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X ray Fluorescence in the IAEA and its Member States

In This Issue

Activities in the IAEA XRF Laboratory

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

Handheld XRF analysis of a 16th century Mexican Feather Headdress

Introduction

The 16th century feather headdress in the Weltmuseum Wien (WMW), an affiliated institution of the Kunsthistorisches Museum (KHM) in Vienna, is the most renowned of the few remaining pre-Columbian "Arte Plumaria" artefacts, which were made by feather artisans (Amantecas) using traditional techniques in the territory of present day Mexico [1]. The recorded history of the headdress begins in 1596, when it is first mentioned in the estate inventory of the art collection of Archduke Ferdinand II of Tyrol at Ambras Castle [2]. Due to its age, the variety of materials used, its history and former restoration treatments, the artefact is today one of the most sensitive and demanding care objects of the museum.

Fig. 1. Feather headdress from ancient Mexico (Photo: Christian Mendez, February 2010, Kunsthistorisches Museum, Wien)

Despite the object's long history, very little documentation on past interventions exists. From 2010-2012, a binational research project between Mexico (Instituto Nacional de Antropología e Historia) and Austria (Weltmuseum Wien) performed a systematic investigation focused on the identification of manufacturing techniques and the various materials, the old restoration measures and its conservation [1, 3].

Handheld x-ray fluorescence (XRF) spectrometers are extremely useful for the study of art works in museum collections [4]. The possibility of bringing the instrument to inspect the objects on-site facilitates the study of artefacts that cannot be moved either due to their extreme fragility or due to their large size and/or weight. In addition, non-destructive analysis constitutes a preferred alternative to invasive sampling techniques, which are usually not allowed in the study of unique or extremely valuable objects. The aim of the XRF analysis was twofold: to investigate the possible presence of inorganic toxic elements that could be associated to the use of pesticides in past conservation interventions and; to characterize the chemical composition of the authentic gold and the gilded brass ornaments, which were added in the 19th century. The results of the XRF analytical study on the Mexican Feather Headdress were published recently in the X-Ray Spectrometry journal (2014) [5].

Experimental

The handheld XRF analyzer utilized during the in-situ measurements uses a miniaturized air-cooled transmission X-ray tube with a thin Ag layer as anode material. The tube can be operated up to 50 kV and 200 µA, providing that a maximum power of 2.5 Watts is not exceeded. The tube current is automatically adjusted for each measurement so that the detector counting rate does not lead to a maximum dead-time fraction. The analyzer is equipped with a Silicon Drift Detector (30 mm^2) with energy resolution better than 178 eV (Mn-Kα). Different excitation conditions can be selected to optimize the elemental sensitivity for low, medium or high atomic number elements by using different settings of the high voltage and by introducing different filters in the excitation beam path. The analyzed area can be considered to have a circular shape with a diameter of about 8 mm.

During the measurement, the feather headdress was lying horizontally on a supporting acrylic glass table, allowing its investigation under minimal risks of damage (see Figure 2, XRF measurements performed by Dr. Padilla-Alvarez Roman).

Fig. 2. Dr. Roman Padilla-Alvarez (IAEA) performing handheld XRF analysis of the feather headdress lying horizontally on a specially constructed acrylic table.

Results

a) Analysis of the feathers for pesticides

In the Museum of Ethnology Vienna the use of pesticides is documented since the 1950s, but its introduction could date much earlier. The feather headdress consists of a combination of different organic and inorganic materials and exhibits substantial damages caused by a former insect infestation (in all probability cloth moths). These facts make a contamination with pesticides most probable. Three characteristic spectra collected in the main condition of the handheld XRF operational mode are shown in Figure 3.

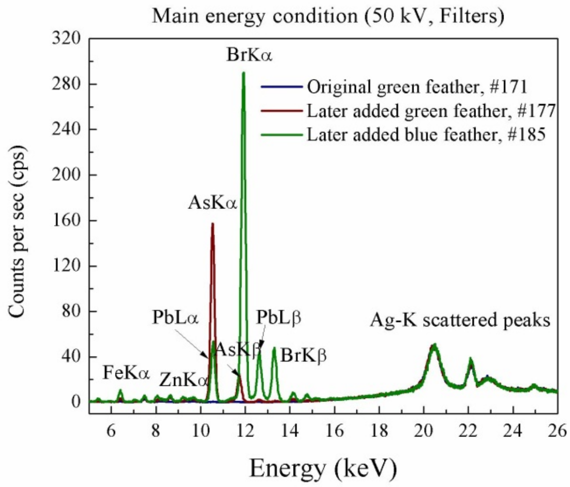

Fig. 3. Spectra collected in the main operational condition of the handheld XRF analyzer (enhanced sensitivity for medium atomic number elements)

The spectrum 171 (blue line) corresponds to the measurement in a spot of green feathers that are supposed to be the originally used in the making of the headdress. The measurement 177 (brown line) corresponds to the measurement of green-feathered bird skin fragments, whereas the measurement in the spot 185 (olive line) corresponds to blue-feathered skin fragments. Both of these skin fragments were presumably added to the headdress in 1878 as part of the first documented restoration. New feathers have been integrated to the headdress especially in those areas, which were damaged by a previous insect infestation. About one third of the whole front side of the headdress shows feathers added during the restoration process (1878). The spot 177 contains high intensity arsenic peaks, whereas bromine and lead peaks are also noticed in the measurement at spot 185. Such elements could be indicative of the use of arsenic, bromine and lead containing pesticides such as arsenic soaps, bromadiolone and lead arsenate (as both elements Pb and As were detected in other spots).

b) Analysis of the metal ornaments

The use of the x-ray radiography performed by Dr. Manfred Schreiner, Institute for Natural Sciences and Technology in the Arts, Academy of Fine Arts Vienna revealed two different chemical compositions for the metal ornaments; one corresponding to a highly absorbing material (gold alloy) and another one of much lower atomic number. The XRF measurements were performed to assure the classification based on microscopic investigation and the limited quantitative results obtained using wet chemical analysis [6].

For each gold ornament one single measurement (see Figure 4) was performed by carefully targeting the inspected area. In some cases replicate measurements were done to ensure that there were not elements detected from adjacent ornaments.

The composition of the original ornaments was calculated using one of the factory calibrations provided with the instrument, which accuracy has been verified through the measurement of two sets of reference 14kt to 23kt gold alloys. The quantification results of the gold ornaments using the instrument pre-existed calibration ("Precious Metals" mode) are presented in Figure 5.

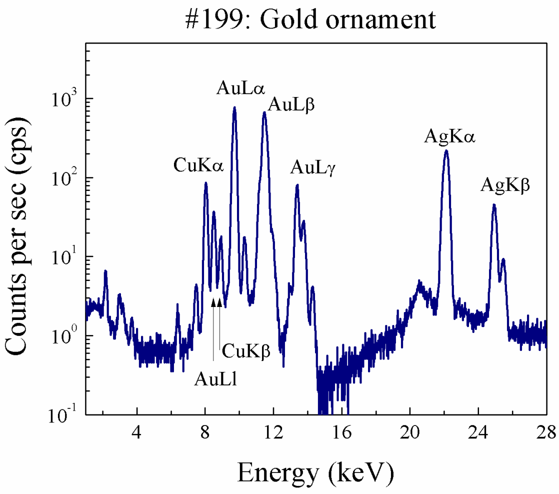

Fig. 4. An XRF spectrum of a gold alloy from the feather headdress (reading #199) obtained by the XL3t GOLDD handheld XRF analyzer operated at the main condition (50 kV, filtered excitation)

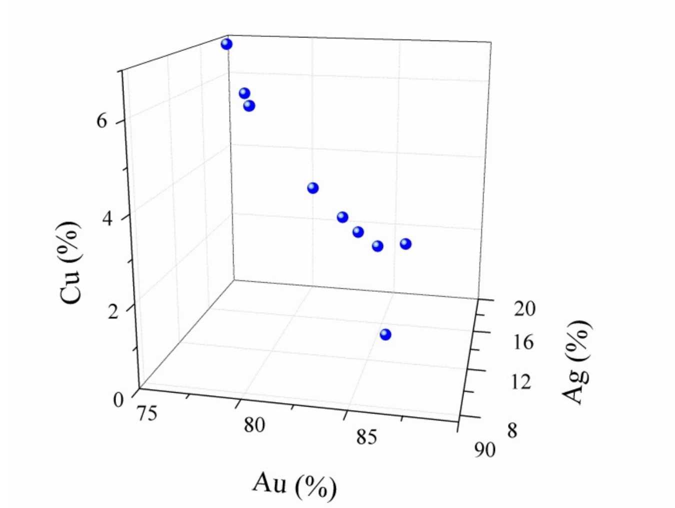

Fig. 5. Elemental composition of the original gold ornaments measured by means of the handheld XRF analyzer

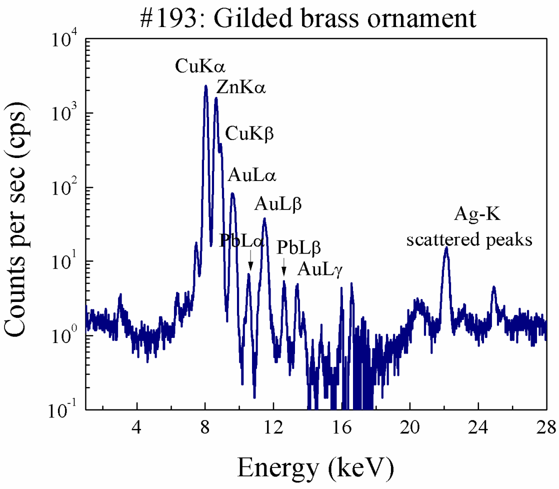

Fig. 6. An XRF spectrum of a plated brass alloy form the feather headdress (reading #193) obtained by the XL3t GOLDD handheld XRF analyzer operated at the main condition (50 kV, filtered excitation)

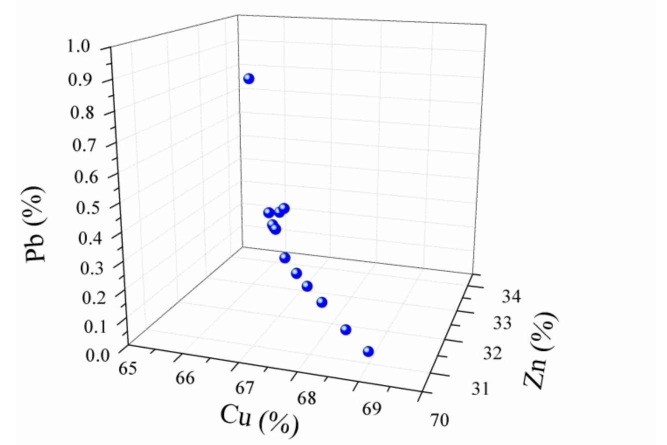

Fig. 7. Elemental composition of the gilded brass ornaments measured by means of the handheld XRF analyzer

The measurements taken from the later added ornaments revealed high intensity peaks for Cu, Zn and to a less extent of Pb, as well as smaller Au peaks as compared to the spectra from the gold ornaments (Figure 6).

