pollution in the border region of Germany-Poland-Czech Republic, uranium in soils, etc.

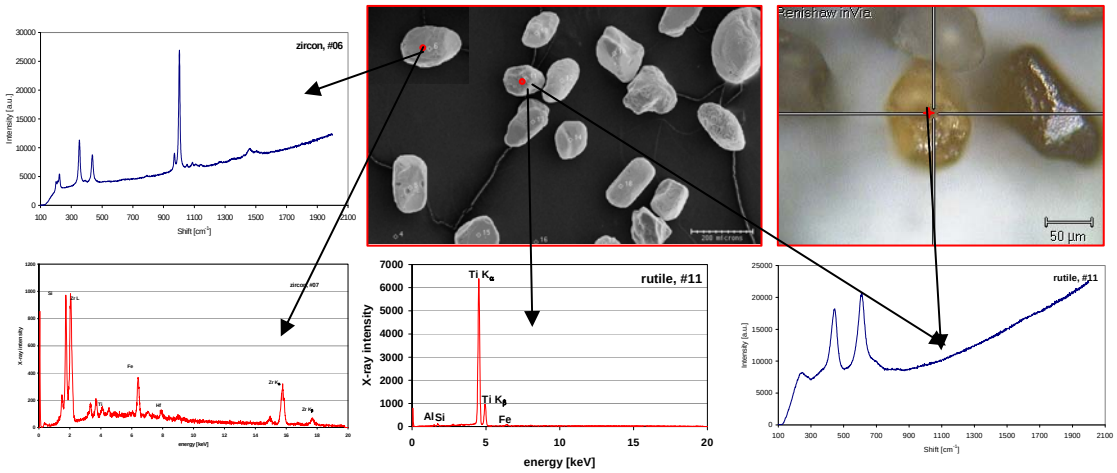

Fig.3. Heavy minerals sands: the combination of EPXMA and MRS spectra allows unambiguous identification of the minerals in the two indicated particles.

Methodological advances concerning the integrated methods of analyses will be discussed here in a bit more detail, namely for the interfacing of EPXMA and MRS in one instrument, and the interfacing of EPXMA with micro-XRF and Auger electron spectrometry in another, always in view of aerosol particulate matter characterisation. While the applicability of stand-alone EPXMA or SEM-EDX and MRS instruments is undisputed, although not without restrictions, a hybrid instrument combining these techniques will transform the EPXMA into a powerful material characterisation tool. Such combination of two well-established

technologies allows morphological, elemental, chemical and physical analysis without moving the sample between instruments. The 'two-in-one-unit' offers a number of doubtless advantages, and provides a solution for several fundamental and analytical problems. Although such interfaced instrument can be obtained commercially for a number of years now, there still is no literature concerning its use for individual environmental particles. Our research indicates that the application of this type of instrument to individual particles of heterogeneous nature, especially in the micrometer size range, is less obvious than originally expected. To use this analytical approach further and more sophisticated optimisation is required. The most important aspects regard the following: (a) beam damage and molecular changes; (b) stability of image in case of very fine features (1-4 μm) and (c) the success of relocating a particle correctly. The damage of individual particles with the EPXMA/MRS interface seems to be more problematic than in stand-alone instruments. Some electron beam sensitive particles appeared resistant to the laser beam (e.g. ammonium nitrate and ammonium sulphate are not damaged during MRS analysis) and as long as one works with a 'cold stage' to collect X ray and MRS spectra of these particles, there is no problem during measurement with the EPXMA/MRS interface. On the other hand, we determined that some particles that are stable under the electron beam are damaged by the laser beam, so their analysis was obstructed. The physical and chemical phenomena that lie underneath the damage with a laser still remain unclear. The successful relocation of the same particle is also connected with the compatibility of the two spots, laser and electron beam, as well as the probing depth. The diameter of the electron beam has to be correlated with the laser spot size, in order to cover precisely the same area of interest. The laser spot can be smaller than 0.5 μm, which makes it comparable with the area analysed by the electron beam. If the object has been relocated correctly, we can assume that the excited area is also covered by both beams. Another aspect inseparable from the spot size is the probing depth. In case of EPXMA, it is controlled by the energy of the beam electrons and the nature of the sample. For MRS, the collected volume of scattered light can be limited by a high-magnification objective and also by applying the confocal mode. With an appropriate instrument setup, the probing depth can be controlled, but it is always achieved at the expense of the quality of the optical image. Objectives of a large magnification are characterized by a small depth of field, which can cause loss of detail in the particle morphology and – consistently – lead to the incorrect recognition of the object. In other words, there has to be a –not always trivial- compromise between the successful relocation of the spot and the compatibility of the two beams. In essence, the spot relocation is an x-, y- and z-resolution issue that is greatly influenced by the mechanics of the system and depends on the precision with which the Raman probe retracts to allow electron beam analysis.

The preliminary work with the advanced field-emission EPXMA, micro-XRF and Auger electron spectrometry (AES), shown in Fig. 4, combined in one novel instrument, has led to the following preliminary conclusions: (1) the high resolution SEM enables to obtain high quality images of both sub micrometer and nano scale size with their fine detail revealed, (2) the micro-XRF technique can not be reasonably applied to single aerosol particle analysis because its spatial resolution does not match the size of relevant atmospheric particles, and (3) the Auger electron escape depth does not exceed 2 nm while the sharply focused electron beam has a lateral diameter of 2-3 nm, thanks to the superbly performing electron-optical column. In other words, the instrument is a unique Auger 3D-nanoprobe. The local AES technique can be successfully applied for the composition test of particles of any size and for obtaining the element distributions along a line (line profile), in an area (Auger mapping) and in depth with the help of ion etching (depth profile). The preliminary aerosol samples were all urban aerosols, and AES indicated e.g. a strong enrichment of N in the surface nm layers, undoubtedly the result of interactions with gaseous NOx in the air, as illustrated in Fig. 5. The quantification of the results should be studied further.

Fig.4. The advanced instrument which combines: field-emission gun SEM/EDX, micro-XRF with capillary optics and Auger electron spectrometry with an argon-ion gun.

