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XRF Newsletter

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X ray Fluorescence in the IAEA and its Member States

In This Issue

Activities in the IAEA XRF Laboratories

The NSAL 3D Micro-XRF Spectrometer for Elemental Imaging of Paint Layers Composition in Roman Period Plaster Fragments

From the development of a confocal x ray geometry set-up back in 2003 at the synchrotron radiation facility BESSY II and the realization of depth-resolved measurements of x ray signals[1], the analytical capabilities of XRF were significantly expanded adding a new capability to look into the interior of materials with few tens of micrometers resolution. Nowadays, 3D Micro-XRF analysis has reached a certain degree of maturity and has been already developed on a laboratory scale by several groups[2-5]. The implementation of the confocal geometry requires at first a focused exciting x ray beam with size down to the micrometer scale and a restricted field of view for the x ray detector. Usually, for laboratory x ray sources, a polycapillary x ray lens is utilized to offer a focused exciting beam, whereas a half lens or a polycapillary conical collimator (PolyCCC) attached in front of an x ray detector can localize its field of view. The alignment of the two foci regions creates the so-called probing microvolume, i.e., a 3D region sensitive to x ray signals. By scanning the investigated sample with a few μm step size through the probing microvolume depth-sensitive XRF

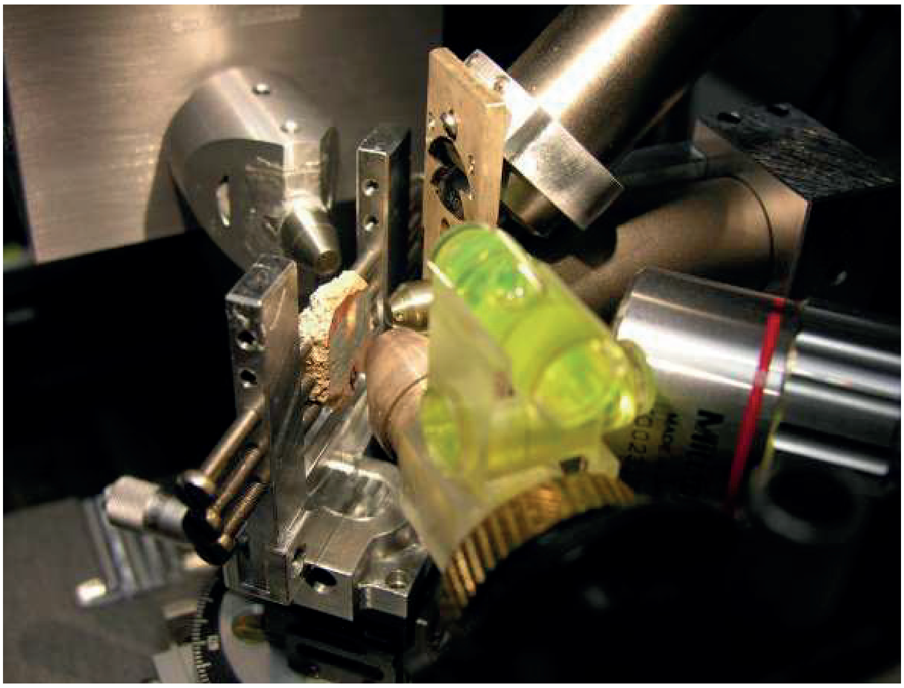

Fig.1. A Roman painted plaster (kor43b) placed in the 3-axis motorized sample stage for 3D Micro-XRF measurements.

measurements can be obtained. Obviously, the technique, due to its non-invasive character of application, found immediate and wide applicability in the field of cultural heritage; the archaeological materials are considered in general quite heterogeneous, presenting a complicated surface structure that can be extended even more than hundred micrometers below the surface.

The wall paintings fragments studied in the present work originate from the Roman Corinth (Greece) and are dated to the early Imperial period through late antiquity. The wall paintings were decorating private and public buildings, one area east of the theater and two domestic buildings, located southeast of the Roman forum. The original motifs included figural representations, floral and geometric ornaments and architectural motifs[6]. Previous analyses[7] of wall painting micro-samples by means of OM, SEM-EDX and XRD techniques revealed a limited pigment palette, composed of Egyptian blue, naturally occurring iron-based ochres (limonite, goethite, hematite), cinnabar, celadonite and lead white. SEM-EDX analyses on cross-sections identified the presence of minor elements (like As, Pb) dispersed in yellow or red pigments and Cr rich mineral grains within the ochre or in Green Earth rich painted layers. In-situ XRF results were rather confusing regarding the role of Pb and As. 3D Micro XRF analysis was applied in a non-invasive manner aiming at: 1) reconstructing the arrangement of the various painted layers and 2) revealing and confirming, with spatial resolution of few tens of µm, 3D spatial correlations between major and minor/trace elements in the individual pigments.

Experimental

For the laboratory 3D Micro XRF measurements the modular experimental set-up of the Nuclear Spectrometry and Applications Laboratory (NSAL) at IAEA Laboratories, Seibersdorf was utilized[2]. The set-up is composed by the following main components: high power (3 kW), line focus, Mo-anode, diffraction X ray tube (operated at 45kV/40mA); three silicon drift X ray detectors (SDD), each serving a different purpose, namely: (1) detection of X ray fluorescence (XRF) radiation in a 'standard' geometry, (2) detection of XRF radiation in a confocal geometry, (3) detection of the transmitted beam; X ray polycapillary lens focusing the primary beam emerging from the X ray tube; polycapillary conical collimator positioned in the confocal channel; computer controlled, motorized stages for sample 3D translation and rotation and for the confocal lens alignment in 3-spatial dimensions; a laser triangulation position sensor; optical microscope coupled to a CMOS camera providing a real time image of the analyzed region of the sample. Fig. 1 shows a close up of the sample holder and optics arrangement during the measurement of a Roman painted plaster.

The scanning and the data acquisition were controlled by the SPECTOR/LOCATOR software[8] developed by the IAEA. Spector also supported the extraction of the net characteristic X ray peak areas, whereas AVIZO 6.04 visualization software was used for volumetric reconstruction of the collected data. The depth resolution was 23 µm at Cu-Kα with a filtered exciting beam (50 µm Ni + 12.5 µm Mo composite filter).

XRF screening measurements

In-situ XRF analyses carried out by means of a portable XRF spectrometer, but also laboratory based micro XRF measurements, were rather confusing regarding the position of certain elements appearing in elevated amounts. For example in the XRF analysis of painted plaster Cor43b (Fig. 2a, blue on red on white ground), the XRF spectrum (Fig. 2b) shows strong presence of the Pb and As characteristicc x ray intensities. The measurement of the surface cannot provide any clue if these two elements are correlated with the red or blue paint layer or another association exists with another paint layer (for example a lead white preparation layer).

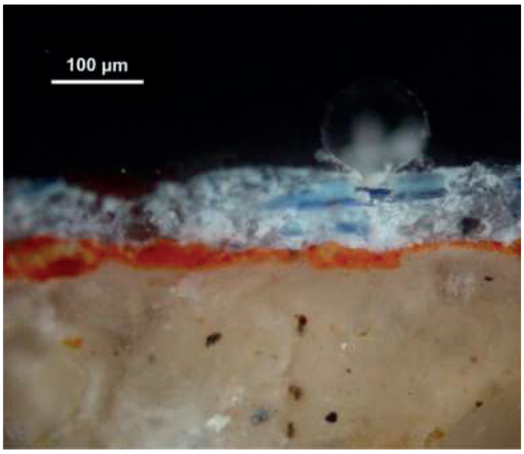

Fig. 2a. Optical image of the painted plaster Cor43b (blue on red on white ground)

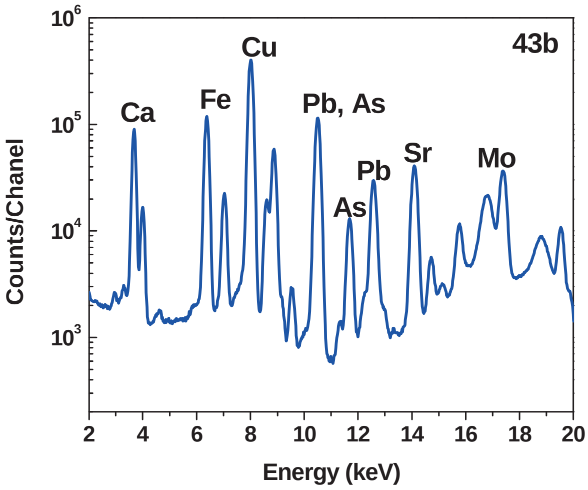

Fig. 2b. Micro-XRF (total) spectrum from the analysis on extended scanned area of the sample Cor43b indicating significant presence of Pb and As.

Therefore, due to the difficulties in properly interpreting the preliminary surface XRF results, 3D Micro XRF analysis was applied in a non-invasive manner aiming at: 1) reconstructing the arrangement of the various painted layers and 2) revealing and confirming, with spatial resolution of few tens of micrometers, 3D spatial correlations between major and minor/trace elements in the individual pigments.

Results of 3D Micro XRF measurements

3D Micro XRF measurements were performed for five painted plaster fragments. Single or composite painted layers with various combinations of blue, green, red and white pigments were examined. Two examples that will be presented here highlight the potential of confocal micro-XRF analysis to reveal hidden associations within the matrix of the examined sample.