The presence of these peaks in the spectra suggests that such ornaments are replacements made from gilded brass pieces. The two layered system, namely the presence of a gold gilding layer on the top of a brass alloy cannot be handled by the equipment quantitative analysis software in a straight forward manner. Thus, an analytical methodology was followed with the aim to determine the thickness of the gilding layer and to correct the brass elemental concentrations as obtained by the instrument software for the effect of attenuation of the radiation trough the gilding layer [5]. The chemical composition of the gilded brass is presented in Fig. 7 and the thickness was found to be in general less than 1-2μm.

Conclusions

The in-situ examination allowed the determination of the chemical composition of the original gold ornaments and that of the gilded brass replacements including an estimation of the thickness of the surface gold layer. Furthermore, it was noted that the added feathered-bird skin fragments were treated with various pesticides prior to their integration during the first documented restoration in 1878. The results of the pesticide analysis indicate a potential risk for museum staff and appropriate precautions should be followed when getting in contact with contaminated material or dust.

The results of this study demonstrate the usefulness of handheld XRF measurements, when interpreted following a well-sustained analytical methodology. Fast screening results can be produced on the spot to answer different questions arising from a prior detailed documentation of the artefact to be analyzed or even during the in-situ investigation, whereas a more detailed interpretation of the measurements carried out can be performed “off-line” to enhance significantly the information gathered from of the analysis.

Acknowledgments

We wish to thank the following institutions for extensive support: The International Atomic Energy Agency (IAEA), the Instituto Nacional de Antropología e Historia (Mexico), Weltmuseum Wien (Austria), the Kunsthistorisches Museum Vienna (Austria) and the Mexican Embassy in Austria.

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Nuclear Spectrometry Instrumentation for 2D and 3D imaging applied to characterization of materials of potential for nuclear power sector (Technical Meeting)

The meeting was held at IAEA headquarters in Vienna from October 01-04, 2013. The objectives of this meeting were to review the relevant experience and current status of nuclear instrumentation and methods for 2D-3D characterization of materials and to prepare a report / guidelines for the effective utilization in developing Member States, including technical and managerial requirements and possible role of the IAEA. Eight participants from Algeria, Brazil, Croatia, Cuba, Italy, Jamaica, South Africa and USA discussed the following topics:

- State-of-the-art instrumentation, developments and relevance for improved performance of the techniques, Analytical methodologies and applications, including ion beam, neutron and x-ray–based imaging techniques,
- Role of national and international collaboration to provide access to analytical facilities, and
- Role of the IAEA in support of the developing Member State activities to effectively apply nuclear instrumentation for 2D-3D imaging.

The Meeting concluded that the state-of-the-art instrumentation and techniques for 2D and 3D imaging could play an even more important and competitive role in the current and future research in comprehensive characterization of materials of importance for the nuclear sector. 2D and 3D imaging techniques provide unique possibilities to obtain chemical-, physical- and structural information at micro- and nano-scale levels which is increasingly important in the development of advanced technologies and materials for the study and protection of the environment. The existing infrastructure for imaging techniques, in terms of measurement equipment and sources for irradiation, requires continuous upgrade.

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A Report summarizing the conclusions reached from the discussions and addressing recommendations to the IAEA and its Member States is available upon request (R.Padilla-Alvarez@iaea.org).

Technical Meeting on
The application of micro-analytical techniques based on nuclear spectrometry to the characterization of materials of importance for the nuclear power
TM-44779
IAEA Headquarters, Vienna, Austria, Room 7–11 October 2013

The nuclear power is utilized by many IAEA member countries to cover a considerable part of their urban and industrial energy needs. Its generation is strictly controlled and monitored in order to minimize the operational risks and limit the environmental impacts. The efforts of the international scientific community are mainly targeted to:

- a strict and more demanding quality control of different nuclear materials (e.g. nuclear fuels, structural materials, coolant, moderator),
- strengthening of the efforts to produce in the future, cleaner and safer electricity using nuclear fusion.

The micro-analytical techniques based on nuclear spectrometry can play an important role and contribute to the achievement of these goals. The various nuclear radiation probes (e.g., x-rays, charged particle and neutron beams) can support through a plethora of associated analytical techniques an advanced characterization of nuclear materials fulfilling the requirements imposed by their functional or structural use.

The amount of trace element impurities which can be tolerated in different types of reactor fuels, their density and quality, the composition of the cladding, moderator and absorber but also the investigation of the structure and environmental behavior of the fission fragments and the actinides produced during the nuclear fuel cycle are extremely important areas where the application of nuclear spectrometry based micro-analytical techniques can play a dominant role. High sensitivity (down to the ng/g level or below) and selectivity, multi-elemental capability, short duration of the measurement are just a few of the many advantages of these techniques. Novel X-ray spectrometry techniques and equipment can extend and complement the capabilities of the conventional chemical analytical and spectroscopic techniques for nuclear materials characterization. Moreover, since some of these materials are radioactive, the analysis should be ideally non-invasive or at least use a minimum of sample (microgram level) so that the radioactive waste generated, and radiation exposure to the detector and operator are minimal. X-ray spectrometry techniques like the Total Reflection X-ray Fluorescence Analysis (TXRF) can fulfill these requirements to a great extent even at the laboratory scale. New instrument and method developments are exploring the applicability of X-ray spectrometry techniques for Pu assay of spent fuel through high resolution X-ray spectrometry (hiRX) with the use of doubly curved crystals (DCC) or through the Synchrotron Induced Ultra-high energy X-ray fluorescence (UHEXRF) to provide spatially resolved non-invasive analytical characterization of nuclear fuel within the Zircaloy cladding.

On the other side, the surface- (e.g. X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), secondary ion mass spectrometry) and the accelerator-based (e.g. Rutherford backscattering spectroscopy (RBS), nuclear reaction analysis (NRA), and particle induced X-ray or gamma ray emission (PIXE, PIGE)) analytical techniques can offer information on the composition of surface and near-surface layers. Other micro-analytical techniques (e.g., the scanning and transmission electron microscopy (SEM and TEM), the X-ray diffraction and small angle neutron scattering (SANS)) can provide valuable and complementary information for the morphological and structural characterization of nuclear and fusion materials. These techniques are continuously exploited to offer as much information as possible regarding the processes taking place during irradiation.

The Technical Meeting aimed at providing a discussion forum among specialists having the following objectives: 1) To review the current status and trends in the development of nuclear spectrometry based micro-analytical techniques for nuclear materials characterization, 2) To identify new areas where nuclear spectrometry based techniques can effectively address analytical requirements imposed on nuclear materials, 3) To support exchange and sharing of cross-cutting information and know-how between scientists working in R&D of nuclear spectrometry based micro-analytical techniques for nuclear materials characterization and 4) To provide recommendations to IAEA and Member States how to support further development and optimization of nuclear spectrometry based micro-analytical techniques for fulfilling requirements for more advanced and integrated characterization of nuclear materials

The meeting was attended by eight experts from the following Member States: Croatia, Egypt, Jamaica, Kenya, Portugal, Syria, Tunisia and USA. The participating experts presented material relevant to Ion Beam Analysis techniques, X-ray Fluorescence and in-situ gamma ray spectrometry highlighting recent advances and current status of each technique emphasizing applications relevant to the nuclear energy sector for materials characterization. These techniques offer unique solutions to existing issues and offer potential growth to the efforts to establish alternative energy sources (fusion reactors) and in addressing nuclear energy operations ranging from fuel performance to waste management issues.

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

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Invitation to join the European Radiation Detection and Imaging Technology (ERDIT) activities

The goal of ERDIT is to create a bottom-up network with leading scientists in the field of radiation detection and imaging to exchange information between different application areas and to promote research in relevant fields at the European Commission and national funding agencies.

ERDIT MISSION STATEMENT

The mission of the European Radiation Detection and Imaging Technology Platform is to promote the research on radiation detectors and imaging at European level. The aim of this platform is to synergistically implement a common strategy across research infrastructures involving research laboratories, academy and industry, which would benefit fundamental science, promote innovation in industry and would feed into the crucial European societal challenges. This would be implemented through a process of guidance, prioritization and promotion of research, innovation and education with respects to fundamental science principles and contemporary benefit to society and growth of global competitiveness of European industries

BACKGROUND

The demand for advanced radiation detectors will increase dramatically in the next few years. A number of large research institutes including CERN, GSI, ESRF, XFEL, ITER, JET, ESS and others are either being built or are planning for substantial upgrades before 2020. In addition the concept of quantum imaging is used for materials testing in industry and has gained interest from the medical imaging industry with an expected annual market exceeding 10 billion euros. The challenge addressed by this Platform concerns both the development of high performance detectors and the ability to produce them by European industries. The aim is to create an academy-industry platform to address the key scientific challenges for development of high-performance radiation detectors, to coordinate the research on radiation detectors with competitive edge at European level. Strong interaction between leading scientists in academy, industry and end-users is necessary to remove overlaps in research topics, increase piloting of new ideas and facilitate access to national and international R&D funding.