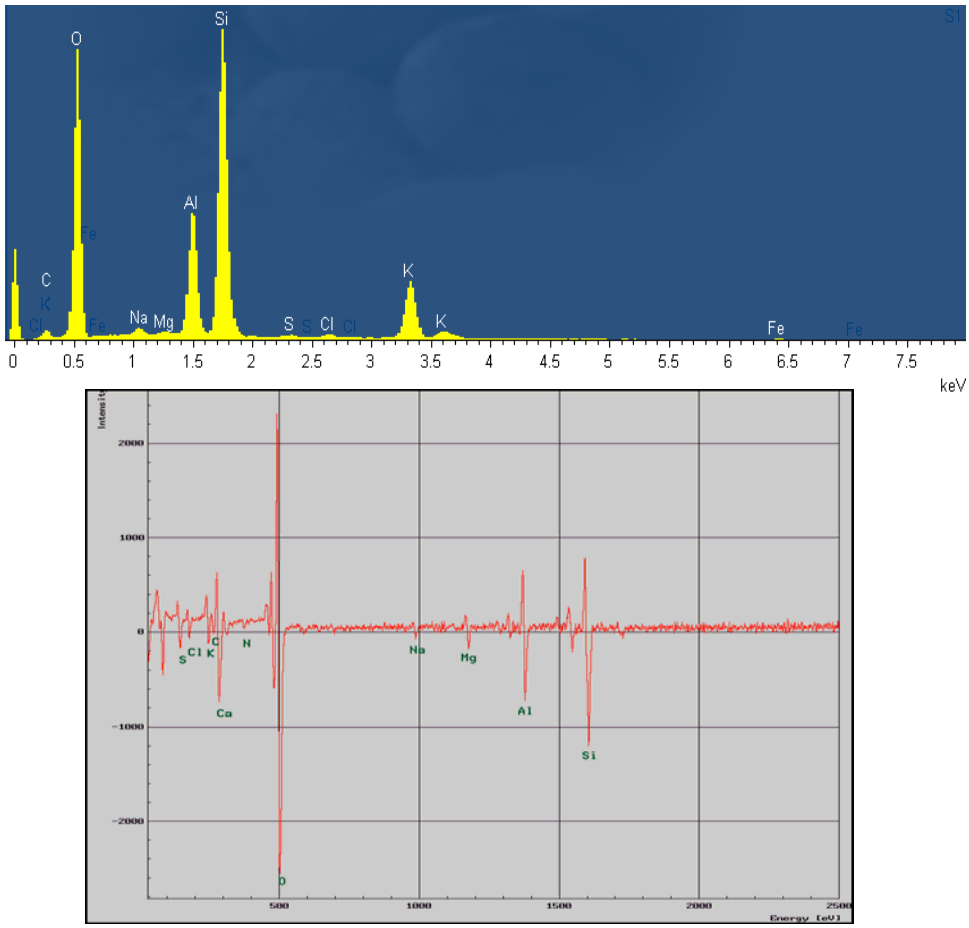

Fig.5. Some results of the novel instrument shown in Figure 4: EPXMA data for one urban aerosol particle (depth information in the order of 1 µm), and Auger electron spectrometry (depth information of a few nm) for the same particle. The Auger electron data show a nm layer enrichment of nitrate on this particle.

(iv) Conclusions

As expected, the combination of EDXRF with EPXMA and with other bulk and microanalysis techniques appeared to be much more powerful than using only one individual technique, in various applications, mostly preventive conservation and atmospheric aerosol characterisation. Unexpectedly, several problems were encountered in the application of a commercial interfaced EPXMA/MRS instrument and these led to a need for further optimisation and evaluation of the procedure.

The following combinations of nuclear and non-nuclear techniques have been applied successfully (between brackets: the number of publications during the last 3 years, in which a given combination has been employed):

- EDXRF/EPXMA (5),
- EPXMA/MRS (3),
- EPXMA/XRD (1),
- EDXRF/aerosol-mass-determination (1),
- EDXRF/gas-analysis (1),
- EDXRF/EPXMA/aerosol-mass-determination (1),
- EDXRF/EPXMA/gas-analysis (1),
- EDXRF/EPXMA/MRS (3),
- EPXMA/MRS/secondary-ion-mass-spectrometry (1),
- EDXRF/soot-determination/aerosol-mass-determination (1),
- EDXRF/gas-analysis/aerosol-mass-determination (1),
- EDXRF/ion-chromatography/aerosol-mass-determination (1),
- EDXRF/EPXMA/gamma-spectrometry (1),
- EDXRF/EPXMA/ion-chromatography/aerosol-mass-determination (1),
- EDXRF/EPXMA/gas-analysis/aerosol-mass-determination (2),
- EDXRF/µ-PIXE/MRSa/Fourier-transform-infrared (1),
- EDXRF/EPXMA/XANES/TXRF (1),
- -EDXRF/ion-chromatography/gas-analysis/soot-determination/aerosol-mass-determination (1).
-

Other and full references can easily be found in our homepage: http://webhost.ua.ac.be/mitac1

Poland

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In September 2009 our group has been moved to the Department of Medical Physics and Biophysics. Although this change occurred recently the focus of our group has been on biomedical and environmental research for a long time. Currently the research conducted by the Group encompasses the development and applications of X ray spectrometric methods for investigation of the role of trace and essential chemical elements in biological process, monitoring the levels of hazardous elements of anthropogenic origin in the environment, and in situ/ex situ characterization of materials by X ray fluorescence (XRF) techniques.

BIOMEDICAL RESEARCH

(by J. Chwiej, M. Lankosz)

Since few years, our Group, in cooperation with the Department of Neuroanatomy, Faculty of Biology and Earth Sciences, Jagiellonian University, Cracow, Poland, carries out research on the role of metals in the pathogenesis and progress of epilepsy. Our previous results confirmed the existence of significant changes in elemental composition of rat brain tissue occurring as a result of pilocarpine induced seizures. Now, our investigation has been focused on the compounds that can minimize the effects of brain injury by increasing the ability of nerve cells to survive under pathological conditions. The influence of FK-506 (tacrolimus), being one of such neuroprotective factors, on the distribution of metallic elements in the areas of rat brain that undergo neurodegeneration in case of epilepsy has been investigated. The preliminary results showed many statistically significant differences in elemental composition between epileptic animals treated and non-treated with tacrolimus. They concerned the accumulation of P, K, Fe, Cu and Zn. The findings obtained in frame of this study suggested that the neuroprotective action of FK-506 in epileptic rat brain may involve not only the inhibition of calcineurin but also blockade of the K+ channel.