At first, a detailed examination was undertaken for sample Cor 43b (Fig. 2a). The 3D reconstruction of the morphology of the painted plaster (Fig. 3) provides clear evidence for an association of both Pb and As elements with the Fe-ochre rich layer. Additional fine tuned 3D Micro-XRF scans were selected in order to reconstruct in more detail the local element specific morphology. The results of such a detailed reconstruction in the case of an Fe rich region (Fig. 4) confirm not only the association of Pb and As with the red paint layer as minor elements within the iron rich compound, but also the co-existence of Pb and As (most likely included in the same compound or mineral).

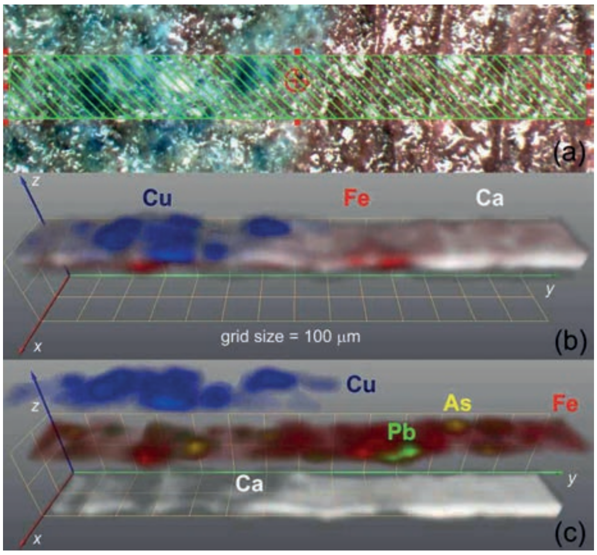

Fig. 3. (a) Optical image of Cor 43b with scanned region dimensions: 120 µm x 1440 µm x 293 µm, xyz scanning spacing: 40 µm x 40 µm x 3 µm; (b) Volumetric reconstruction of 3D spatial distribution of Cu-Kα (Egyptian blue), Fe-Kα (red ochre), Ca-Kα (Egyptian blue, ground, Pb-Lβ and As-Kβ characteristic peak intensities; (c) Translation in z-axis of the elemental distribution patterns.

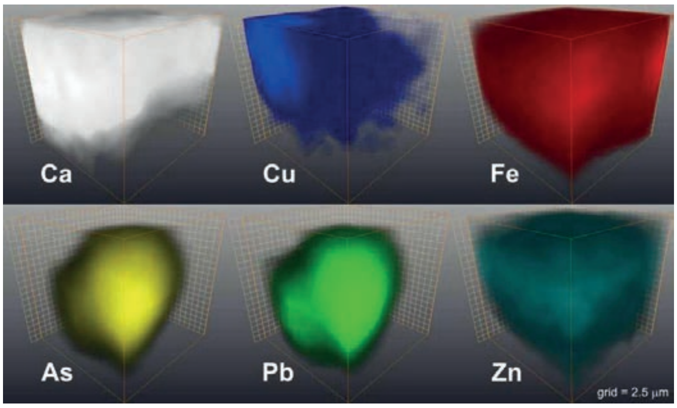

Fig. 4. Fine-tuned 3D Micro-XRF scans of selected regions of sample Cor43b. The volumetric reconstruction refers to a blue on red rich micro-volume, respectively. Scanned region dimensions: 56 µm/ 55 µm/55 µm, scanning spacing 5.6 µm/5.5 µm/5 µm. (Maximum counts: Fe-Kα=1950, Pb-Lα=1200, As-Kα=3030).

Another example refers to the 3D Micro-XRF examination of a goethite ($FeO(OH)$) top layer on white ground (Fig. 5, sample Cor13). Previous SEM examination in the backscattering mode has revealed the presence of large grains, whereas EDX analysis further confirmed the presence of chromite ($(Mg,Fe^{2+})(Cr,Al)_2O_4$) grains together with other more abundant mineral phases such as goethite, biotite, calcite with Pb, dolomite, gypsum, calcitic matrix with dispersed Pb and Egyptian blue.

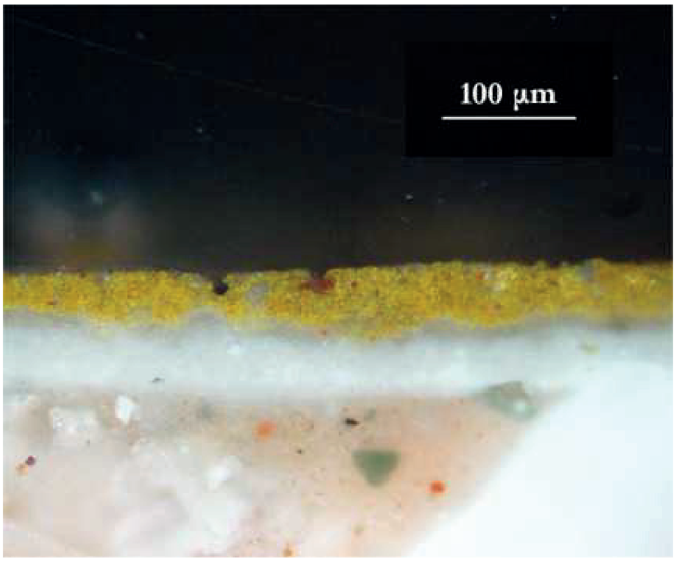

Fig. 5. Optical image of the sample Cor13, yellow ochre on white ground (Kor 13).

The 3D Micro-XRF analysis (scanned region dimensions: 0 µm/1500 µm/243 µm, scanning spacing 0 µm/25 µm/ 3 µm) revealed a strong evidence for the co-existence of Cr in the Fe-ochre rich layer. It is noted that all acquired spectra were analyzed by means of AXIL software in order to account properly for the spectral interference of Fe-Kβ escape peak (5.32 keV) with Cr-Kα (5.41 keV). The measured relative intensity ratio of Cr and Fe characteristic x-rays, was found at the level of 10^{-3} thus highlighting the sensitivity of the technique to identify with

3D spatial resolution associations even amongst major and trace elements within the sample matrix. The presence of chromite clearly marked the formation of the Fe-oxides/ hydroxides from the ultra-basic parent rocks.

Conclusions

The laboratory 3D Micro XRF non-invasive analysis of Roman period painted plaster fragments offered 3D reconstruction and imaging of the various pigments and painted layers. The 3D analysis confirmed the existence of important elemental correlations with micrometre resolution.

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Contributors - Acknowledgements

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Detailed Assessment of Uncertainty of PIXE Results in the Analysis of Environmental Samples

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Particle-induced X ray emission (PIXE) is a technique that has been widely used for determination of the elemental composition of samples of diverse nature and origin. The advantages of multi-elemental capability and high sensitivity allowing determination of the elemental composition in the range of fractions of micrograms per square centimeter in thin samples or in the range of micrograms per gram in bulk samples make the technique very suitable to support the environmental studies.

In monitoring atmospheric pollution no special sample preparation is needed for the analysis of airborne particulate matter collected on filters. To analyze soil sediments or plants, pellets are pressed from grinded dry material to form a homogeneous sample with a flat surface facing the irradiation beam.

Obtaining reliable analytical results in terms of trueness, precision and well assessed uncertainty becomes more important nowadays, in particular in the environmental pollution related studies. The results are compared with threshold, target or reference concentration values to check compliance with guidelines and/or standards set by state or international bodies or legislation (EC Directive, etc). Several actions have been taken since the establishment of PIXE laboratories to improve the quality of the analytical results. An overview of various possibilities of quality systems, describing their main features and impact on laboratory operation was provided in reference [1] where the author admitted that "...whereas rather formalized approaches to quality management were developed during the nineties, their use in PIXE laboratories is extremely rare...".

The ISO standard (ISO/IEC 17025:2005) addresses a series of recommendations for method validation, among which a correct assessment of the uncertainty of the obtained results constitutes an unavoidable step. Advice on uncertainty budget for ion beam analysis has been formulated since 2000 but, according to our knowledge, there are no texts presenting a detailed assessment of uncertainty sources and uncertainty estimation for the analysis of the various elements measured by PIXE in environmental samples.

The IAEA has a collaborative agreement with the Laboratory of Ion Beam Interactions at the Institute Ruder Boskovic (LIBI-IRB), Zagreb, Croatia. As a result of this collaboration a beam line has been established and applied for PIXE analysis and Rutherford backscatter spectrometry (RBS), with particular emphasis on samples of environmental origin [2, 3]. The agreement also includes a possibility to facilitate access to the ion beam accelerator facility for the IAEA Member States that do not have such facilities at the national level. Recent work was carried out to assess the uncertainty budget in the PIXE analysis of environmental samples, as well as to provide recommendations for calculating the uncertainty of the results. For this purpose, specific PIXE experiments were designed and conducted at LIBI-IRB and an integrated mathematical approach was developed for detailed estimation of uncertainty budget by PIXE users. The results have been submitted to the X ray Spectrometry for publication.