There is a common understanding that the development of radiation detectors is lagging behind and that the lack of high performance detectors is the limiting factors in many applications. An explanation is that the research is truly multidisciplinary and that it does not fit into any of the major research programs. There are only a few cross program calls where this type of research is possible.

It is now time to consider whether the various involved communities would be interested in joining forces to establish a Technology Platform at European level. This would be done together with industries to raise the awareness of the common needs and to promote a detector roadmap for future research and innovation.

THE ERDIT PLATFORM WILL…

- Collect information on important challenges for the development of high performance radiation detectors
- Collect information on the shortcomings of the current detectors as seen by the applications
- Work on common strategies for research and development in Europe.
- Develop technology roadmaps for radiation detector development
- Raise the awareness of the needs for radiation detectors and their impact on societal challenges
- Promote the field of research, education, innovation and knowledge transfer at national and European level

ERDIT ACTIVITIES SO FAR

Initial meeting at CERN in April 2013

- Collect information from the different fields
- Discuss the objectives of ERDIT

Second meeting at IAEA in October 2013

- Present the results of the survey on common challenges
- Information from the European Commission on Horizon 2020
- Discussion on a proposal for a COST action

Third meeting in Freiburg in April 2014

- First open meeting, previous meetings were by invitation only
- First meeting with industrial partners
- Proposing further actions from the network

You may also visit the ERDIT website and register at: http://www.erdit.eu/content/subscribe-erdit

You are invited to ERDIT next meeting in November 2014 at Stockholm. For more information please contact Mr. Yacouba Diawara (Y.Diawara@iaea.org)

X ray Fluorescence in Member States

Indonesia

Application of ED XRF in supporting national program of air quality improvement in Indonesia

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Abstract

Since 1997, the National Nuclear Energy Agency, BATAN has been involved in the IAEA's RAS projects for the application of nuclear analytical techniques to characterize airborne particulate samples. The measurement of the elemental composition of the particulate matters is a key factor in utilization of the data for the determination of possible sources, which the process of identification and apportionment of pollutants to their sources is an important step in air quality management. Nuclear analytical methods such as XRF and PIXE are suitable for characterizations and need to be applied to produce large data sets of elemental compositions of APM. To maintain the sustainability of research in supporting the national program of air quality improvement in Indonesia, in 2011, BATAN has proposed new equipment, Energy Dispersive X-Ray Fluorescence (ED-XRF) Epsilon 5. During the last two years, based on MoU between BATAN and the Ministry of Environment, the assessment and monitoring of air quality has been expanded into 15 cities in Indonesia. In this review, we present the research activities related to the application of XRF in APM samples characterization.

Introduction

In Indonesia, air pollution control programs have been conducted through several actions i.e unleaded gasoline policy, vehicle emission testing, car free day and launching environmental programs in national and local regions such as blue sky program and urban Air Quality improvement (UAQi). But, increased air pollution is still present in several cities and needs serious attention from the government, stakeholders and the public, in order to avoid health impact and greater financial losses.

The National Nuclear Energy Agency of Indonesia, BATAN has contributed in solving air pollution problems through the application of nuclear analytical techniques for the characterization of airborne particulate samples. BATAN is involved in regional research activities in application of nuclear analytical techniques in airborne particulate matter characterization and source identification under IAEA cooperation in RAS project since the 1990s.

Fig. 1. Sampling locations

NAT's such as neutron activation analysis, X-Ray Fluorescence and particle induced X-ray emission have simultaneous capabilities to detect various elements present in airborne particulate matter with fraction sizes less than 2.5 µm ($PM_{2.5}$), producing a set of data concentration of 25-30 key elements in identification of air pollutant sources.

In this review, the elemental composition analysis of airborne particulate matters by EDXRF Epsilon 5 and comparison with the Particles Induced X-ray Emission - PIXE results from the same samples will be presented. Quality assurance of the method using standard reference material SRM NIST 2783 airborne particulate on filter media and the detection limit of elements are also discussed.

Sampling activities

The APM samples were collected using a Gent stacked filter unit sampler [1]. During the last two years, the sampling locations covered 12 cities in Indonesia, i.e: Sumatra (Pekanbaru), Java (Jakarta, Serpong, Bandung, Yogyakarta, Semarang, Surabaya), Borneo (Palangka Raya, Sulawesi (Makassar), Bali (Denpasar), Maluku (Ambon) and Papua (Jayapura), and in the end of 2013 the sites were expanded into other 3 cities: Lombok, Menado and Balikpapan. Sampling activities were carried out once a week in each location, in a year that will be totally 780 pairs of samples collected, consisting of fine filter ($PM_{2.5}$) and coarse filter ($PM_{10-2.5}$).

Sampling activities were done by the local EPA in each region whose staff has been trained and supervised before in a national training/workshop. After sampling, samples were sent back to BATAN Bandung to be analyzed for gravimetric and black carbon concentrations, then analyzed for elemental compositions.

Fig. 2. Characterization of APM using Epsilon5 in BATAN Laboratory

Elemental composition using ED-XRF Epsilon5

The elemental composition analysis was all carried out at BATAN Bandung which has implemented ISO/IEC 17025:2005 accredited by the National Accreditation Body since 2006. The analysis was conducted using an Epsilon 5 EDXRF spectrometer from Panalytical, which has a 100kV excitation source and a polarising optical path, giving detection limits in the low ng/cm^2 range for most elements [2].

A special sample insert enables air filters to be fitted directly into the sample cup. No additional sample preparation is needed and the sample changer makes continuous analysis possible. The calibration was set up using a multi standard reference material, standard Micromatter® and a blank standard for each element, Mg, Al, Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As and Pb. The method validation of this application was done by analyzing the SRM NIST 2783. The EDXRF Epsilon 5 installed at BATAN Bandung has 9 secondary targets i.e: Al_2O_3, Fe, CaF_2, Ge, Zr, CeO_2, Mo, Ag and Al. EDXRF Epsilon 5 with its polarization method produces an indirect exitation/secondary target excitation giving significantly lower background.

For method validation, the result for SRM 2783 is shown in Figure 3, it has a good agreement with the certificate value with ratio 0.92-1.09.

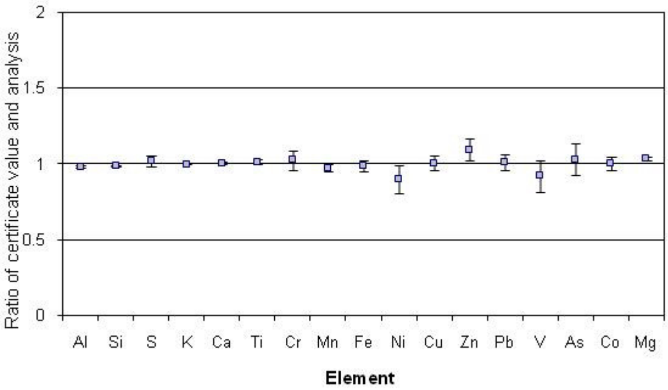
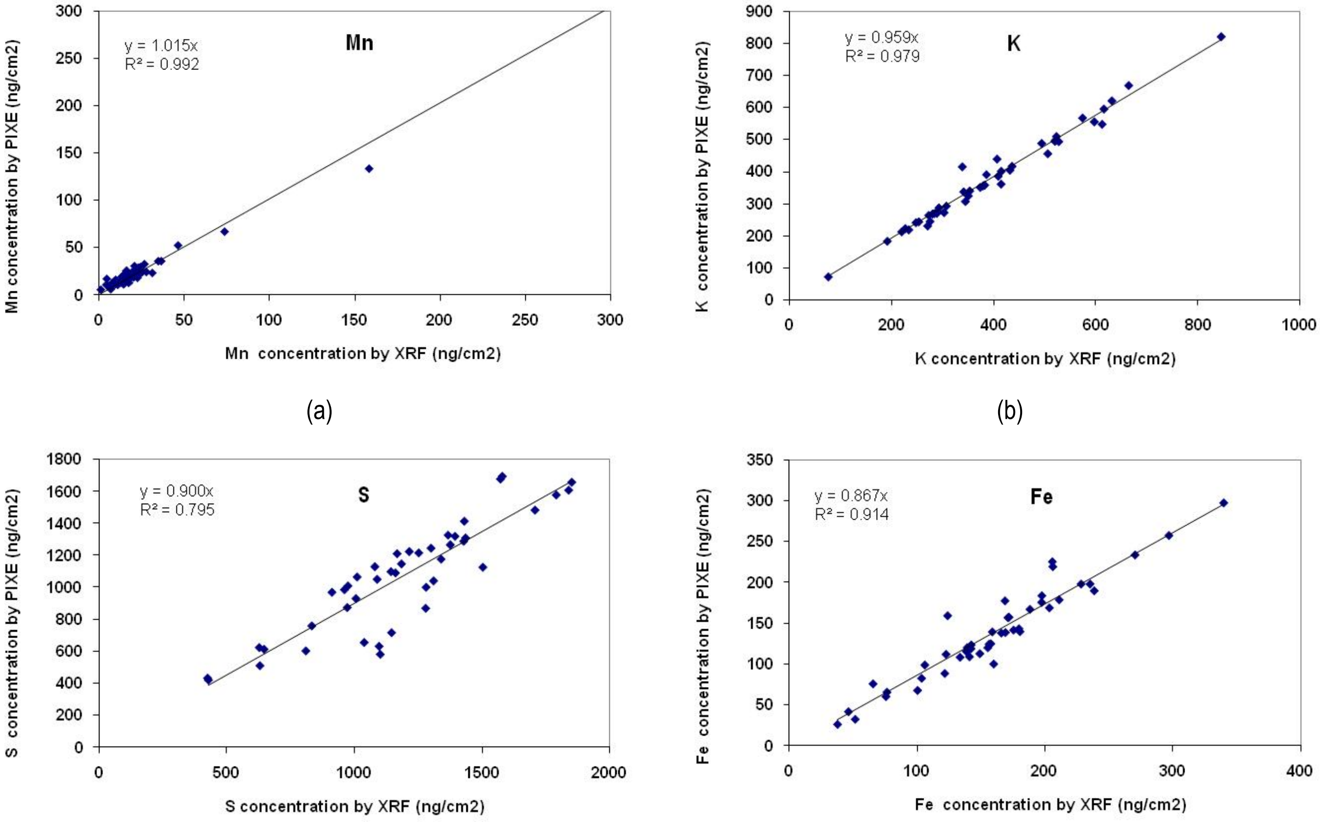


Fig. 3. The ratio of certificate value of SRM NIST 2783 and the analysis result by ED-XRF[3].