QUANTIFICATION PROCEDURES

(by M. Czyżycki, M. Bielewski, M. Lankosz)

Recently, a considerable interest in investigation of particle composition by micro-beam X ray fluorescence analysis has been triggered. The sources of these micro-samples are mostly diversified. These samples come from space dust, air and ash, soil as well as environment and take the shape of sphere or oval. Geometrical effects caused by different sizes and shapes influence accuracy of results. This fact arises from the matrix effects. For arbitrary grain shape it is not possible to find analytically appropriate absorption correction factors. Hence, a way out is to approximate the real sample shape with a fake one or to use Monte Carlo (MC) simulation method.

An iterative MC simulation was applied to determine chemical composition of individual particles. A set of glass micro-spheres, made of NIST K3089 material of known chemical composition, with diameters in the range between 25 and 45 μm was investigated. The micro-spheres were scanned with X ray tube primary radiation. Results of MC simulation were compared with these of some analytical approaches based on particle shape approximation.

The investigation showed that the low-Z elements (Si, Ca, Ti) were the most sensitive to the changes of particle shape and size. For high-Z elements (Fe - Pb) concentrations were nearly equal regardless of method used. However, for all the elements considered, results of MC simulation were more accurate than these obtained from analytical relationships.

References:

M. Czyzycki, M. Bielewski, M. Lankosz, Quantitative elemental analysis of individual particles with the use of micro-beam X ray fluorescence method and Monte Carlo simulation, X ray Spectrom., (2009) - accepted for publication.

AIR POLLUTION MONITORING

Intelligent system for air pollution measurement as instrument for predicting air protection

(by L. Samek, M. Lankosz)

A research is carried out on monitoring air pollution. A 3-years project entitled ‘Intelligent system for air pollution measurement as instrument for predicting air protection’ has been financed by Polish Ministry of Science and Higher Education in 2007-2009. Our part

concentrates on collecting air size fractionated particulate matter, evaluation of concentration of particulate matter and concentration of elements in particulate matter by X ray fluorescence method. Statistical analysis is applied for data interpretation. Backward trajectories of air mass are also prepared.

A project entitled 'Influence of meteorological conditions on elemental content of particulate matter', financed by AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, has been carried out in 2007-2009. In the frame of this project samples of particulate matter were collected in Cracow, Poland. Particulate matter was separated according to grain size: 0.4 μm-2.0 μm, 2.0-8.0 μm, and greater than 8 μm. The mass of particulate matter was evaluated. For analyses of concentration of elements in particulate matter energy dispersive X ray spectrometry (EDXRFS) method was applied. Meteorological data were collected at the place of air particulate matter sampling.

In 2009 a Regional IAEA Project 'Seasonal variations of concentrations of elements of particulate matter in European urban and rural areas having different climatic conditions' has been started. The project, coordinated by L. Samek, has been foreseen for 2009-2011. The aim of the project is to evaluate the concentrations of PM10 and concentrations of elements in PM10 collected during warm and cold seasons of the year in order to find correlation with meteorological conditions. Some urban and rural areas were chosen for investigations in Eastern, Southern and Western Europe (Albania, Bosnia and Herzegovina, Croatia, Greece, Hungary, Montenegro, Poland, Portugal, Serbia). The research will help to explain the possible sources of air pollution in these areas. The data will be used in the future to elaborate effective strategies for reduction of emission of air pollutants. The data will also be used to harmonize the air sampling protocols with the EU requirements. The analyses will be carried out by energy dispersive X ray fluorescence technique.

CHARACTERIZATION OF ARCHAEOLOGICAL GLASS ARTIFACTS

(by L. Samek)

A project entitled 'Study of elemental content of archeological glasses by XRF method', financed by AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, was carried out in 2007-2009. This project was conducted in cooperation with Institute of Archaeology, Rzeszow University, Rzeszow, Poland. Evaluation of concentration of elements in glass samples was performed by EDXRFS technique. The main research goals of the work were: identification of the materials used to melt glass and determination of their origin employing chemical analyses, reconstruction of the methods of modification of glass coloration by changing the conditions in the furnace and the time of melting, and determination of the chemical characteristic of glass artifacts to find the origin/places where they had been produced.

Morocco

Examples of TXRF Activities in the XRF Laboratories of CNESTEN

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1. Introduction

TXRF is founded on the same principles of the EDXRF; the main difference with respect to common XRF-spectrometers is the use of monochromatic radiation and the total reflection optic. Illuminating the sample with a totally reflected beam reduces the absorption as well as the scattering of the beam in the sample and its matrix. Resulting benefits are a largely reduced background noise, and consequently much higher sensitivities and the significantly reduction of matrix effects.

In CNESTEN, we set up a TXRF module (Fig. 1) with a 2 kW power fine-focus X ray tube with a molybdenum anode operating in most case at 30 mA and 50 kV. X ray beam is monochromatized by using a multilayer (W/C) crystal. The fluorescent X rays of the sample are detected by a Si(Li) detector with a resolution of 165 eV at 5.9 keV and next analyzed by a

Canberra S100 multi-channel analyzer card coupled to a computer for data storage and analysis.

Fig. 1: TXRF module installed in CNESTEN.

The following studies have been carried out:

a. Evaluation of metal contents in particulate matter collected from Meknes city (Morocco);

b. Diagnosis of a contamination by trace metal elements in the spinach (Spinacia Oleracea) cultivated on market-gardening soils of the Abidjan city (Ivory Cost) amended with poultry droppings;

c. Determination of trace element contents in gnetum spp intended for national consumption in Cameroon.

2. Evaluation of metal contents in particulate matter collected from Meknes's city (Morocco)

The objective of the work was to characterize particulate matter in the Meknes's city (Morocco). Sampling was carried out 24 h once a month (from June to November 2006) at three sites characterized by their proximity to the principal roads and the industrial sectors.

Particulate matter was collected by using Gent sampler with 2 fractions according to their size:

- The breathable particles (PM10) with a diameter between 2.5 µm and 10 µm.
- The inhaled particles (PM2.5) with a diameter lower than 2.5 µm.