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ICT Modules for Training in Nuclear Spectrometry

The IAEA Nuclear Spectrometry and Applications Laboratory (NSAL) has hosted a substantial number of fellows, under national and regional IAEA Technical Cooperation projects, for training in different EDXRF techniques. The demand for such training as well as for the development and/or adaptation of analytical procedures based on EDXRF spectrometry is still observed. In this context Information and Communication Technology (ICT) can be a useful tool to better respond to the relevant needs by creating new learning opportunities. The ICT based training modules can also serve as self-learning materials to transfer knowledge to the fellows willing to receive introductory training prior to a more advanced practical training programme. Extensive use of animations and visual tools makes the process of learning very motivating and exciting. The NSAL, in cooperation with external consultants, has recently developed two ICT based materials.

The first module provides an overall introduction to total reflection XRF (TXRF) analysis, including detailed discussion on instrumentation, quantification, sample preparation and selected applications. Several animations are used to facilitate comprehension of fundamentals of the technique and experimental arrangements, including the alignment of x ray optics.

The second module provides materials and recommendations for QM and quality control in EDXRF and is addressed to technical specialists and laboratory managers. The module presents two different levels: (i) **basic** - for laboratories on early stage of organization, and (ii) **advanced** on Implementation of QMS compliant with ISO/IEC 17025, for laboratories which offer services to the open market and require official accreditation to certify the quality of the services and to demonstrate technical competence. The training materials are presented using numerous graphic/animation tools, to facilitate the understanding of the concepts and to illustrate their practical applications in the field of the EDXRF analysis. Several utilities for quality control and a comprehensive set of examples of QM documentation are included.

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Coordinated Research Project (No. 1752)
‘Improvement of portable instruments and analytical techniques for in-situ applications’
(2011– 2014)

1. Background

Considerable progress has been observed in recent years in the design of portable instruments for in situ applications. The recent developments in the semiconductor detector industry have produced low weight Dewar detectors for gamma spectroscopy, as well as different types of advanced new generation thermoelectrically cooled detectors for both gamma and x ray spectroscopy. Low power and compact X ray tubes offer optimum excitation geometry conditions for x ray fluorescence analysis, and miniaturized X ray optics with improved performance have made possible the microanalysis with spatial resolution in the order of several tens of microns. The developments in FPGA design have led to the production of digital pulse based spectrometers for spectrum acquisition, which benefit from very compact dimensions and increased input count rate capability without decreasing the spectral energy resolution.

The efficiency of the analytical work for studies requiring extensive sampling has improved considerably by incorporating the in-situ analysis as one of the initial stages in the work. In-situ analysis improves management decisions by providing quasi real time, densely spaced, and repeatable characterization data. In situ measurements, although having comparatively less accuracy than laboratory analysis, are less expensive and allow achieving an effective screening in the study. In the cases when taking portions of the samples for laboratory analysis is unfeasible in situ techniques are the only alternative.

The following nuclear spectrometry (and related) techniques can be used for in situ analysis: (i) X ray fluorescence (XRF), (ii) total reflection X ray fluorescence (TXRF) (iii) neutron activation analysis (NAA), (iv) X ray diffraction and (v) micro-Raman spectroscopy, among others.

The range of applications of in situ analysis is very wide and covers, among others, the following fields:

- Geological exploration in the search of resources for both radioactive and non-radioactive minerals.
- Screening of different valuable or toxic elements in industrial or domestic wastes
- Assessment of environmental pollution and radio-ecological hazards in waste disposal sites related to past mining and milling facilities for remediation purposes
- Characterization of environmental baseline values as part of environment risk assessment studies.
- Monitoring of industrial discharges to the environment, including mining, milling and mineral processing plants
- Applications in archaeology, art and conservation science, by providing non-invasive characterization of monuments and artworks, museum objects, characterization of corrosion and alteration products of artefacts in support of their conservation, restoration and future preservation.
- Forensic applications
- In controlling the quality of food products and for screening soils and fertilizers in agriculture.

Taking into account the importance of the in situ analytical techniques based on nuclear spectrometry in different fields, the IAEA organised several activities in the past. A Coordinated Research Project was conducted on site characterization techniques used in environmental restoration activities (T23013, 1995 - 2001) and another CRP was conducted on in-situ applications of x ray fluorescence analysis (CRP F11009, 2000-2003). Two technical meetings were held in Vienna on current status, developments and trends in nuclear spectrometry methods for in-situ characterisation of materials (19-23 May, 2008) and on use of in-situ methods for contaminated site characterization (05-09 July, 2010). The participants of these meetings reviewed the current and future role of the IAEA in promotion and effective use of in-situ techniques based on nuclear spectrometry and one of the recommendations was to foster new Coordinated Research Projects (CRP) on improvement of portable instruments and analytical techniques for in-situ applications in order to coordinate and support the research efforts in this field. In response to this recommendation a new CRP has been proposed under IAEA project 1.4.3.4. Nuclear Spectrometry for Analytical Applications (2010-2011 P&B). It is expected that the CRP will contribute effectively to meet the objectives of the Nuclear Spectrometry project, i.e., *to enhance the capability of interested Member States to effectively utilize nuclear spectrometries for analytical services in environmental pollution monitoring and other applications, including nuclear energy system-related needs*.

2. Overall objectives

The CRP proposed under IAEA project 1.4.3.4. Nuclear spectrometry for analytical applications will help Member States laboratories to enhance their analytical capabilities to effectively utilize in-situ nuclear spectrometry techniques, and to implement improved analytical services in environmental pollution monitoring and nuclear energy systems related applications through new and extensive use of portable instruments and in-situ analytical techniques.

The specific objectives of this CRP are:

- To develop portable instruments featuring more efficient instrumental response, reduction in noise and time signal processing to achieve higher input count rate capabilities and energy resolution, in designs with the lowest possible weight and power demands
- To implement and validate robust analytical procedures including solutions to correct the inaccuracies in the results arising

from differences in sample geometry, matrix and other characteristic features of in-situ analysis

- To contribute to enlarge the spectrum of in-situ applications of nuclear spectrometry methods in support of research and technological development in nuclear science and technology, industry, environmental pollution monitoring, among other fields.

3. Expected research outputs

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

- Improved performance portable nuclear spectrometers.
- Improved analytical methodologies for in-situ measurements.
- Standardized harmonized analytical procedures.
- New applications in support of research, innovation and technological development.
- Publications, including IAEA-TECDOCs and papers in national/international scientific journals.

4. Proposed action plan

The activities under the CRP will include:

- Evaluation and award of research contracts and research agreements 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/agreements.
- Holding a first Research Co-ordination Meeting (RCM) in the second quarter of 2011.
- Conducting research and publishing the results (continuous).
- Submission of the annual reports to the IAEA, evaluation of requests for renewal of research contracts (2012 and 2013).
- Holding a second RCM in the second half of 2012.
- Holding a final RCM in the first half of 2014.
- Preparation and distribution of RCM reports (two months after RCM).
- Publication of an IAEA-TECDOC in the second half of 2014, publications in national/international scientific journals, conference contributions (continuous).

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Meetings and Conferences

XIII Workshop on Nuclear Physics (WONP' 2011) and VII International Symposium on Nuclear and Related Techniques (NURT' 2011), Havana, Cuba, 7-11 February 2011

The participants from Argentina, Belgium, Colombia, Cuba, Italy, Mexico, Montenegro, Venezuela, Pakistan, Portugal, Switzerland and Turkey attended the Workshop and Symposium. Special talks were given by the lecturers from Austria (IAEA), Brazil, Canada, France, Germany, Norway, Russian Federation and Spain. The workshop and symposium were held in the Ambos Mundos hotel in old Havana (see Photo 1). The events attended by the Cuban and international experts created a good forum to discuss the progress and current research results in the fields of high energy physics, radiation physics, medical physics and nuclear analytical techniques. The scope of the workshop and symposium overlapped with the activities of the IAEA. The IAEA participant delivered two lectures. A special talk was on the IAEA activities related to the application of nuclear analytical techniques for environmental monitoring (authors: A. Markowicz, E. Chinea-Cano, A.G. Karydas and R. Padilla-Alvarez). The contribution presented major modalities of the IAEA activities in the field of environmental monitoring including regular program activities, coordinated research projects, Technical Cooperation projects, experimental activities of the IAEA Nuclear Spectrometry and Applications Laboratory (NSAL) and IAEA Collaborating Centers. Emphasis was on the programmes on environment, nuclear instrumentation and spectrometry and TC projects. Moreover, the activities of the NSAL related to training, adaptive research and development and direct services to the laboratories in Member States were described together with selected examples of the results obtained. NATs are often used as the 'methods of choice' for environmental monitoring. In a second talk on QC/QA procedures for analytical techniques (PIXE, XRF) used in the characterization of APM (authors: A. Markowicz, E. Chinea-Cano, A.G. Karydas and R. Padilla

Photo 1. Session of the Symposium

Alvarez) major components of the quality management system developed at the XRF Laboratory at Seibersdorf were presented. Selected methods for evaluation of the interfering effects in XRF analysis of filters loaded with APM such as absorption and enhancement effects as well as particle size effect were described including the accuracy of a calibration procedure for XRF spectrometry and accuracy of the emission-transmission method for XRF analysis. In case of PIXE a method to assess the total uncertainty of the results for environmental samples was presented. Careful and rigorous calculation of the total uncertainty of the results provides information on individual contribution of various sources of uncertainties and helps in selection of an optimum analytical strategy by intentional reduction of the influence of the dominant source. Finally some MS-Excel based tools for calculation of uncertainty and assessment of trueness and precision as well as the available information communication technology (ICT) based materials for teaching/learning in the field of QC/QA for EDXRF were introduced.