To ensure the analysis method, beside method validation using SRM NIST 2783, the comparison with the Particles Induced X-ray Emission - PIXE results was also carried out from the same samples. The comparisons for some elements are shown in Figure 4. PIXE analysis to the same samples was done previously in the Geological Nuclear Science, New Zealand. It can be seen for some elements such as S, K, Fe and Mn were in good agreements between EDXRF and PIXE method as shown in the figure. PIXE offers higher sensitivity and quicker analysis time than ED-XRF which requires long time measurement to meet the good results and low detection limit. At present, a PIXE accelerator based nuclear analytical technique facility is not available in Indonesia. Using PIXE, it could analyze one filter of APM in 5-6 minutes compared with XRF that will need times around 1-1.5 hours.

The results of elemental analysis of Pb concentrations during 2013 are shown in Figure 5. The box represents 25 to 75% of the distributions of the concentration. The box represents 25 to 75% of the value. The horizontal bar in the box indicates the median and the plus symbol (+) denotes the mean data. The points lying outside the range defined by the whiskers are plotted as outlier dots. From this figure, it can be stated that Surabaya sampling sites is detected for lead pollution which is higher than Serpong area. Preliminary results related to Pb pollution in Serpong showed that the highest concentration of Pb in the $PM_{2.5}$ and $PM_{2.5\text{-}10}$ in industrial areas, respectively 5 and 8 times higher than the residential area.

Identification of pollutant source analysis showed that more than 80% concentrations of Pb in $PM_{2.5}$ are estimated from the metal smelting process [3]. The Pb concentrations in Surabaya from this monitoring could be beneficial to show an early warning of lead pollution in Surabaya, and quick response should be taken to control this pollution. Lead concentrations during the period ranged from 11.0 to 1911 ng/m^3 with an average of 427.3ng/m^3. Some samples were almost in violation to the 24–hour Indonesian standard for total suspended particles, 2 µg/m^3.



(a)

(b)

(c)

(d)

Fig. 4. Comparison of element Mn, K, S and Fe by PIXE and EDXRF

The pollution of heavy metals in Surabaya was also detected for Fe and Zn as shown in Figure 6. The concentrations of Fe and Zn in Surabaya were higher than in other cities. This could be attributed to industrial sources, for more detail and comprehensive discussion, source identification research related to this matter is needed.

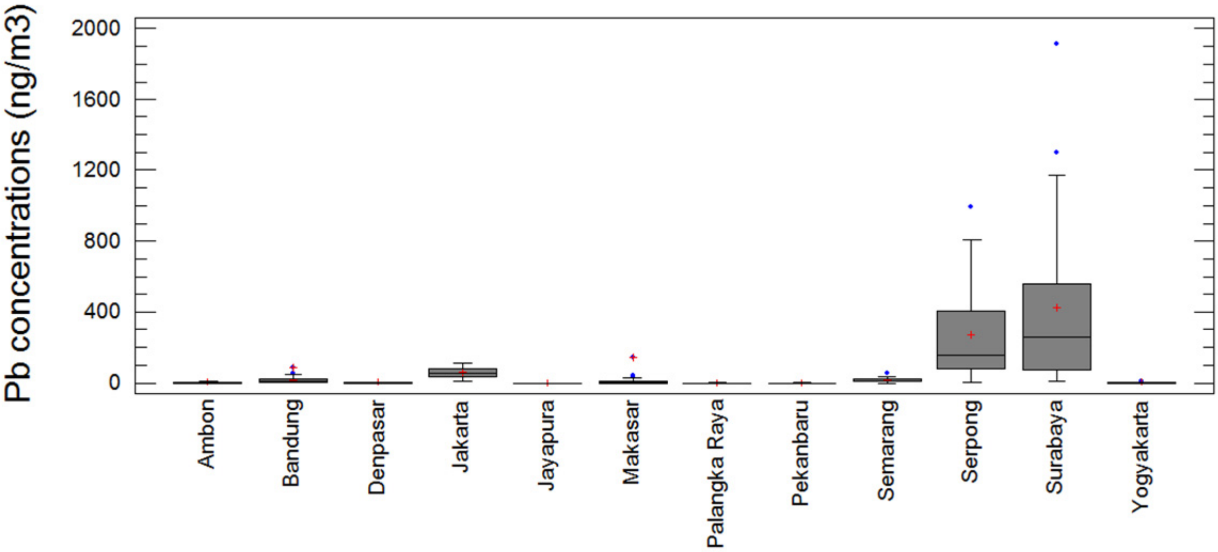
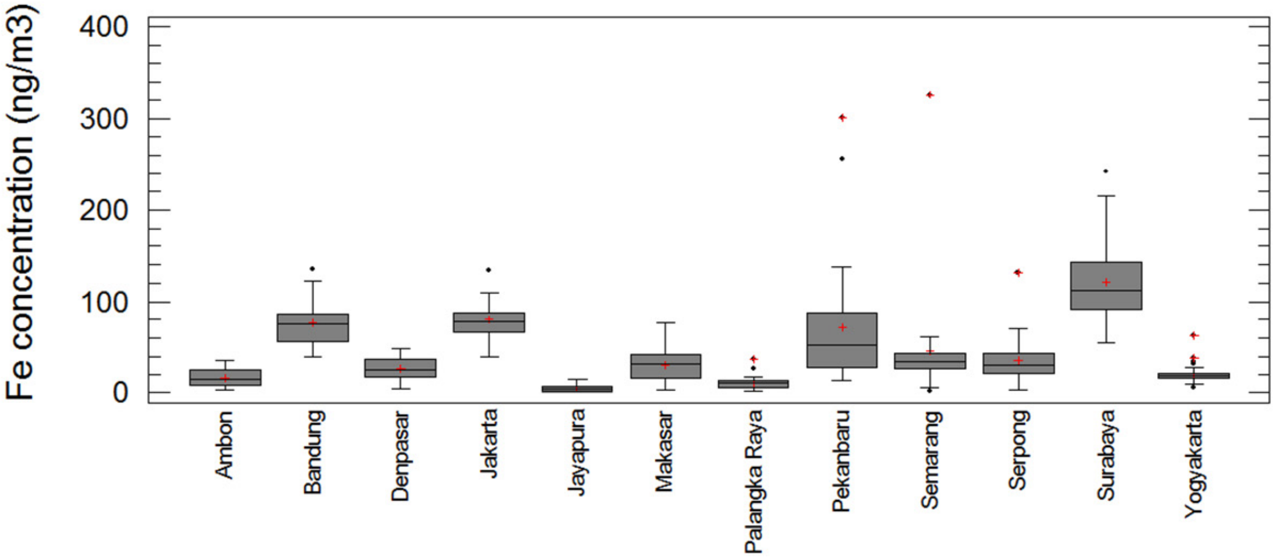
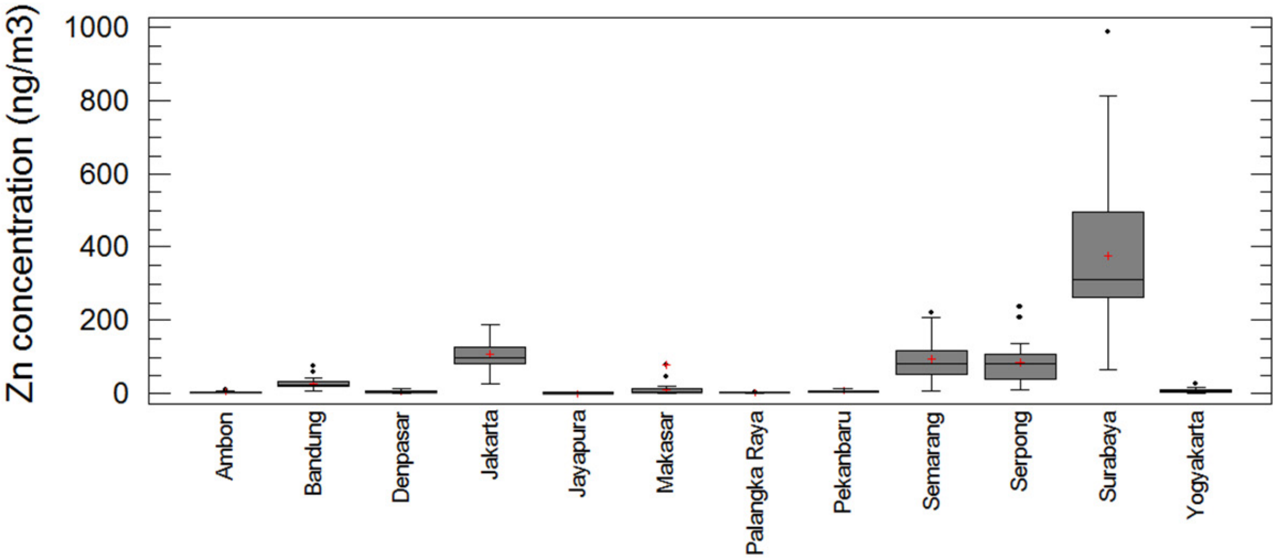