The elemental composition was determined by Atomic Absorption Spectrometry (SAA) and Total Reflection X ray Fluorescence (TXRF).

Our results show that the average mass concentrations in the sites of survey present weak variations between the campaigns of sampling. For elemental composition, Pb, Cd and Cu show the highest concentrations in road axes; whereas Mn shows important contents at the industrial sites. Similar variations were observed for Cr for the three sites of sampling.

The comparative study between the values recorded in Meknes's city and those founded in other Moroccan cities [1,2] shows that there is no significant difference for PM, Fe, Cr and Mn (major constituents originated from earth's crust) but there is a great difference for Pb, Cu and Cd (different anthropogenic sources).

3. Diagnosis of a contamination by trace metal elements in the spinach (Spinacia Oleracea) cultivated on market-gardening soils of the Abidjan city (Côte d'Ivoire) amended with poultry droppings

Ivory Cost, following the example of many African countries, undergoes a development of the urban agriculture last years. In Abidjan's city, market garden production and more exactly those of vegetables leaves took an important part in this activity. It contributes to the supply of the markets of ten municipalities of the city in fresh products. The market garden soils are amended with poultry droppings, which, as many other wastes used in agriculture, contain organic matters and mineral elements essential for the cultivated soils [3]. However, the presence of trace elements in the droppings represents a major constraint to its use in agriculture because these elements might be hazardous for consumers of the agricultural products [4]. Deposit of trace elements on market garden soils can also be attributed to fertilizers, domestic activities or atmospheric pollution in Abidjan city [5].

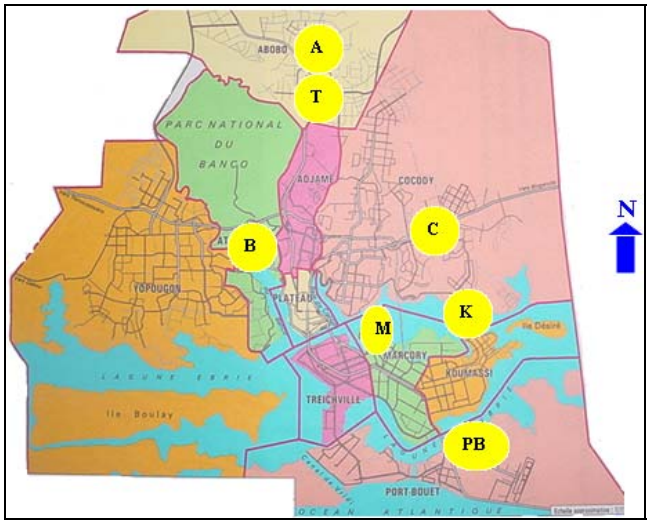

Fig. 2: Distribution of the market garden zones within the agglomeration of Abidjan.

This study is a contribution to evaluation of health impact of these market-garden products by estimating the contents of Cd, Cu, Pb, Zn and Ni in the spinach (Spinacia Oleracea) which is one of the most cultivated species considered as accumulator of trace metals [6,7]; and also in poultry droppings and surface layers of the market garden soils.

Abidjan city possesses six important sites of truck farming (A, B, C, K, M, PB) (Fig. 2) all exposed to urban and agricultural pollutions. This study was carried out in the market garden sites of the Anoumabo district of the Marcory municipality (M) and of M' Pouto's district of the Cocody municipality (C) and a pilot site (T).

The study was carried out on the area of 60 m × 45 m in Marcory and Cocody and of 15 m × 15 m in the pilot site. Three sampling sessions, from July 2006 to July 2007, were carried out. The elemental composition of the collected samples was determined by SAA and TXRF.

The results obtained from this study shows that the average contents of Cd and Cu in Cocody and pilot sites are lower than the values recommended by FAO and WHO [8]. However, the Pb, Zn and Ni contents exceed the recommended values. The spreading of poultry droppings is a source of trace metal enrichment in market garden soils. In all sites under investigation, the spinach leaves show concentrations of Zn, Pb and Ni higher than the recommended values whereas the Cd and Cu contents do not seem to present a danger for the consumers.

4. Determination of trace elements contents in Gnetum spp intended for national consumption in Cameroon

Gnetum spp is a sub-spontaneous liana in forest fallows. There are about thirty species of Gnetum in the tropics [9]. In Africa, particularly in Cameroon, there are two species: Gnetum africanum and Gnetum bucholzianum. Consumers and traders do not distinguish these two species easily. Like other NTFPs, Gnetum ssp has some value as food, medicine and cultural product [10].

Using the TXRF and SAA, it was possible to determine the mean concentrations of several elements as K, Ca, Mn, Fe, Ni, Cu, Zn, Sr and Pb.

This paper aims to investigate the potential intake of mineral elements and the bio-availability of the oligo elements in gnetacae plants. This information is of great importance for the detection of a potential metal contamination of the vegetables which may be collected in suburban forests.

Sampling was made during September and October 2008 in two regions of Cameroon: a forested region situated in the center province, and a coastal region situated in the littoral province. The center province is one of the main zones of production and collection of the leaves of gnetum spp intended for national consumption and export. In this region, sampling was made in the following five cities: Yaounde, Mfou, Monatelé, Okola, Sa'a. In the coastal region, the collection of samples was made in the city of Douala which is an industrial city. The Table 1 shows the number of sampling sites by city. For every site, leaves, stalks, roots and soils were sampled. Two or three plants in the mature state were collected and the set is mixed to form a homogeneous sample.

Table 1: Sampling sites

City	Douala	Mfou	Monatele	Yaounde	Okola	Sa'a
Number of sites	3	2	3	1	1	3

Other eatable leaves were collected in different local markets in Cameroon, such as Vernonia Amygdalina, Vernonia Calvoana and Vernonia Richadiana. The soil and rock samples were also collected from different regions of Cameroon.

The results obtained in this study are still under evaluation and interpretation. The preliminary results indicate the presence of elements like K, Ca, Mn, Fe, Ni, Cu, Zn, Rb and Sr in the leaves collected in Cameroon. Within this list, K, Ca, Mn and Fe represent 99 % of the total concentrations.