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Consultants meeting on applications and trends in the use of nuclear spectrometry techniques for the assessment of the impact of mining and milling sites on human health and the environment

A consultants meeting was held in Vienna, November 23-26, 2010. The meeting allowed gathering and reviewing of information on recent applications and trends in the use of nuclear spectrometry techniques for the assessment of the impact of mining and milling sites on human health and the environment. The participants also discussed topics related to the objectives of environmental investigations and monitoring programmes, as well as to integration of sampling strategies and statistical interpretation of the analytical results.

Comprehensive characterization of environmental impact arising from mining and milling activities requires a proper assessment programme based on an interdisciplinary approach. At different stages of any environmental assessment large amount of data on the nature, concentration and distribution pathways of the investigated contaminants of concern is required.

The meeting concluded that nuclear analytical techniques allow determining the contents and distribution of common inorganic contaminants and radiation hazards resulting from mining and milling operations in the exploitation of both radioactive and non-radioactive mineral resources. The basic principles of detection often ensure a high selectivity, with the additional advantages of detecting more than one analyte in a single measurement, a wide working range and in many cases no need for a complex sample preparation procedure. The recent developments in nuclear instrumentation have made possible the release of portable instruments with sensitivity comparable to that achieved with laboratory instruments, thus allowing the use of in-situ techniques as a cost effective approach to determine the spatial distribution of the contaminants and radiation hazard. A technical report was prepared and is in the process of publication.

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Technical meeting on the infrastructure needed for use of nuclear instruments in the laboratories of developing Member States for environmental sampling

The meeting was held at IAEA Headquarters in Vienna from 09-13 May 2011 with the objective of reviewing the current status, shortcomings and infrastructure needs in developing Member States to achieve more efficient use of nuclear instruments in environmental studies.

Nine participants from Cameroon, Cuba, Ghana, Jamaica, Lebanon, Pakistan and South Africa discussed the following topics:

- Tools and instruments required for sampling of air particulate matter, water, soil, sediments, bio-monitors and other environmental compartments;
- Sampling designs and optimization of sampling campaigns;
- Requirements related to the installation and operation of environmental monitoring stations;
- In-situ and laboratory analysis of environmental samples by nuclear analytic techniques (instrumentation and analytical procedures);
- Devices and software required for the collection of supplementary data (geographic location, meteorological and geophysics information) and its further integration in interpretation and modelling studies;
- The role of the IAEA in support of the improvement of infrastructure in developing Member States for a sustainable use of nuclear instrumentation in environmental studies.

The meeting concluded that there is a need to complement existing infrastructure for environmental monitoring, in terms of both human resources and equipment hardware. There are shortages of nuclear instruments and environmental monitoring stations. Awareness of the need for development of methods for suitable and cost effective environmental sampling campaigns and measurement techniques was emphasized. Collaboration among member states and regions for sharing of knowledge, methods and data related to environmental monitoring shall be promoted, and the national & regional capabilities for environmental monitoring and risk assessment must be enhanced. A report summarizing the conclusions reached from the discussions and addressing recommendations to the IAEA and its Member States is under preparation.

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IAEA consultants meeting on status and trends in nuclear instrumentation for synchrotron radiation research

A consultants meeting on Status and Trends in Nuclear Instrumentation for Synchrotron Radiation Research took place at International Atomic Energy Agency Headquarters, Vienna, Austria, from 10-12 November 2010. The aim of the meeting was to review the current progress of nuclear instrumentation (NI) at synchrotron radiation (SR) and FEL sources, to discuss state of the art developments and identify future needs and research directions.

The experts from Germany, Italy, Thailand and USA attended the meeting and presented the recent research activities in the field of nuclear instrumentation for SR and FEL research, reviewed the current status and the state of the art developments for energy dispersive X ray detectors, imaging detectors (hybrid pixel detectors, CCD, CMOS), integrated imaging and spectroscopy detectors (pn-CCD), high resolution X ray spectrometry, cryogenic and wavelength dispersive X ray detectors, data acquisition systems for SR and FEL sources and the X ray optics in SR.

The participants have identified the future trends and needs in detectors and nuclear instrumentation for SR, such as improvements of the analytical performance (stability, higher energy and/or spatial resolution, higher throughput, larger detection area, etc.), embedded intelligence and introduction of functions (databases) for more integrated approaches and operating modes, the need for software tools and developments to improve interface to the users (calibration, data mining, data analysis) and to increase data compression methods and FPGA based systems.

Finally the meeting participants concluded that SR and FEL sources drive new developments in nuclear instrumentation and techniques.

During the consultants meeting some of the developments have been highlighted emphasizing their role in extending the analytical capabilities of SR radiation and FEL sources in various disciplines. Some of the developments can also be transferred to small or medium scale laboratories upgrading significantly their capabilities and improving the analytical results. Taking into account the significant time (many years) and cost spent for research and development of advanced detector arrays with high-count rate capabilities, high energy resolution, and high spatial resolutions over large areas based on single pixel high quality read-out electronics, the meeting participants recommended that the international efforts, synergies and various funding resources will be required in order to develop complex next generation detectors. Development of a technology roadmap for nuclear instrumentation has been requested, taking into account that the NI for synchrotron radiation is very similar with respect to the one used in the fields of environmental radionuclide monitoring, security safety inspections etc. Further, it was also suggested that the support and enhancement of young scientists training should be considered not only in the utilization of nuclear instrumentation but in particular in the R&D of advanced instrumentation by means of specialized schools (with demonstration experiments and hands on experience), workshops, fellowships, etc..

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X ray fluorescence in Member States

Morocco

Application of TXRF to the Analysis of Particulate Matter Collected in the City of Meknes (Morocco)

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1. Introduction

The atmosphere is a complex environment in which gas species, solid particles and liquid droplets coexist. The air quality is an extremely important field of study due to its impact on the environment and human health. The air quality is estimated in terms of common pollutants such as sulphur dioxide (SO_2), nitrogen oxides (NO_x), tropospheric ozone (O_3) and suspended particulate matters.

In Morocco, air pollution is not sufficiently estimated. The completed studies have a local character. These studies were initiated in the beginning of the 1990s by the Department of Environment in the cities which suffer from atmospheric pollution [1-5].

To complete and expand the Moroccan air quality database, academic research in the field of the control of air quality has been carried out or is in progress in several Moroccan cities [6-13]. In the same context, the present study aims to evaluate and to monitor the air quality in the city of Meknes (city located in the center of Morocco). In our work, we were interested in the study of several types of atmospheric pollutants, mainly gaseous pollutants (sulphur dioxide and ozone), particulate matter (fine and coarse fractions) and heavy metals contents. To achieve these objectives, many sampling campaigns were conducted from 2005 to 2008. For the campaigns carried out from 2005 to 2006, the objective was to select a representative site for the atmospheric pollution in the city of Meknes. From 2007 to 2008 our choice was restricted to one sampling site representative of the road traffic pollution in this city.

In the present study, we will present just the results obtained from the analysis of particulate matter (fine and coarse fractions).

2. Methods and Materials

2.1 Presentation of the study area

The city of Meknes suffers from continental influences during the summer and winter seasons. However, the geographical diversity of the region causes each of its natural zones to present particular climatic nuances. The climate of this region is also characterized by its irregularity. The summer is usually hot and dry, and the winter is mild and rainy [14].

From March to October 2007, the travel agency (Moroccan Transport Company 'CTM'), situated in the FAR Avenue, was chosen as the study site. This site is situated in the center of Meknes city, near a taxi station and not far from rail traffic. The samplers (Gent sampler and Dichotomous [1-17]) were placed at a height of about 5 meters. This site is representative of an urban environment with dense road traffic.

For logistics reasons, since November 2007, we have changed the sampling site to another similar site which is not very far from the first site. This site, also located in the centre of the city, is less narrow than that of FAR Avenue; it is characterized by dense road traffic, especially during the rush hours, the presence of bus and taxi stops and traffic with a one way street.

2.2 Presentation of the used TXRF module

In CNESTEN, we have a TXRF module (Fig. 1) with a 2 kW power fine focus X ray tube with a molybdenum anode mostly operating at 30 mA and 50 kV. The 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. With this technique, we have determined the following elements: Ca, Cl, Cr, Cu, Fe, K, Mn, Ni, Pb, S, Sr, Ti and Zn.

To complete this study, we have used type SpectrAA 220FS (Varian) atomic absorption spectroscopy (AAS), to evaluate the contents of Al.

Fig. 1. TXRF module installed in CNESTEN

3. Results and discussion

3.1 Seasonal variations of particulate matter

Figure 2 shows the averages and the variation intervals of mass concentrations of fine and coarse fractions.