Fig. 5. Pb concentrations in $PM_{2.5}$ at several sampling locations



(a) Fe concentrations

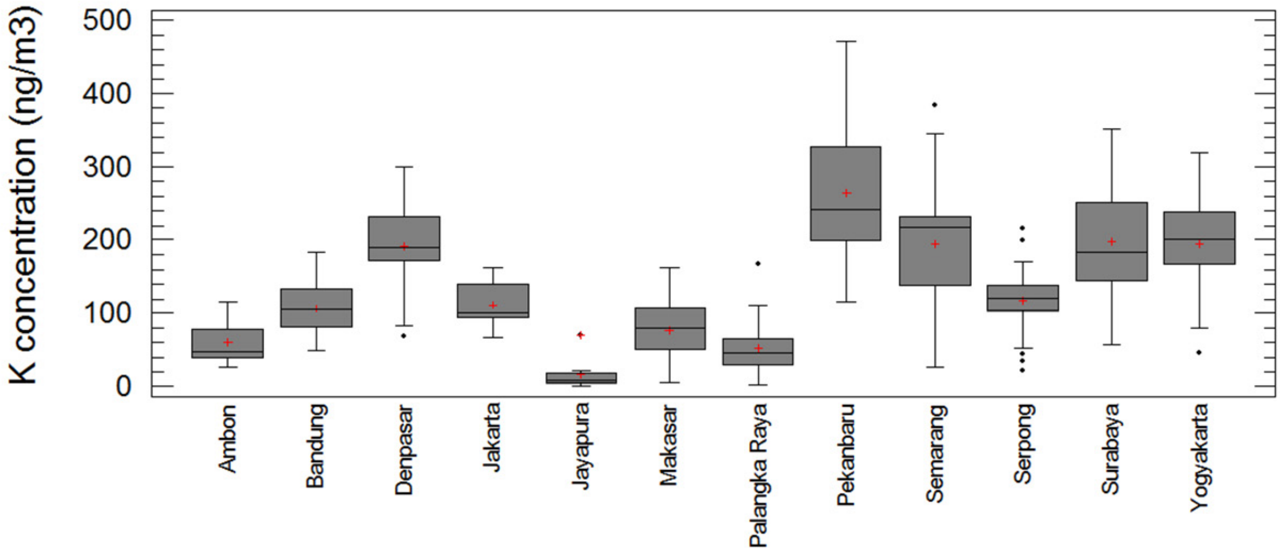


(b) Zn concentrations

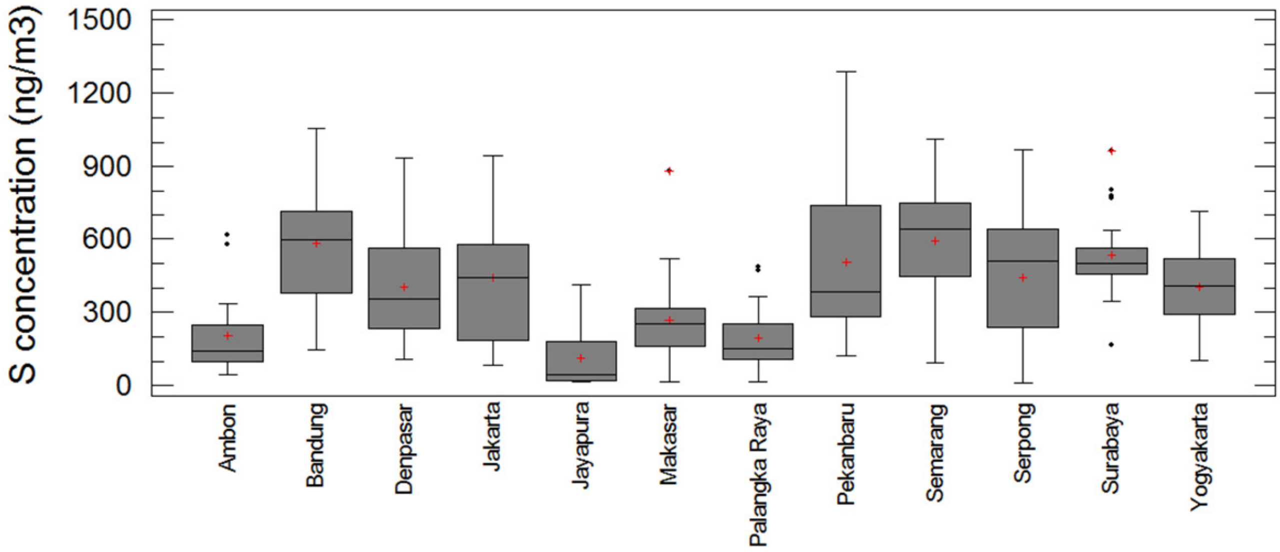
Fig. 6. Fe and Zn concentrations of $PM_{2.5}$ during 2013 in several locations

S and K concentrations are shown in Figure 7. From the figure it can be seen that Pekanbaru has higher S and K concentrations. This could be related to forest fires which occurr occasionally. Pekanbaru is one of the cleanest big cities in Indonesia. In 2011, it received the "Adipura" ('clean city') award in the category of large city for the seventh consecutive time.

However, Pekanbaru regularly suffers from smoke or smog due to forest fires, particularly in the dry season. Forest fires from uncontrolled burning of large areas of lands are a major problem for air quality. Tropical peat/forest fires in Indonesia are generally caused by illegal human activities including land clearing, converting to agricultural lands through heavy logging and slash and burn techniques [5]. Most of the fires are intentionally started but often unintentionally grow dangerous. The highest concentrations of S and K were observed in Pekanbaru, and those elements are assumed to originate from peat forest fires. Peat is the earliest stage of transition from compressed plant growth to the formation of coal and contains high amounts of sulfur [6]. K concentrations were also high in Denpasar, despite of lower mass concentrations ($PM_{2.5}$ ranged 3.44 - 14.74 $\mu g/m^3$). Potassium was also high in Semarang, Surabaya and Yogyakarta. More comprehensive research related to this matter is needed and still on going.



(a) K concentrations in $PM_{2.5}$



(b) S concentrations in $PM_{2.5}$

Fig. 7. Concentrations of S and K in $PM_{2.5}$ at several sampling locations

Source Apportionment

Source identification of pollutants has been applied to several cities data in Indonesia, using Positive Matrix Factorization (PMF). One of the source apportionment results in Serpong has been published [3], and it reveals that more than 80% of Pb concentrations in $PM_{2.5}$ are estimated to originate from the metal smelting process. Figure 8 shows the source apportionment in Serpong, and the first factor shows a high value of lead. The lead in this factor dominates more than 80% of lead in the samples. It should be noted that S also appears along with Al, Ca, Fe, and Si suggesting contaminated road dust. This factor could be represented by lead industry mixed with road dust that represented 12% of fine fraction composition. There are industrial facilities involved in metal lead processing and battery recycling plant to the northwest of sampling sites.

The source apportionment in Jakarta, Bandung and Lembang has been published elsewhere, and the source apportionment needs the large data sets of elemental concentrations [7,8].

Conclusions and future plans

The application of nuclear analytical techniques such as XRF contributed to the national air quality program of Indonesia. The results of our research have shown that ED-XRF is an effective tool and enables the characterization of multi elemental composition and could produce large data sets for source identification. However, to meet good sensitivity and low detection limit, it needs longer measurement times than accelerator based nuclear techniques such as PIXE. In the next three-five years, the air quality assessment research will be expanded into 33 cities covering all the capital of province in Indonesia, therefore to cover and accomplish the project it will need other complimentary analysis tools that enable characterization in a short time and with good quality. To make this project sustain, BATAN will assess the possibility of PIXE development in Indonesia. Some visibility studies have been conducted and hopefully in the near future, PIXE will be available in BATAN Indonesia to be utilized for environmental, materials, and other related research to emphasize the role of nuclear analytical techniques in a broad field, to solve national problems through enhancing the collaboration with several numbers of end users.

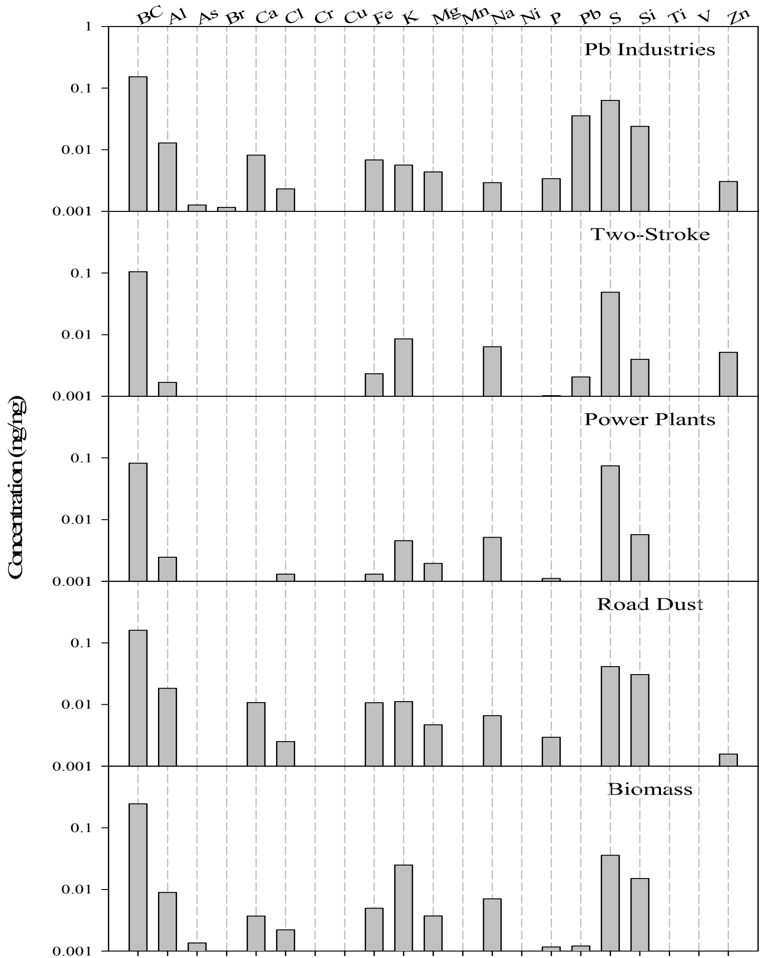


Fig.8. Source apportionment in Serpong area [3].