References

[1] M. Bounakhla, A. Fatah, K. Embarch, M. Ibn Majah, R. Azami, A. Sabir, A. Nejjar, R. Cherkaoui, A. Gaudry, Air pollution assessment of Salé's city (Morocco), Journal de Physique IV – France, 107 (2003) 211–214.

[2] M. Bounakhla, A. El Hamdaoui, K. Embarch, M. Ibn Majah, Fluorescence X pour l'évaluation de la pollution atmosphérique des villes de Safi et El Youssoufia, Rencontre Franco-Marocaine de Physique Nucléaire, El Jadida – Morocco, (mars 1999) 10–13.

[3] M. Legret, L. Divet et C. Juste, Migration et spéciation des métaux lourds dans un sol soumis à

des épandages boues de station d'épuration à très forte charge en Cd et Ni, 1998.
[4] M. Legret, 1984. Les métaux lourds dans les boues de station d'épuration. Valorisation agricole et extraction des métaux toxiques, Bull. Liais. Labs. P. et Ch., 129 (1984) 35-40.
[5] A. Rico, Pollutions et pratiques agricoles. Deux concepts : dose journalière admissible et chimiodéfense, Comptes Rendus de l'Académie des Sciences, Paris, Sciences de la vie / Life Sciences 323 (2000) 435-440.
[6] C. Juste, P. Chassin, A. Gomez, M. Linères, B. Mocquot, I. Feix, J. Wiart, Les micro-polluants métalliques dans les boues résiduaires des stations d'épuration urbaines, ADEME Editions, Angers, 1995, pp. 209.
[7] V. Khader and S. Rama, Selected mineral content of common leafy vegetables consumed in India at different stages of maturity ». Plant foods for Human Nutrition, 53 (1998) 71-81.
[8] FAO and WHO, Report on the 32nd session of the Codex Committee on Food Additives and Contaminants, ALINORM 01/12, Beijing, People's Republic of China, 20–24 March 2000.
[9] A. Dutta, Botany for degree students, 5th ed., Oxford University Press, Dellin, 1981, pp 286-288.
[10] J. Hutchinson, J. M. Dalziel, Flora of West Tropical Africa. Millbank. London, 1954; p 33.

Spain

Activities at the Laboratory of X ray Analytical Applications (LARX)

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1. Determination of metal residues in active pharmaceutical ingredients according to current legislation by using XRF spectrometry

Eva Marguí[1], Ignasi Queralt[1], Clàudia Fontàs[2], Manuela Hidalgo[2], Katleen Van Meel[3] , Rene Van Grieken[3] and Angel Buendía[4]

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Safety and efficacy of pharmaceuticals are two fundamental issues of importance in drug therapy. Therefore, the determination of potential impurities in different stages of the manufacturing processes, and especially in the final product, is necessary to prevent potential risk to human health. Metals can be introduced in the active pharmaceutical ingredients (API) through different sources (raw materials, reagents, catalysts, reactors, etc) and, consequently, they are potential impurities in the drug substances and are routinely monitored.

All international pharmacopoeias include a test for heavy metals, which is commonly based on sulphide precipitation in a weakly acidic medium. Serious limitations of this visual semiquantitative test are the lack of sensitivity, specificity and recovery to monitor properly the actual levels for some metals according to the European Agency for the Evaluation of Medicines (EMEA) [1].

Therefore a great effort is currently being devoted to the development of new procedures to control metals in pharmaceuticals that rely on modern instrumental techniques such as atomic absorption spectrometry and inductively coupled plasma emission spectrometry. However, when using these techniques a prior dissolution of the solid drug sample is required, leading to a time consuming and elaborated sample treatment. A promising alternative could be the use of solid state techniques such as X ray fluorescence spectrometry.

At present, one of the research activities in our group is focused on the possibilities of XRF instrumentation for the determination of metal residues in APIs according to the current legislation. In a former work [2], with collaboration with the Department of Chemistry of the University of Antwerp, we developed a simple, rapid and reliable analytical strategy for the determination of Pd-catalyst residues in a triazole antifungal API by means of high-energy polarized-beam energy

dispersive X ray fluorescence spectrometry (HE-P-EDXRF) (Fig. 1). In that study, the use of several synthetic cellulose standards made of cellulose to simulate the API matrix appeared to be an effective mean to obtain reliable calibration curves when no suitable pharmaceutical reference materials were available for this propose. The achieved limits of detection and quantification (0.11 and 0.37 mg kg-1 Pd, respectively) meet rigorous requirements and the methodology was successfully applied to the determination of Pd in three different batches of the target API (see Table 1). In another publication [3], the applicability of a conventional wavelength dispersive X ray fluorescence spectrometer (WDXRF) to the determination of other inorganic impurities (Fe, Zn, Ni) in APIs with different chemical structures was studied. Results showed that the API matrix (i.e. neutral organic compound or sodium salt) significantly influences the determination of metals by WDXRF spectrometry and this fact has to be taken into consideration when selecting the best compost candidate to prepare the synthetic calibration standards for quantification purposes (Fig. 2).

In both studies, typical validation characteristics that should be considered (specificity, limit of detection, limit of quantization, linearity and range, accuracy, precision) according to the International Conference on Harmonization of Technical Requirements for Registration of Pharmaceuticals for Human Use (ICH) were also evaluated and successful results were obtained.

Therefore, analytical methodologies based on X ray spectrometry are very attractive for the implementation in the pharmaceutical industry to increase the productivity of the laboratory, offering an interesting and easy alternative to the complicated digestion/dissolution methods described so far for this type of pharmaceutical samples.