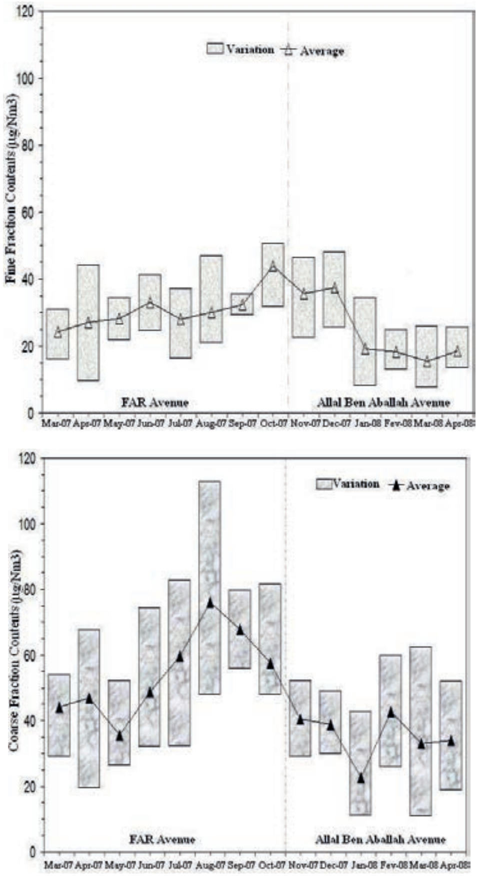

Fig. 2. Averages and variation intervals for contents of fine and coarse fractions.

With the exception of the autumn when the average concentration is about 37.21 µg/Nm^3, the fine fraction concentrations don't show significant seasonal variations (the averages vary from 23.41 µg/Nm^3 in spring to 30.42 µg/Nm^3 in summer). These concentrations are lower compared to those recorded for coarse fractions where the average values vary from 35.12 µg/Nm^3 in winter to 61.47 µg/Nm^3 in summer. So, the average ratio (fine/total) is lower than 0.5. This could be an indication of an important contribution of natural particles or particles previously deposited and aggregated to soil dust.

For monthly variations, it is clear that the variations are more significant in the case of coarse fractions than for fine fractions. The average values increase from May to August 2007 and then decrease until November. For fine fractions, the variations are less important and the average contents are generally more constant.

The comparison with the international recommended values indicates that the annual average (75.38 µg/Nm^3) is considerably above the limit values fixed by the European Directive (40 µg/Nm3/year) [18-20] and the WHO guide value (20 µg/Nm^3/year) [21]. For fine fractions, the limit value (25 µg/Nm^3/year) is slightly exceeded [20].

3.2 Chemical characterization of particulate matter

To better distinguish the distribution of the elemental contents for the fine and coarse fractions, the results in four seasons have been presented in Figure 3.

Globally, the variation between the elemental distribution of fine and coarse fractions is very low. Nevertheless, there are some fluctuations in distributions for some elements between the two fractions. Thus, Ca and Fe are distributed a little more on the coarse fractions. Al, contrary to what we expected, is more concentrated in fine fractions while Cl, Cr, Cu, Pb, S, Sr, Ti and Zn are equally distributed in the two fractions. However, K, Mn and Ni change their distribution from one season to another. So, Ni in winter and in summer show the same distribution in fine and coarse fractions; in spring and autumn they have a slight tendency to dominate in the fine fractions. Mn is more present in coarse fractions, with the exception of spring when it is more distributed in fine fraction. Finally, K in winter and in spring shows quite equal distributions in the two fractions while in summer and autumn, it presents a preferential distribution on coarse fractions.

Table 1 complements the observations by presenting the elementary fraction ratios (fine/total) for the four seasons. In fact, when the elementary ratio (fine/total) is equal to 0.5, we could say that we have an equal distribution on fine and coarse fractions. If this ratio exceeds 0.5 the distribution is more predominant in fine fractions (it's the case of terrigenous or natural particles). However, if this ratio is lower than 0.5, coarse fractions are more important (it's the case of anthropogenic sources).

3.3 Mass concentrations of particulate matter

Seasonal variations of mass fractions for fine and coarse particles are shown in Figure 4. The highest mass fractions are recorded for Al, Ca and Fe. The seasonal variations are not very significant; nevertheless a low variation for some elements can be observed. Thus, for coarse fractions the increase observed mainly for Ca in winter could be explained by the decrease of the mass balance of coarse fractions as a consequence of pluvial periods encountered during this season.

The different statistical parameters of mass fractions of fine and coarse particles are listed in Table 2.

The mass fractions of Ca and K are slightly more important in the coarse fraction which might be the result of their terrigenous origin. The mass fractions of Cr, Pb, S, Sr and Zn are slightly higher in the fine fraction. In case of Al the fine and course fractions correspond to 19% in 9%, respectively. For other elements, the mass fractions are equal for both fractions.

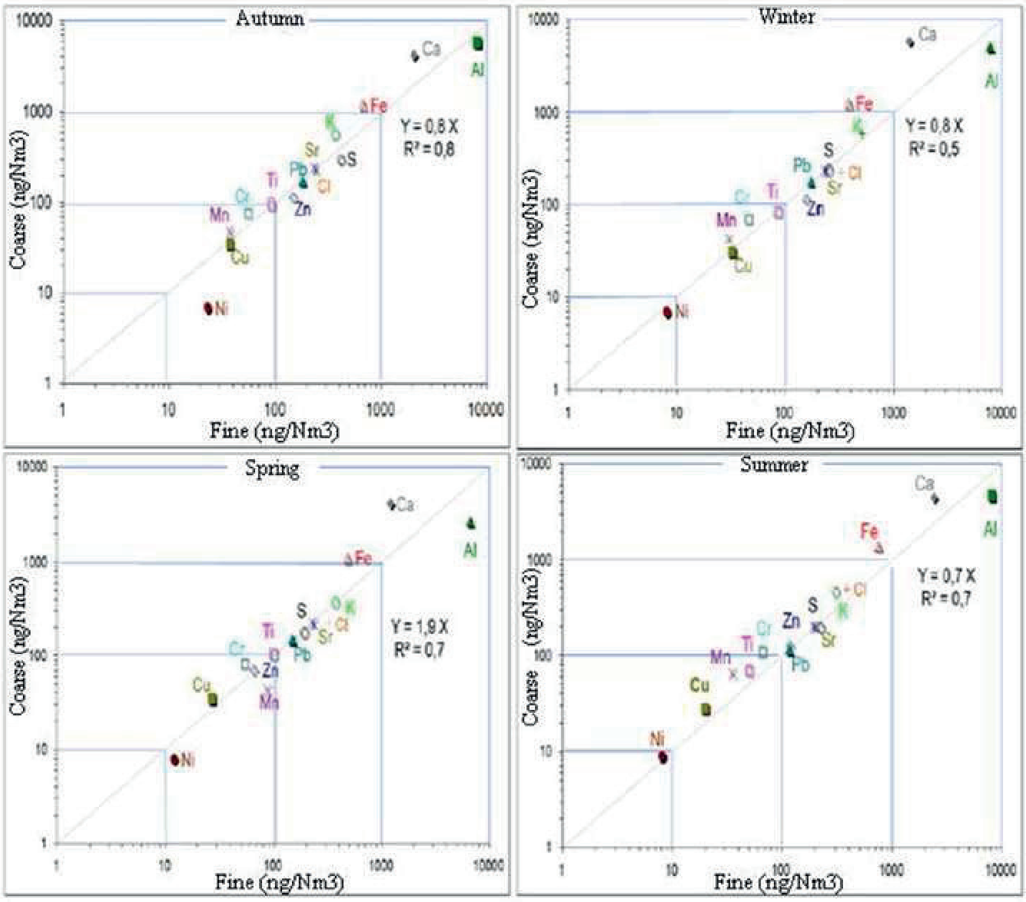

Fig. 3. Relations between the elemental concentrations of fine and coarse fractions.

Period	**Al**	**Ca**	**Cl**	**Cr**	**Cu**	**Fe**	**K**	**Mn**	**Ni**	**Pb**	**S**	**Sr**	**Ti**	**Zn**
Autumn	0.58	0.34	0.56	0.47	0.51	0.37	0.41	0.45	0.53	0.51	0.56	0.48	0.39	0.55
Winter	0.61	0.22	0.55	0.50	0.51	0.25	0.44	0.41	0.60	0.49	0.52	0.50	0.42	0.55
Spring	0.70	0.23	0.45	0.51	.48	0.32	0.40	0.47	0.54	0.50	0.54	0.50	0.42	0.48
Summer	0.66	0.35	0.46	0.42	0.43	0.35	0.39	0.35	0.50	0.50	0.53	0.49	0.39	0.48

Table 1. Elementary fraction ratios (fine/total).

All the analyzed components represent about 19% and 23% of the masses for the fine and coarse fractions. So, the analyzed elements are less abundant compared to those which are not analyzed (such as secondary aerosols and organic matter).