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Italy

Portable EDXRF in a multi-technique approach for the analyses of large paintings

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Energy-dispersive X-ray fluorescence (EDXRF) with its portable capability, generally characterized by a small X-ray tube and a Si-PIN or Si-drift detector, is particularly useful to analyze works of art. The main aspect that characterizes the EDXRF technique is its non-invasive character.

This characteristic that makes the technique so powerful and appealing is on the other hand the main source of uncertainty in XRF measurements on Cultural Heritage. This problem is even more evident when we analyze paintings because of their intrinsic stratigraphic essence.

As a matter of fact a painting is made of several layers: the support, which can be mainly of wood, canvas, paper; the preparation layer, mainly gypsums, white lead or ochre; pigment layers and at the end the protective varnish layer. The penetrating power of X rays allows that most of the times the information of all the layers reaches the detector. Most of the information that is in the spectrum arrives from deep layers of which we have no clue. In order to better understand this concept, let us use the equation of A. Markowicz [1]:

$$\sigma^2_{\text{tot}} = \sigma^2_{\textit{sample representation}} + \sigma^2_{\textit{sample collection}} + \sigma^2_{\textit{sample handling}} + \sigma^2_{\textit{sample preparation}} + \sigma^2_{\textit{analysis}}$$

in which the various uncertainties that influence the analyses with portable EDXRF are reported.

Let us adjust this equation for *non invasive* portable EDXRF analysis. The second, the third and the fourth term do not exist, for obvious reasons. Only the first and the last term influence the total uncertainty of an EDXRF analysis. The ways to reduce the influence of the fifth term is known by any scientist: good stability of the system, long measuring time, correct standard samples, good energy resolution etc. But what about the first term when we are executing a non invasive analysis?

An example that shows the influence of the sample representation in the increasing of the uncertainty of a XRF analysis is the case in which we are asked to determine the original pigments used in a painting. If we have no clue of where restoration areas are dislocated on the painting, the probability of analyzing a “wrong” pigment is surely high and therefore high is the probability of having a high uncertainty in our results. Without a good representation of the painting to analyze, the total uncertainty could be very high even applying correctly all the analytical procedures for XRF analysis.

The only way to reduce the influence of the sample representation in the EDXRF technique is to backup the EDXRF analysis with different kinds of techniques that help reduce the total uncertainty. These techniques, totally non invasive such as EDXRF, can be the imaging techniques such as UV light, IR reflectography and X radiography. These techniques have already an independent application in Cultural Heritage with their own prototheir results to the fact that: UV light is able to detect surfaces restorations, IR reflectography intercepts restorations in deeper layers while X rays define deeper problems. These imaging techniques gain new importance from a scientific point of view when they help choosing the right spot of analysis and therefore reduce the total uncertainty of EDXRF analyses. Surely the sample representation of a specific surface of the painting is greatly increased when, prior to any EDXRF analysis, we are able to fulfill non invasive imaging techniques.

In a few words, we can state that Markowicz's equation demonstrates that portable non invasive EDXRF in Cultural Heritage needs a multi-technique approach to reduce the total uncertainty of its results.

When dealing with large surface paintings, regardless whether on canvas, on wood or mural, before starting with instrumental measurements, it is necessary to define a strategy to reduce the number of expensive and time consuming analyses to the minimum and at the end reduce to a minimum, or better eliminate, the necessity of destructive sampling. The working session must start with deep visual examination together with an art historian and a restorer and define the targets of the analyses. After this, it is necessary to divide the large painting in sections internally coherent for problems and expectations.

The next step is to define what technique is necessary to apply to which section starting from quick and cheep techniques like the imaging ones, such as grazing light, UV light, IR reflectography, X Rays and then move to more expensive analyses such as XRF and Raman and only at the end, and only if really necessary, do some micro sampling for OM stratigraphy, SEM/EDS and micro FTIR. The best way to deal with big paintings is therefore to manage them as a mosaic of smaller ones. That means, it is necessary to divide the painting with the help of an art historian and restorer into several scenes coherent within each other and apply to each one of them the procedure proposed.

To show the importance and necessity of a multi technique approach when using EDXRF on large paintings we describe the cases of:

- Caravaggio, "Calling of Saint Matthew" in the Contarelli Chapel in Rome, Italy
- Luca Signorelli, "The altarpiece of Paciano" in the National Gallery of Perugia, Italy

On this occasion, we are going to discuss only the case in which EDXRF is applied to determine the original pigments used by the painter. As it is easy to imagine, there are many more applications of EDXRF and for all of them, the methods and procedures for the multi technique approach are different.

"Calling of Saint Matthew" by Caravaggio in the Contarelli Chapel in Rome, Italy [2]

In 1559, Caravaggio was asked to decorate the Contarelli Chapel in the Church of San Luigi dei Francesi in Rome. One year later, the "Calling of Saint Matthew" was delivered. The painting is 322 cm x 340 cm. The highlight of the painting, which had an immediate success, is the beam of light that enters the picture from a window following the arm of Jesus and depicting the change of the destiny of Saint Matthew. 38 EDXRF analyses were conducted on the painting.

In Figure 1 we show the painting, a red dot marks the point of interest.

Fig. 1. Calling of Saint Matthew

Wanting to define the pigments used by Caravaggio to paint the shades, we chose a spot pointed out by a red dot, just above the right hand of Jesus. In Figure 2, we see an IR reflectography of the painting just around the red dot. It makes the presence of an important "pentimento" clear. It is evident that the interpretation of the XRF spectrum is very different with the correct awareness of an under painting as compared to not knowing about the presence of an under painting. In the second case, it would be difficult to understand why Caravaggio used lead white and red cinnabar to build a dark shade and the uncertainty of our result would be very high.

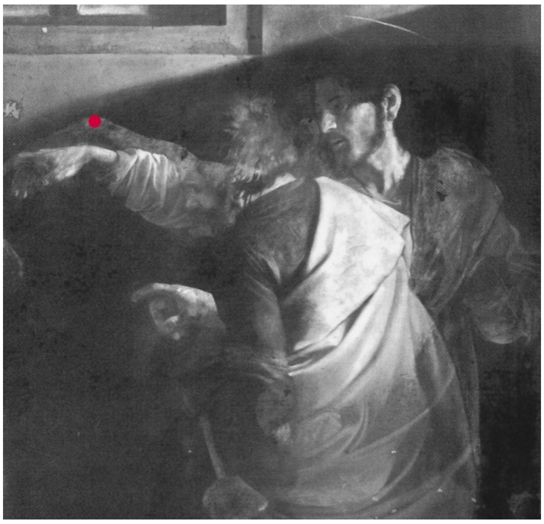

Fig. 2. IR reflectography of the painting

"The altarpiece of Paciano" by Luca Signorelli in the National Gallery of Perugia Italy [3]

The altarpiece of Paciano is a large painting (215 cm x 310 cm) now located at the National Gallery of Perugia in Italy. The painting is signed by the painter and is dated 1517, at the bottom of the painting, it is possible to see the old city of Paciano that commissioned the work. In Figure 3, you can see a full view of the altarpiece with indicated points where XRF was done. 51 EDXRF analyses were conducted on the altarpiece.

We want to define the right positions to study the work with portable EDXRF to characterize the pigments used by Signorelli for the incarnate. As already stated, it is of fundamental importance to determine which areas are original and which are retouched. In Figure 4, results for the head of the Holy Mother analyzed by different imaging techniques are aligned. It is easy to see areas with "pentimento" such as the crown of the Holy Mother and areas with restorations such as on her right eyebrow.

Only after careful study of these images, it is possible to choose the right spots to apply EDXRF to be sure that we are analyzing only original areas and by that reducing the total uncertainty that influences the analyses with portable EDXRF devices on paintings.