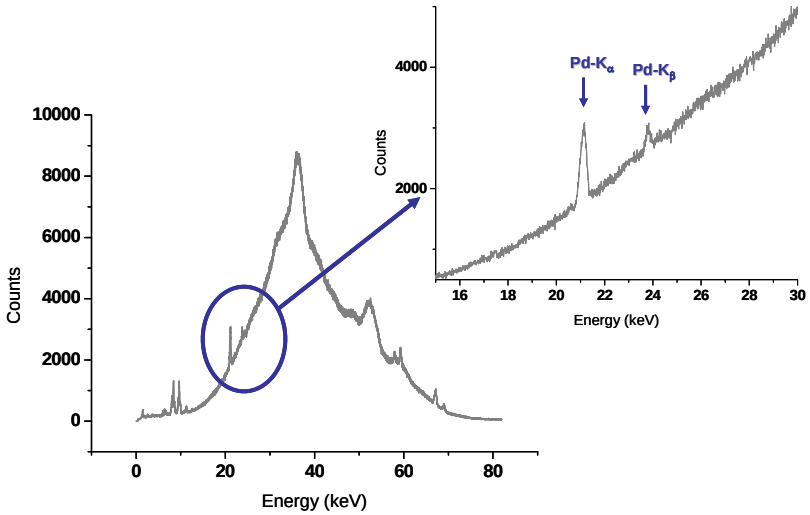
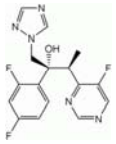


Fig. 1. Spectra for a Pd standard of 2 ppm using Al_2O_3 Barkla target (HE-P-EDXRF)

Table 1
Comparison of mean Pd concentrations (n=3) in three batches of the target API analyzed by the proposed method (HE-P-EDXRF) and the reference method (acid digestion plus ICP-OES).

	Pd (ppm), n=3	
	This method (HE-P-EDXRF)	Ref. method (ICP-OES)
API-1	0.35±0.06	0.34±0.16
API-2	0.86±0.07	0.79±0.06
API-3	0.30±0.02	0.25±0.09

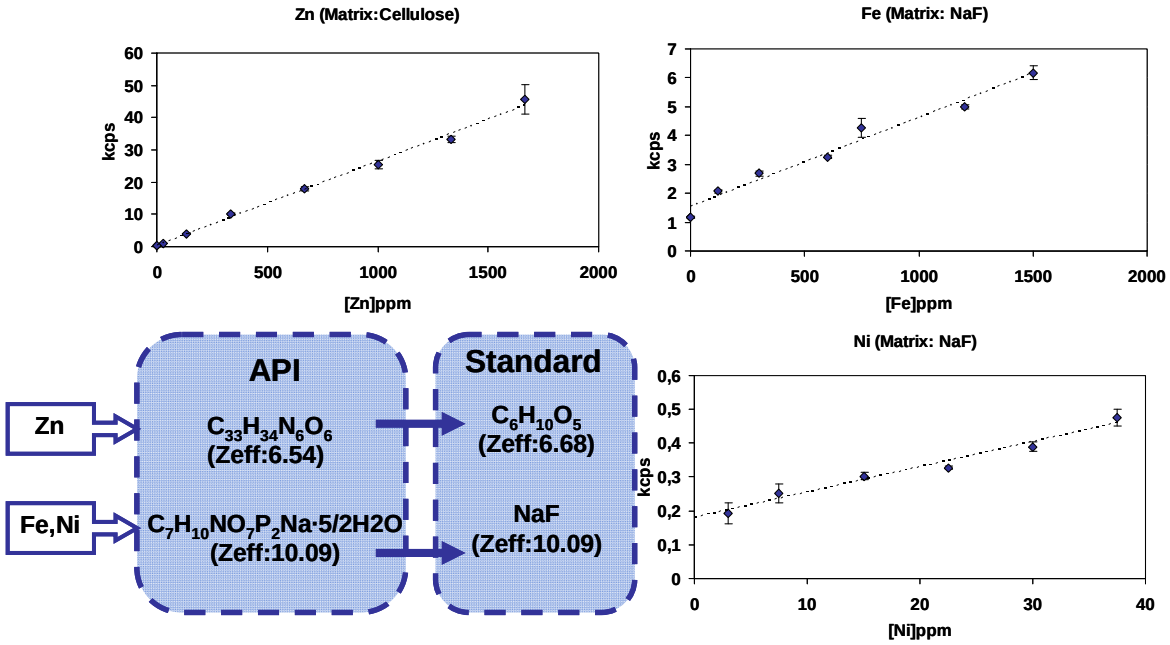


Fig. 2. *Calibration curves for Zn, Fe and Ni using different chemical compounds to simulate the API matrix (each point in the curves represents the average of the three pellets measurements).*

2. Application of XRF spectrometry in phytoremediation activities around mining areas

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In the last decade, the use of plants for the stabilization (phytostabilization) and clean-up (phytoremediation) of metal contaminated environments has gained popularity among government agencies worldwide, as alternate or complementary cost-effective non-invasive technology to the engineering based remediation methods. In view of the considerable number of analyses necessary in phytoremediation and plant biology studies, it is important that the analytical procedures used for elemental determination in plant tissues should be fast and cheap, with simple sample preparation, and of adequate accuracy and precision. Last years, we have developed several analytical methodologies, using diverse configurations of XRF spectrometers (EDXRF, WDXRF, HE-P-EDXRF), to determine elemental composition of vegetation grown in mining areas [4-8]. Recently, in collaboration with a research group from the Department of Chemical Engineering, Agriculture and Food Technology of the University of Girona (Spain), we have studied the possibilities and limitations of a low-cost benchtop energy dispersive X ray fluorescence (EDXRF) instrument to be employed as analytical technique for studying the potential use of sunflowers (Helianthus annuus) for the phytoremediation of an abandoned Pb/Zn mining area located at the North East of Spain (Fig. 3).

The simplicity, ability to operate at room temperature and open air conditions provides a flexible set-up for the rapid analysis of vegetation material without complicated previous sample pre-treatments. Moreover, due to the low power X ray tube (max. 50 W), the EDXRF instrument exhibits very low sample heating and thermal damage to the samples and associated problems of redistribution of elements when performing the analyses are avoided.

The modest lateral resolution of EDXRF system (from 200 μm to 1mm) was sufficient enough to study metal accumulation and distribution between parts of the vegetation specimens (roots, stems and leaves) providing biologically relevant information not available from standard bulk techniques such as plasma spectrochemistry and atomic absorption spectroscopy. Although, the brilliance and the sensitivity from the conventional X ray tube used is several orders of magnitude lower than the synchrotron source, it is still possible to generate moderate spatially resolved elemental maps from such a device and thus, obtain information of the spatial distributions of elements in plant tissue (Fig. 4). In addition, absolute limits of detection achieved (0.6 ng for Zn and 3.0 ng for Pb) prove to be suitable for the intended purpose [9].