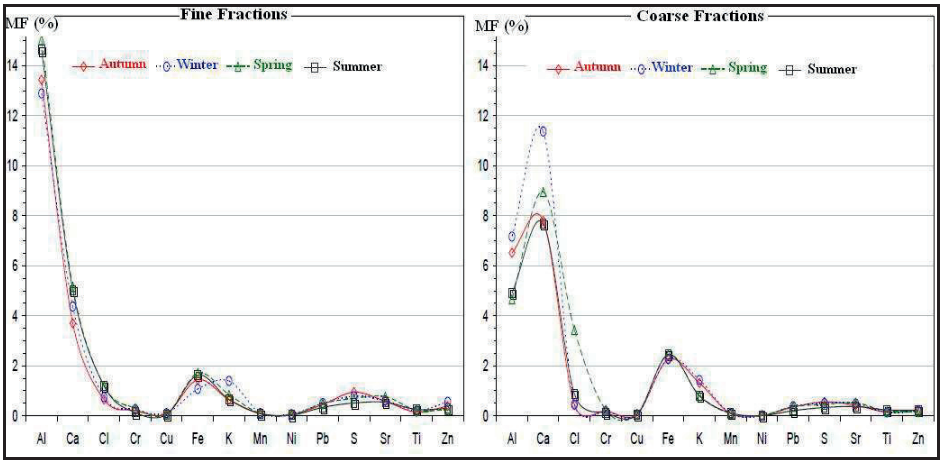

Fig. 4. Profiles of the seasonal variations of mass fractions for fine and coarse particles.

MF(%)		Al	Ca	Cl	Cr	Cu	Fe	K	Mn	Ni	Pb	S	Sr	Ti	Zn
Fine	Min	10.37	1.19	0.27	0.06	0.56	0.03	0.34	0.03	0.01	0.24	0.20	0.43	0.05	0.12
	Max	22.82	9.56	4.61	0.42	8.54	0.78	3.30	0.55	0.15	2.36	4.33	3.65	0.72	1.30
	Ave	19.26	4.48	1.40	0.35	2.18	0.13	0.23	0.14	0.05	0.64	1.02	0.95	0.21	0.43
	S.D.	2.83	1.79	1.13	0.26	1.71	0.13	0.89	0.11	0.04	0.39	0.87	0.62	0.14	0.26
	C.V.	15	40	81	72	78	101	72	74	87	61	85	65	67	60
MF(%)		Al	Ca	Cl	Cr	Cu	Fe	K	Mn	Ni	Pb	S	Sr	Ti	Zn
Coarse	Min	0.98	1.35	0.10	0.05	0.27	0.02	0.11	0.02	0.01	0.13	0.08	0.20	0.04	0.07
	Max	20.80	18.26	7.71	1.10	8.90	0.33	7.46	0.53	0.09	1.43	1.64	2.12	1.51	0.72
	Ave	8.81	8.98	1.02	0.25	2.86	0.08	1.21	0.13	0.02	0.41	0.52	0.59	0.21	0.24
	S.D.	4.30	4.05	1.34	0.19	1.68	0.06	1.09	0.09	0.02	0.25	0.32	0.38	0.21	0.13
	C.V.	49	45	132	76	59	78	90	68	85	63	62	65	100	52

Mi: Minimum; Max: Maximum; Ave: Average; S.D.: Standard Deviation; C.V.: Coefficient of Variation

Table 2. Averages and intervals of variations of mass fractions of fine and coarse particles.

4. Conclusion

For particulate matter, coarse fraction concentrations are more important than those of fine fractions. The latter do not show significant variations along the sampling days. For coarse fractions, the seasonal variations are well marked by a decrease in winter and an increase in summer indicating the importance of terrigenous contributions and the resuspension of the soil particles. An excess of the WHO guideline values was also noted.

For elemental compositions, the majority of the analyzed elements show the same distributions for fine and coarse fractions and generally do not show significant variations between the four seasons. The studied chemical elements represent only 19 to 23% of the total mass of particles for fine and coarse fractions, respectively.

A second part of this study is related to evaluation and identification of the principal sources of emission in the city of Meknes. To reach this objective, different statistical tools were used, mainly principal component analysis (PCA), hierarchical classification (CHA) and receptor model, especially positive matrix factorization (PMF). The results of this study will be presented in a future publication.

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Italy

Portable XRF Systems for the Analysis of Outdoor Bronze Equestrian Statues

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The analysis of historical bronzes and particularly outdoor historical bronzes provides a useful solution for difficult analytical problems. The historical bronzes are structurally very complex systems, usually very large and divided into many smaller parts that were casted separately and at the end jointed together. The composition of the different pieces is not always the same and the alloy of the joining metal is different. Moreover, the position of the statue with regard to the wind direction and pollution fluxes is also important. All these heterogeneity effects make both the characterization and conservation of an outdoor bronze statue a very complex issue. A very simple indicator of this situation is the variety of colours that the surface of the metal acquires during a few years of weathering. The classical way of gathering information regarding the alloy and patina composition is through micro sampling. Surely micro sampling with micro stratigraphy connected with analytical techniques such as SEM/EDS and micro-FTIR is the best way to acquire complete information on the samples. However, sampling a bronze object is not an easy task and should be limited to a few points or even avoided. Field portable X ray fluorescence techniques (FP-XRF) either in the high energy mode (6 to 32 keV) or in the low energy mode (2 to 6 keV), can be used in a fully non-destructive way, simply by irradiating the object for which we are looking for information and interpreting the spectra from the structural and conservative point of view. Moreover, combining XRF with faster techniques such as, for example, IACS (international annealed copper standard) method that gives a result proportional to the amount of copper in the alloy it is possible to map the entire statue in a quick and inexpensive way and decide where to perform micro-sampling.

The following bronze statues were examined by this procedure:

- The Colleoni equestrian statue by Andrea del Verrocchio (1437-1488) in Venice;
- The Garibaldi equestrian statue by Emilio Gallori (1895) in Rome;
- The Vittorio Emanuele II equestrian statue by Alfonso Balzico (1897) in Naples;
- The Amedeo di Savoia equestrian statue by Davide Calandra (1902) in Turin.

A series of non invasive measurements were carried out on the statues. In order to map the composition of the alloy and evaluate the deterioration processes of the bronze surface, portable EDXRF and IACS were used. Several XRF instruments are usually used, the lightest in weight is the Amptek system. The characteristics of the Amptek XRF system are as follows:

X ray tube: mini X (Amptek Inc USA) with anode of W, max high voltage 40 kV and max current 100 microA with an aluminium filter of 3 mm with high energy mode and no filter with low energy mode.

Detector: SDD (Amptek Inc USA), with an area of 7 square millimetres, 300 micrometre thickness and 150 eV FWHM, 1 mm collimation with high energy mode and 2 mm collimation with low energy mode. The system was handheld and weighs less than 500 grams.

Figure 1 shows the system applied for characterization of the statue of Garibaldi in Rome.

Fig 1. XRF technique applied for characterization of the Garibaldi statue in Rome.

As mentioned before, an equestrian statue is a complex system composed of various parts. To study the composition of all these parts, it is useful to start with an IACS probe that shows the percentage of copper in the alloy (see Fig. 2 showing the statue of Vittorio Emanuele II in Naples).

With a full mapping by IACS method and statistical data analysis it is possible to divide the subparts of the statue into clusters. With the XRF technique it is sufficient to analyse only one element of every cluster and in this way gather most of the compositional information on the different alloys used in the foundry. On the graph in Fig. 3 one can see the clustering of 31 different pieces of alloy for an equestrian statue.

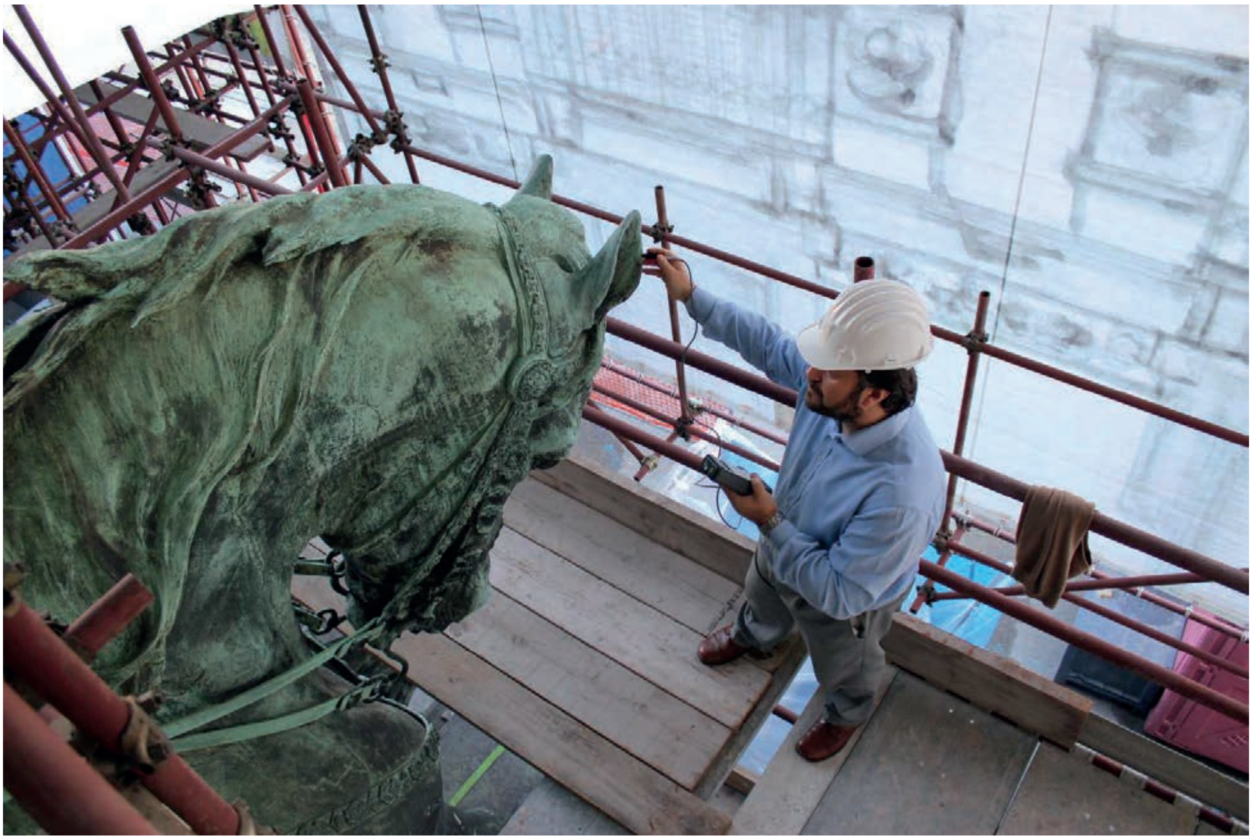

Fig. 2. International annealed copper standard (IACS) technique applied for characterization of the Vittorio Emanuele II statue in Naples.