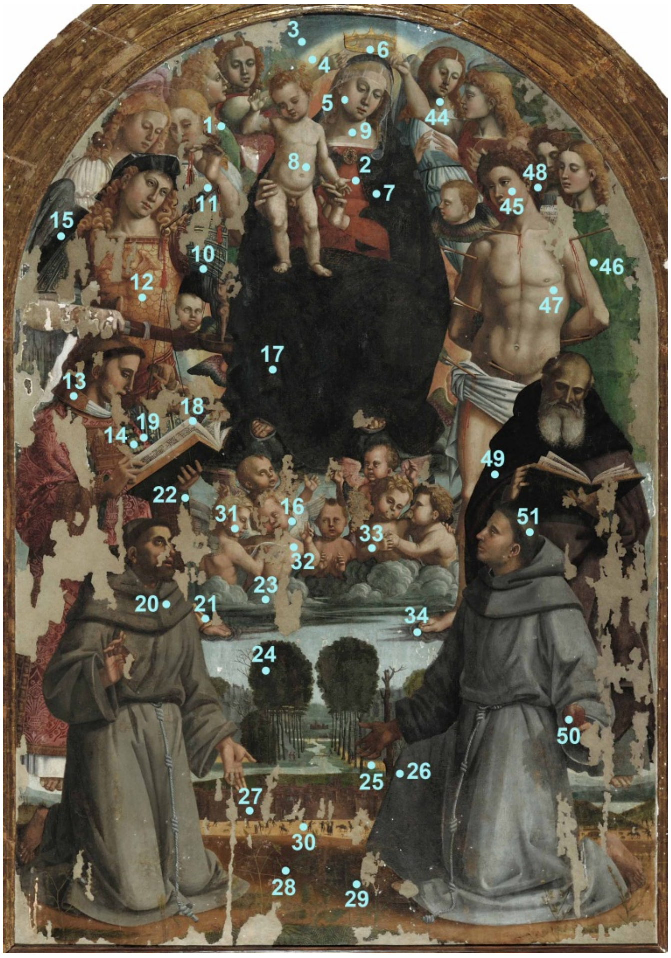

Fig.3. The altarpiece of Signorelli and the XRF points

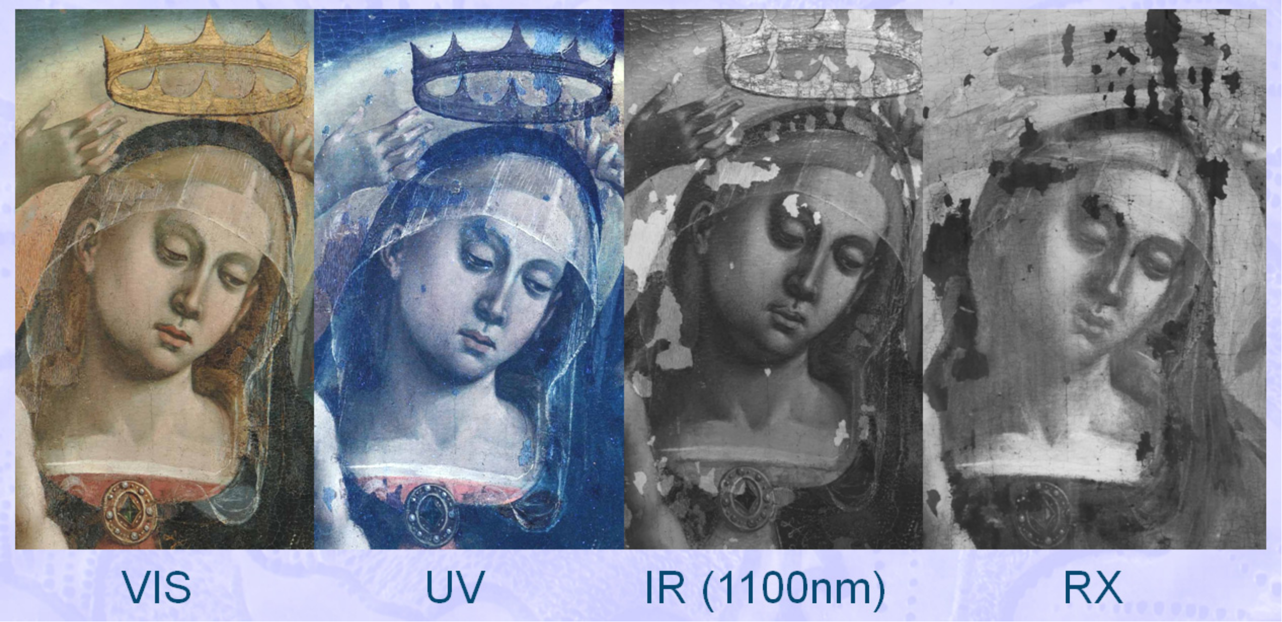

Fig. 4. Detail of the altarpiece of Paciano. The Holy Mother imaging at different energies

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Spain

Main activities related to the use of XRF techniques at the Analytical and Environmental Chemistry Research Group of the University of Girona (UdG)

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Introduction

The Analytical and Environmental Chemistry Group (QAA) is a consolidated research group of the Department of Chemistry of the University of Girona (North-East Spain). The main research topics of the group are related to the development and application of analytical methodologies for the determination of inorganic and organic species in different kind of environmental, clinical and industrial samples.

From the beginning of the 2000's, one of the research focuses of the group, is the use of X-ray fluorescence spectrometry (XRF) for the determination of trace amounts of metals and metalloids mostly in samples related to the environmental and industrial fields. For instance, in collaboration with the Institute of Earth Sciences "Jaume Almera" (ICTJA-CSIC, Spain), we have developed and successfully applied several analytical approaches based on the use of EDXRF (Energy dispersive XRF), WDXRF (Wavelength dispersive XRF) and P-EDXRF (Polarised EDXRF) for the determination of metals at trace levels in complex liquid samples such as sea water or electroplating waters [1-3] in vegetation samples collected around mining environments [4-5] or in active pharmaceutical ingredients [6-7]. At present, the evaluation of the analytical possibilities of TXRF (Total reflection XRF) in the chemical analysis field is also one of the research topics of QAA. In this sense, several contributions related to the use of this technique for element determination in liquid and solid samples have been developed. A summary of these contributions is summarized in the last section of this review.

Instrumentation

As in any analytical chemistry laboratory, our installations are equipped with all the materials and apparatus for sample treatment procedures and pre-concentration strategies for the analysis of solid, liquid and air samples.

In addition to chromatographic techniques (including high-performance liquid chromatography (HPLC), ultra performance liquid chromatography (UPLC) and gas chromatography (GC)), QAA laboratories are also equipped with atomic spectroscopic techniques including inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), flame atomic absorption spectroscopy (FAAS) and electrothermal atomic absorption spectroscopy (ETAAS).

In the field of X-rays, we acquired a commercial benchtop TXRF system (S2 PICOFOX, Bruker AXS) in 2009, in collaboration with the ICTJA-CSIC (Spain). One of the major advantages of this spectrometer is that it is equipped with an air cooled low power X-ray tube (50 W) and a Peltier cooled silicon drift detector and thus, no cooling media and gas consumption are required. These facts make the 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 elements such as Cd and Sb.

In addition, in the framework of a consolidated research unit between CSIC-UdG, some other XRF systems such as a benchtop EDXRF system (S2 Ranger, Bruker AXS) and a EDXRF spectrometer with primary beam focusing capability to perform analysis of small regions, determination of layer thickness and elemental mapping (XDV-SD model, Helmut Fischer GmbH including W target tube and motorized XYZ stage; spatial resolution 0.1-3.0 mm) are also available.

R+D and Educational Activities

Since the creation of the new research line focused on the use of X-ray fluorescence spectrometry techniques, the QAA has actively participated in multidisciplinary collaborative projects and has established close collaborations with different research groups of high national and international prestige in the field of X-rays: ICTJA-CSIC (Barcelona, Spain), CFAUL (Lisbon, Portugal), MiTAC (Antwerp, Belgium) and the Institute of Chemistry (University of Silesia, Poland). During the last four years, scientific collaborations with reference research groups in the field of TXRF have also been consolidated (i.e, Atominsitut, TU Wien).

With regards to educational activities, it is important to remark the co-organization of the biannual “Theoretical and Practical X-ray fluorescence spectrometry workshop” (see Figure 1). This workshop is devoted to the exchange of merging and inventive X-ray spectrometry techniques and their important applications. The program consists on several theoretical conferences, carried out by international and distinguished speakers, and practical sessions. Different XRF instruments are usually available for the later purpose. In the framework of the workshop, assistants (students and professionals working in the field of X-rays) have the opportunity to bring up concrete problems to be solved during the workshop.

Fig. 1. Assistants of the Theoretical and Practical X-ray fluorescence spectrometry workshop held in Girona (Spain) from 28-30 June 2011.

On the other hand, at present, QAA is also cooperating with the IAEA in the training of fellows from the Member States on the use of TXRF for analytical purposes

Recent XRF applications carried out at QAA (UdG)

The use of TXRF in the field of chemical analysis has been reduced in the last years mostly due to the increasing use of ICP-MS instrumentation. Although ICP-MS presents sufficient sensitivity and multi-element capability for the determination of elements at trace and ultratrace levels, the complexity of most environmental matrices significantly hampers the analysis. An additional shortcoming is that several mL of liquid solution are needed to perform analyses and thus, the application to mass-limited samples is restricted. For this reason, in some applications, above all concerning to the analysis of complex liquid samples, mass-limited samples and suspensions, TXRF spectrometry is still unique.

As commented in the introduction, in this last section, a few selected examples of the recent activities and results from QAA research group in the field of TXRF are presented.

A. Determination of environmentally important elements at trace levels in water samples by TXRF

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Despite the advances in the development of highly efficient analytical instrumentation for the end point of determination of analytes in environmental samples, sample treatment is usually necessary to extract, isolate and concentrate analytes of interest from target samples. In this context, it is worth mentioning the development of faster, simpler, inexpensive and more environmental pre-concentration procedures within the framework of the so-called green analytical chemistry such as liquid-phase microextraction (LPME). LPME is a solvent minimized sample pre-treatment 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 tenth or hundreds of mL needed in conventional LLE. Taking into account the micro-analytical capability of TXRF spectrometry, the combination with LPME procedures is an interesting approach to improve analytical performance of trace and speciation metal analysis by using this technique. For instance, we demonstrated the applicability of LPME procedures combined with a transportable TXRF system for the determination of Cd and Sb species at trace levels in different kinds of water samples [8-9]. In Figure 2, the benefits of using LPME+TXRF for the determination of Cd and Sb species at the low μg L^{-1} is shown.