Therefore, data obtained confirmed that the benchtop EDXRF system can be a useful tool to better understands the metal uptake in vegetation species related to biomonitoring and phytoremediation studies. Nevertheless, to increase the efficiency of such technologies, it is important to learn more about the specific plant physiological processes involved, including translocation and tolerance mechanisms, plant-microbe interactions and other rhizosphere processes. For this reason, we have started a new research area focused on the use of μ-XRF and μ-XANES techniques to better understand the mechanisms developed by plants to tolerate metals. Particularly we expect to find information about how the plant modifies the metal speciation in soils, and thus in a way its chemical mobility. This knowledge is essential to understand and develop the effective phytostabilization process in mining environments.

Fig. 3. Location of the studied mining area (North-East of Spain) and impact of abandoned mining activities: (A) ore concentrate tanks, (B) accumulation of mining wastes.

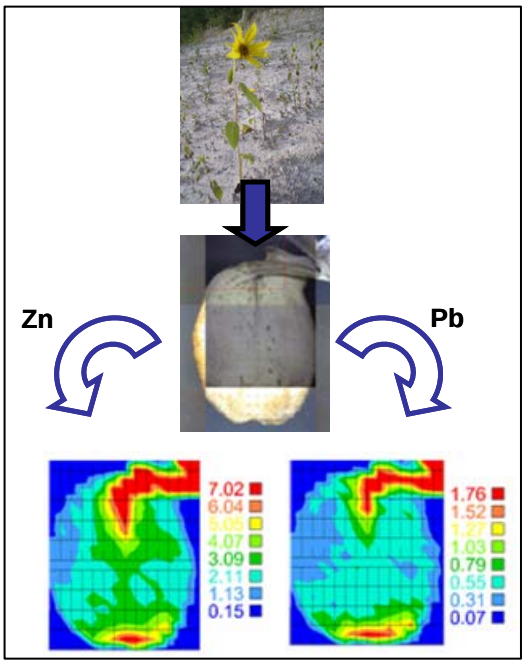

Fig. 4 Two-dimensional Pb and Zn mapping of sunflower leaves by EDXRF spectrometry. Instrument conditions: spot size (200μm), measuring time (200s/spot), griding (15 × 20 points).

3. *Compositional characterization of ancient coins by means of XRF instrumentation*

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Introduction

During the last years, amongst other activities, the Laboratory of X ray Analytical Applications (LARX) has been involved in the analytical applications of XRF spectrometry in the field of Cultural Heritage objects. In the last two years, within the framework of a joined project between LARX and the Catalonian Numismatic Department (GNC) at the National Museum of Fine Arts of Catalonia (MNAC, Barcelona) were undertaken.

Analysis of Greek silver drachmae from Emporion site

A total amount of 132 drachmae coins belonging to the Emporion Greek Colony (Empùries, Catalonia, NE Spain) collection and dated from the 4th to 1st century BC were inspected by non-destructive EDXRF technique, to determine the alloy used in coinage to determine changes in their composition during that period [10].

Measurements were carried out in situ by using a EDXRF spectrometer (X ray XAN, Helmut Fischer GmbH, Germany, equipped with a W target tube). Due to their good conservation, the coins were analyzed directly without applying any cleaning pre-treatment, using an operating 50 W power, a Ni primary filter, a collimator of 3 mm in diameter and a counting time of 180 seconds. Spectra were processed and quantified by using the fundamental parameters method, through the software attached to the equipment (WinFTM 6.20).

From the results obtained by EDXRF technique, the following conclusions could be drawn:

- The drachmae coins showed silver as a main constituent (contributing around of 90% to overall composition) and the presence of minor constituents and trace elements such as copper, tin, lead, gold, platinum, bismuth, iron, chromium, nickel, zinc, manganese and titanium.
- The coins exhibited a great uniformity of the elemental chemistry of its alloys during more than three centuries. The statistical study by means of PCA routine did not allow us to clearly differentiate the drachmae according to their strike period. However, a slight reduction of the mean silver content during the 260-200 BC period was recorded, fact that could be interpreted in the light of the economic decadence suffered by the Emporion colony during this period.
- Finally a change of quality was not recorded during the 2nd century BC, even knowing that the technique of mintage wasn't consistent [11]. On the contrary, there was an increase in the silver content average of the drachmae coins during this period, concluding that variability of the Ag content during this century was very small.

Analysis of Catalonian 19th century silver coins

In this study, we focused our attention on 266 coins minted during the French occupation of Catalonia and dated from the nineteenth century. During this historical period a continuous confrontation between the occupying Government and the local authorities generated different mintages. The study by means of EDXRF technique was useful for the determination of the type of alloy used in the minting process and to determine the differences between the five minting factories (Tarragona, Girona, Lleida, Barcelona, Volant) existing during this period in Catalonia. Likewise, XRF analysis was successful to identify some counterfeits from the true coins.

From the results of the analyses, we can conclude:

- Silver (contributing around of 93% to overall composition) and copper (6%) are found to be the main constituents of the coins from the five minting factories. The presence of minor and trace elements such as zinc, tin, lead, gold, platinum, antimony, nickel and iron have also been determined (Table 2).
- Although the coins were produced under the rule of different authorities and present different styles, they exhibited a great similarity in the elemental chemistry of alloys; even the statistical study by means of PCA routine did not allow us to clearly differentiate them according to their provenance. However, we can observe that the average silver content from the coins of the Girona factory is slightly lower than the other mints, especially the Volant mint. This tendency has allowed us to

differentiate, from a compositional point of view, the coins from both factories.

- On the other hand, some forgeries have been clearly identified among all the analysed coins. In that cases, the most common alloys are: a) bronzes (Cu-Sn alloy) (Fig. 5), b) Silvered bronzes (Cu-Sn-Ag alloy) and c) other less frequent varieties such as Sn-Sb-Ag, Sn-Cu, Cu-Ag-Sn, Ag-Sn and Sn-Ag.

As a main conclusion we can identify the deliberated addition of copper in the alloys in order to debase, reflecting the changes promoted by the difficult economic situation during the occupation war.