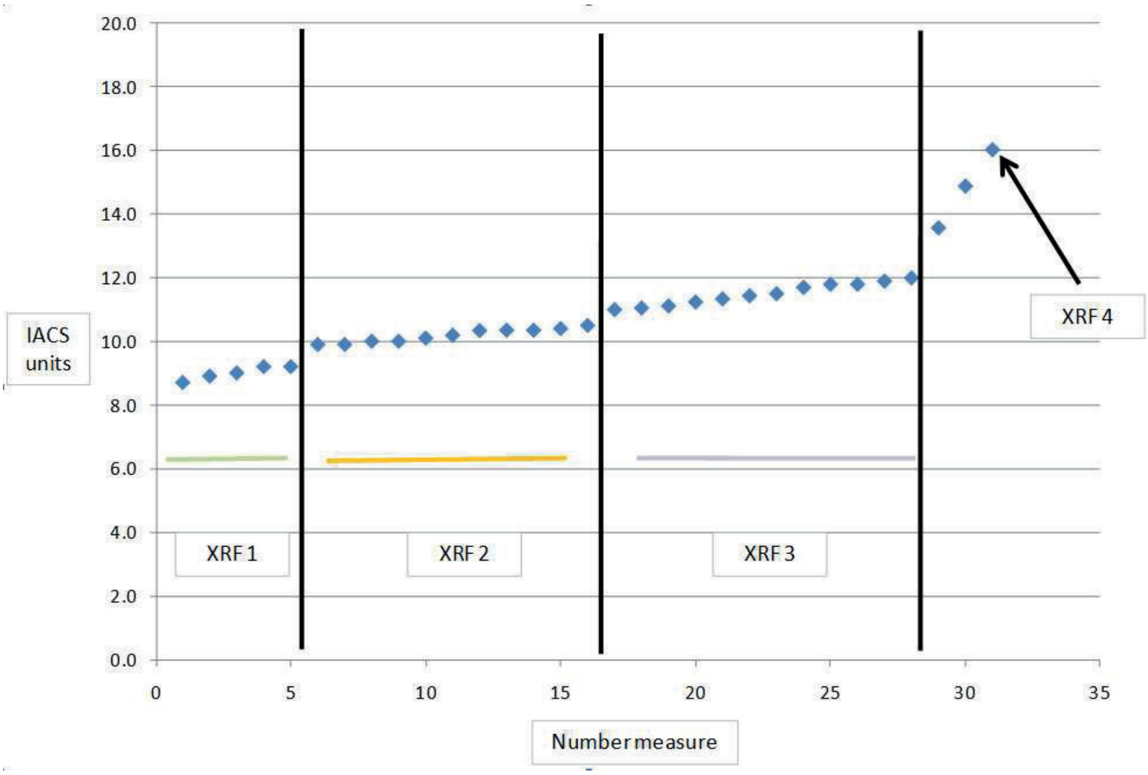

Fig.3. Clustering of 31 IACS results obtained for subparts of an equestrian statue.

The IACS results are shown in increasing order and based on some statistical analysis it is possible to find three main clusters and some outsiders. The XRF results for five alloys are shown in the table below.

	Cu (%)	Zn (%)	Pb (%)	Sn (%)	Ag (%)
XRF 1	85.9	2.0	5.0	7.0	0.1
XRF 2	87.5	2.1	3.2	7.1	0.1
XRF 3	89.7	2.1	2.1	6.0	0.1
XRF 4	99.9	-	-	-	0.1

Table 1. XRF results for alloys

Concerning the use of portable XRF at low energy for the analysis of superficial corrosion to identify the degradation processes (see Figs. 4 and 5) it should be mentioned that the bibliography on the subject is very small. It is mostly because XRF is able to perform only elemental analysis, and therefore it is necessary to integrate other kinds of information to the XRF results such as video microscopic information and colour information.

Fig.4. XRF measurements on the Duca d'Aosta statue in Turin.

Fig.5. XRF measurements on the horse of the Colleoni statue in Venice.

Surely the possibility of mapping the presence of low Z elements (sulphur, chlorine, potassium, calcium, iron and others) and defining their relationship to the corrosion processes is very important and helps to decide where to take micro samples for the destructive analysis. Figures 6 and 7 show XRF spectra for a green and blue patina, respectively. The difference in composition is evident.

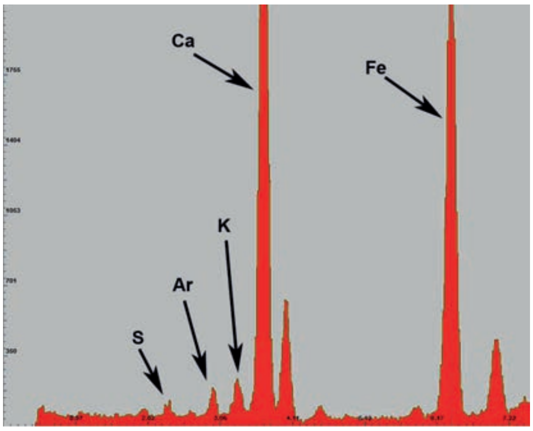

Fig.6. XRF spectrum at low energy for a green patina.

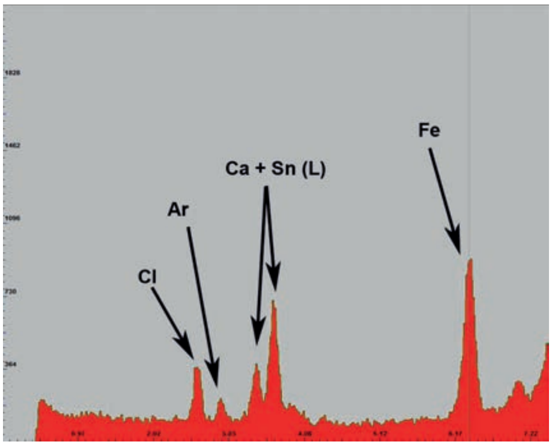

Fig.7. XRF spectrum at low energy for a blue patina.

Spain

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

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Analytical Approaches of TXRF Spectrometry for Trace and Speciation Analysis of Environmental and Industrial Samples

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In 2009, in collaboration with the Department of Chemistry of the University of Girona, we acquired a compact total reflection X ray fluorescence (TXRF) system. One of the major advantages of this spectrometer is that is equipped with an air cooled low power X ray tube (50W) and a Peltier cooled silicon drift detector and thus, no cooling media and gas consumption are required. These facts make this system very attractive for implementation in the industrial field and research laboratories. In this instrument, the use of a W X ray tube allows performing TXRF analysis using K lines of high atomic number elements such as Sn and Cd and thus, both selectivity and limits of detection are improved. Since its acquisition, several research projects have been conducted in order to test the analytical capabilities of this system for trace element analysis of environmental and industrial samples. Comparison with other large-scale instruments with high power X ray tubes has also been performed in collaboration with the Atominstitut of the Technical University of Vienna, Austria (Christina Streli and Peter Wobrauschek).

In our first work, and taking into account the significance of monitoring elemental composition of industrial inlet and outlet effluents, we evaluated the possibilities and drawbacks of the above mentioned benchtop TXRF system for the rapid and simple determination of some inorganic impurities (As, Ba, Cd, Cu, Cr, Sn, Fe, Mn, Ni, Pb, Se and Zn) in inlet and outlet industrial waste water effluents from metallurgical and tanning leather factories. An evaluation of the direct analysis of the raw samples and different simple sample treatments (dilution with water or using a commercial non-ionic detergent and acid digestion) was performed. It was found that for routine and screening analysis of industrial inlet and outlet effluents, TXRF analysis of waste water samples can be directly performed depositing 20 µL of the internally standardized sample on a quartz glass reflector and using a measuring time of 1000 s. A further enhancement of analytical quality of TXRF results can be achieved using more sophisticated sample treatments such as microwave acid digestion [1]. Analytical figures of merit such as accuracy, precision and limits of detection were also carefully studied by analyzing the certified reference material SPS-WW2 (Reference Material for Measurement of Elements in Wastewaters, Spectrapure Standard, Manglerud, Oslo, Norway). In Figure 1 typical TXRF spectra of waste water samples before (inlet effluent) and after the treatment procedure in the industrial treatment plants (outlet effluent) are shown.

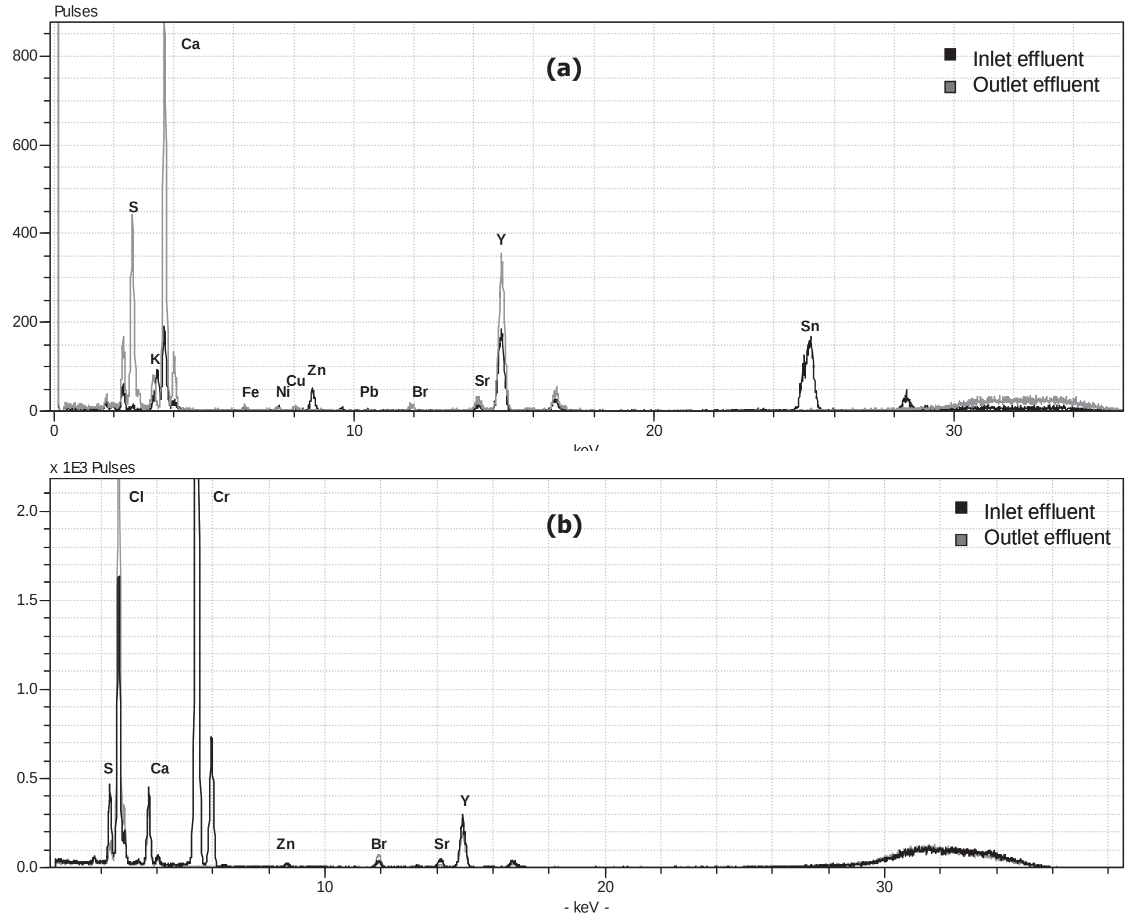

Figure 1. Typical TXRF spectrum of a waste water sample before (inlet effluent) and after the treatment procedure in the industrial treatment plant (outlet effluent): (a) Metallurgical waste water effluent, (b) Tanning waste water effluent [1].

It is interesting to note that through the information obtained with the TXRF analysis we can study the fate of heavy metals throughout the treatment process in the industrial treatment plants. The overall results revealed that a remarkable decrease was achieved in the reduction level of metals in the final wastewater (outlet effluent). The elimination fraction of these metals was higher than 99.8% in some waters (i.e, from ~400 mg L^{-1} Zn to ~0.6 mg L^{-1} Zn). Metal content in all the treated wastewater samples (outlet effluents) was below the regulatory limits for waters to be discharged to a sewage system.

Among the heavy metals, there is considerable interest in Hg monitoring in waste water samples due to its widespread occurrence and the high toxicity of most of its compounds. Hg determination in water samples by means of total reflection X ray fluorescence spectrometry entails some difficulties due to the high vapour pressure and low boiling point of this element that produce evaporation and loss of Hg from the surface of the reflector during the drying process, commonly used for sample preparation in TXRF analysis.

The main goal of a second research project was to develop fast and simple chemical strategies to avoid Hg volatilization during the analysis of waste water samples by TXRF spectrometry. Three different analytical procedures were tested for this purpose: (i) increasing the viscosity of the waste water sample by adding a nonionic surfractant (Triton X-114), (ii) Hg immobilization on the quartz reflectors using the extractant tri-isobutylphosphine (Cyanex 471X) and (iii) formation of a stable and non-volatile Hg complex into the waste water sample. It was found that the best analytical strategy is formation of a Hg complex with thiourea (pH=10) before the deposition of 10 µL of sample on the reflector for the subsequent TXRF analysis. Analytical figures of merit such as linearity (10-1000 µg/L), limits of detection (0.7 µg/L), accuracy and precision were carefully evaluated. Finally, the developed methodology was applied to the determination of Hg in different types of waste water samples (industrial effluents, municipal effluents from conventional systems and municipal effluents from constructed wetlands) [2].

Despite the advances in the development of highly efficient analytical instrumentation for the end point determination of analytes in environmental samples, sample pre-treatment is usually necessary in order to extract, to isolate and to concentrate analytes of interest from complex matrices. In this context it is worth mentioning the recent development of faster, simpler, inexpensive and more environmentally friendly analytical preconcentration procedures within the framework of the so-called green analytical chemistry such as liquid-phase microextraction (LPME). LPME is a solvent minimized sample pretreatment procedure of the conventional liquid-liquid extraction (LLE), in which only several µL of solvent are required to concentrate analytes from the sample rather than hundreds of mL needed in conventional LLE. This procedure has been mostly applied to the analysis of organics and, recently, for the determination of trace metals in water or biological samples using electrothermal atomic absorption spectrometry (ETAAS). However, taking into account the micro-analytical capability of TXRF spectrometry, the combination with LPME procedures is an interesting approach to improve the analytical performance of trace and speciation metal analysis by using this technique. At present, one of our research topics of interest is focused on this method [3].

For instance, we demonstrated the applicability of a LPME procedure using ammonium pyrrolidinedithiocarbamate (APDC) as chelating agent, carbon tetrachloride as extraction solvent and ethanol as dispersant solvent as sample preparation strategy for trace Se determination in soil digests. The effects of various experimental parameters such as sample volume, effect of major elements present in the soil matrix (Fe) and Se concentration in the sample were investigated. The LOD using this analytical methodology (0.05 mg/kg of Se) was comparable or lower than those obtained in previous work using other popular spectrometric techniques such as GFAAS, ICP-MS and AFS. The calculated Se concentration for JSAC-0411 ([Se] =1.32±0.27 mg/kg) using the combination of LPME and TXRF ([Se] =1.40±0.23 mg/kg) was in agreement with the certified value [4]. In Figure 2, TXRF spectra obtained for the direct analysis of a soil extract and after the dispersive liquid-liquid microextraction procedure (experimental conditions: 2 mL of sample, 100 mg APDC, 0.5 mL ethanol, 0.1 mL carbon tetrachloride) are shown.

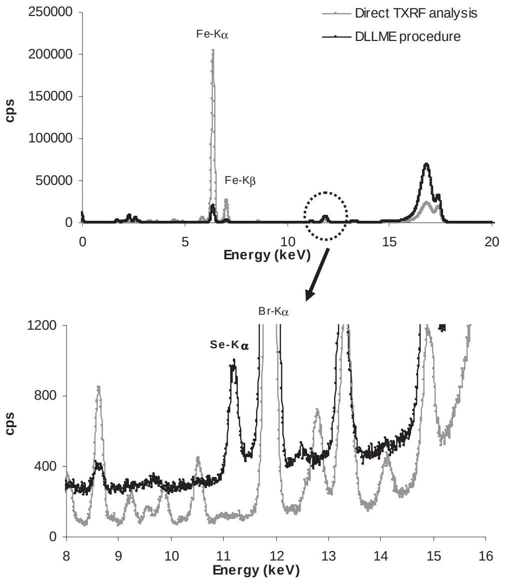

Figure 2. TXRF spectra obtained for the direct analysis of a soil extract and after the dispersive liquid-liquid micro-extraction procedure (experimental conditions: 2 mL of sample, 100 mg APDC, 0.5 mL ethanol, 0.1 mL carbon tetrachloride) [3].

Taking into account that the developed LPME procedure (using APDC) is only effective for selenite (Se (IV)), the concentration of selenate (Se (VI)) could be estimated as the difference between the concentrations of Se obtained for the analysis of the solution with and without a reduction step. This fact is particularly interesting since speciation plays a crucial role in the Se mobility, availability, bioaccumulation and toxicity. Therefore, an additional advantage of the above mentioned preconcentration procedure is the possibility of getting a first indication of the inorganic Se speciation (Se(IV), Se(VI)) in the solution by using TXRF spectrometry [5].

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