Table 2
Analytical data for coins of XIXth century minted at different locations (wt.%)

Location	Ag	Cu	Zn	Sn	Pb	Au	Pt	Sb	Ni	Fe
Tarragona										
mean	92.10	7.25	0.20	0.10	0.26	0.12	0.06	0.10	0.08	0.06
stdev	1.49	1.49	0.05	0.10	0.09	0.07	0.02	0.06	0.02	0.03
Girona										
mean	91.68	7.55	0.17	0.07	0.30	0.20	0.06	0.13	0.09	0.10
stdev	1.11	1.22	0.05	0.05	0.08	0.06	0.02	0.12	0.03	0.20
Lleida										
mean	94.14	5.06	0.15	0.11	0.25	0.22	0.07	0.14	0.07	0.09
stdev	1.65	1.49	0.05	0.11	0.10	0.17	0.03	0.08	0.03	0.15
Volant										
mean	94.94	4.23	0.16	0.09	0.20	0.21	0.06	0.22	0.05	0.07
stdev	0.91	0.91	0.11	0.05	0.06	0.11	0.01	0.13	0.02	0.05
Barcelona										
mean	94.95	4.45	0.12	0.12	0.18	0.19	0.05	0.17	0.06	0.08
stdev	1.33	1.42	0.05	0.12	0.05	0.06	0.02	0.11	0.03	0.05

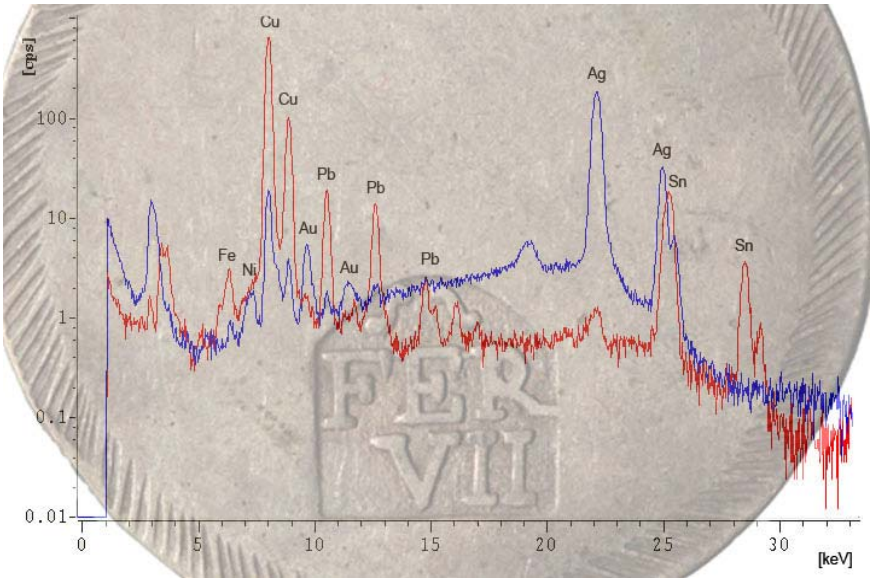

Fig. 5. *Comparison between an EDXRF spectrum of an original coin from Girona (in blue) and an EDXRF spectrum of a counterfeit (in red).*

References

[1] *Guideline on the specification limits for residues of metal catalysts or metal reagents*, (Doc.Ref. EMEA/CHMP/SWP/4446/2000). Committee for medicinal products for human use (CHMP). European Medicines Agency, London, February 2008, pp.1-34

[2] E.Marguí, K.Van Meel, R.Van Grieken, A.Buendía, C.Fontàs, M.Hidalgo, I.Queralt. *Analytical Chemistry*. 81(2009)1404.

[3] E.Marguí, C.Fontàs, A.Buendía, M.Hidalgo, I.Queralt. *Journal of Analytical Atomic Spectroscopy* 24(2009)1253

[4] E.Marguí, I.Queralt, M.L.Carvalho, M.Hidalgo. *Analytica Chimica Acta* 2005(549)197

[5] E.Marguí, M.Hidalgo, I.Queralt. *Spectrochimica Acta Part B* 60(2005)9

[6] E.Marguí, R.Padilla, M.Hidalgo, I.Queralt, R.Van Grieken. *X ray Spectrometry* 35(2006)169

[7] E.Marguí, M.Hidalgo, I.Queralt. *Spectroscopy Europe* 19(2005)16

[8] E.Marguí, I.Queralt, M.Hidalgo. *Trends in Analytical Chemistry* 28(2009)362

[9] E.Marguí, A.Jurado, M.Hidalgo, G.Pardini, M.Gispert, I.Queralt. 'Application of small-spot EDXRF instrumentation in phytorremediation activities around metal mines'. *Applied Spectroscopy*, in press.

[10] A.Pitarch and I.Queralt. Compositional characterization of ancient metals by EDXRF: the case of Greek silver drachmae from Emporion site (Empúries, Catalonia, Spain). Synchrotron Radiation in Art and Archaeology (SR2A), Barcelona (Spain). Abstracts book. 2008

[11] M. Campo (2002) La monetazione dei Focei in Occidente. Acti Dell'XI Centro Internazionale Di Studi Numismatici. Instituto Italiano Di Numismatica, Roma.

[12] A.Pitarch and I.Queralt (2008) Anàlisi de monedes de plata procedents de la col•lecció de la Guerra del Francès (1808-1814) del Gabinet Numismàtic de Catalunya del MNAC. In: Estrada et al. (Eds.) 'Monedes en lluita. Catalunya a l'Europa napoleònica'. Book edited by MNAC (National Museum of Fine Arts of Catalonia).

Publications of potential interest to the XRF community

P. Wobrauschek, C. Streli, P. Kregsamer, F. Meirer, C. Jokubonis, A. Markowicz, D. Wegrzynek, E. Chinea-Cano, Total reflection X ray fluorescence modified for analysis in vacuum, Spectrochimica Acta Part B, 63, 1401-1407, 2008

K. Uhlir, M. Griesser, G. Buzanich, P. Wobrauschek, C. Streli, D. Wegrzynek, A. Markowicz, E. Chinea-Cano, Applications of a new portable (micro) XRF instrument having low-Z elements determination capability in the field of works of art, X ray Spectrom. 37, 450-457, 2008

S. FitzGerald, Forensic applications of X ray fluorescence microscopy, Spectroscopy Europe, 21(3), 16-18, 2009