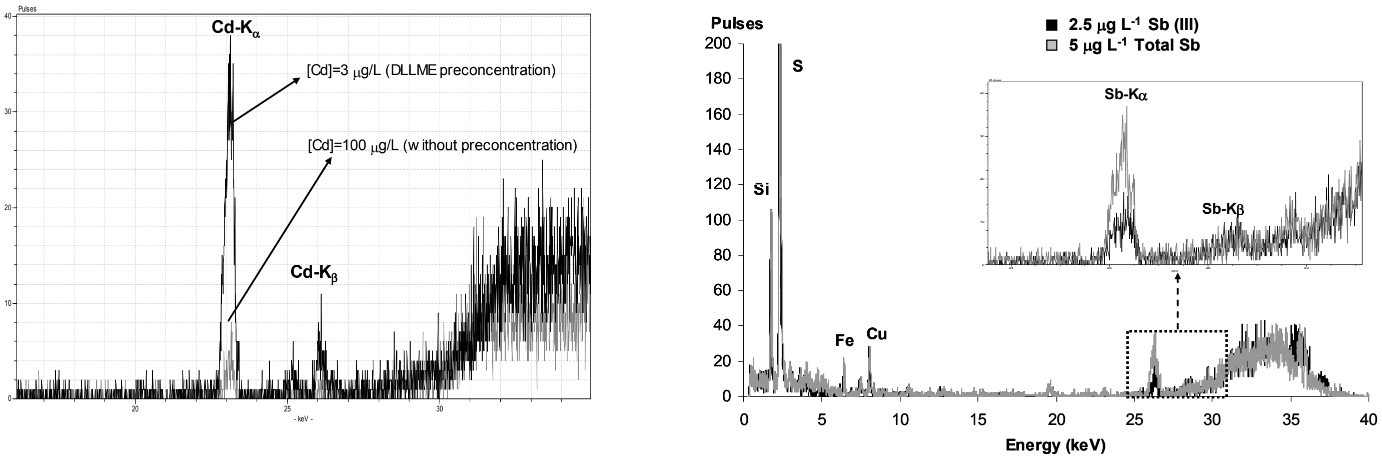

Fig. 2. (A) Comparison between TXRF spectra obtained for the direct analysis of an aqueous standard containing 100 μgL^{-1} of Cd (grey straight line) and of an aqueous standard containing 3 μg/L of Cd after the DLLME procedure (black straight line) and (B) Spectra obtained for the analysis of a river water sample spiked at 2.5 μg L^{-1} Sb(III) and 2.5 μg L^{-1} Sb(V) using the DLLME+TXRF system.

Due to the microanalytical capability of TXRF and the possibility of analysing suspensions, the use of nanomaterials (such as multiwalled carbon nanotubes, MWCNTs) as solid sorbents is also an interesting pre-concentration strategy to be combined with TXRF spectrometry. The very small particle size of MWCNTs made this solid sorbents adequate to prepare a representative suspension to be analyzed by TXRF. In a recent contribution, we evaluate the parameters affecting the extraction process (amount of MWCNTs, pH of the aqueous sample, use of a complexing agent) and TXRF analysis (volume of deposited suspension on the reflector, drying mode and measuring time) for the determination of low levels of Cd (II) and Pb (II) ions in water samples. In Figure 3, a schematic setup for the pre-concentration procedure and the benefits of using it for the determination of Cd (II) and Pb (II) ions in the low μg L^{-1} range is shown.

Under optimized conditions, the detection limits were 1.0 μg L^{-1} and 2.1 μg L^{-1} for Cd(II) and Pb(II) ions, respectively. Both of the examined elements can be determined with quantitative recoveries (ca. 100%) and with an adequate precision (RSD~ 6.0% and RSD~ 10.5% for Cd(II) and Pb(II), respectively) in different types of environmental waters [10].

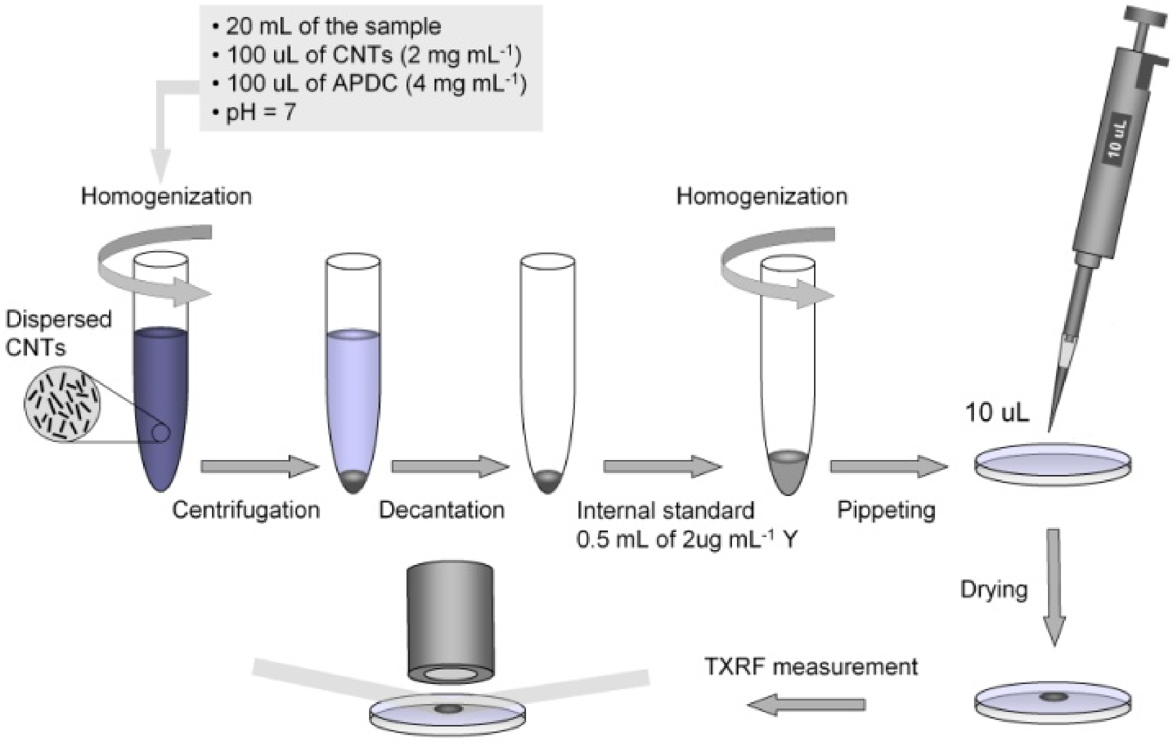

Fig. 3. (A) Schematic setup for pre-concentration procedure using MWCNTs combined with TXRF analysis and

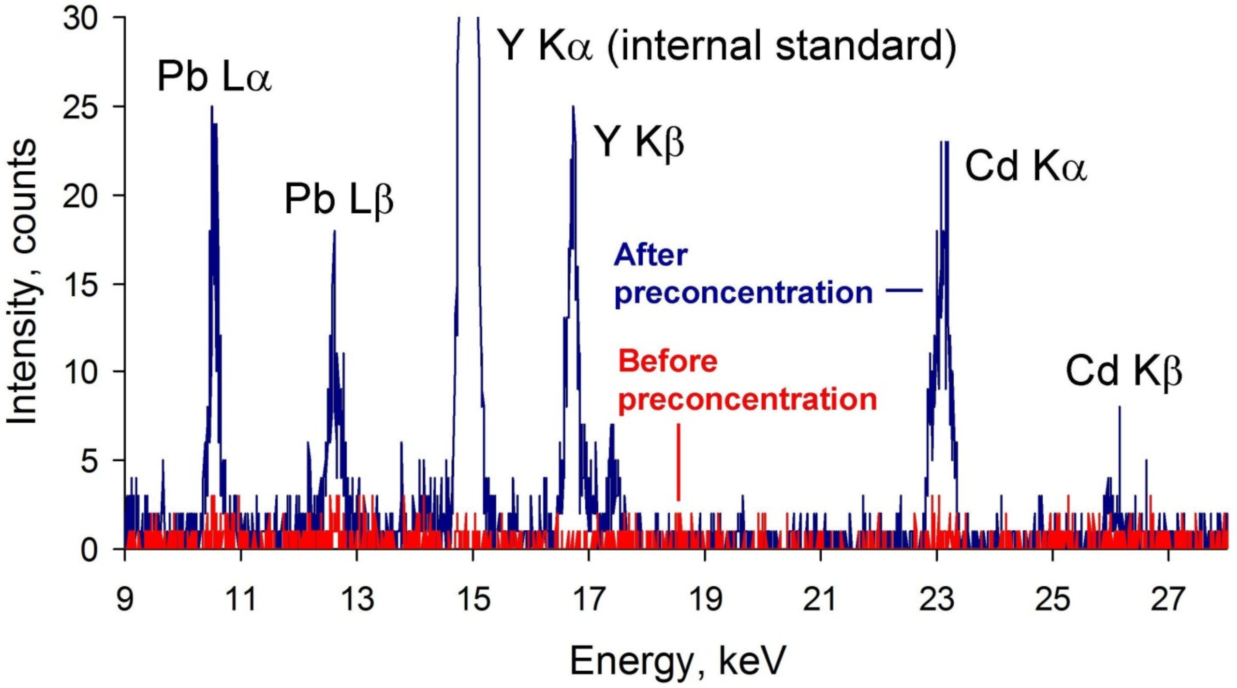

Fig. 3 (B) Comparison between TXRF spectra obtained for the direct analysis of an aqueous standard solution containing 20μg L^{-1} (red line) and after the DMSPE+TXRF procedure (blue line).

B. Application of TXRF for element determination in samples related with geochemical studies

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The selenium (Se) around volcanoes has implications for human health given the high population density close to volcanoes and the narrow range between essential and toxic Se intake. To study the Se mobility during interactions between volcanic derived acid rain and volcanic ash, new analytical approaches are required. Fresh volavailable in low mass amounts. As a result, for kinetic adsorption experiments of mass-limited samples, where aliquots have to be extracted several times in order to get the trends of Se concentration over time, an analytical technique with micro-analytical capabilities is essential.

In a recent contribution, we explored Total Reflection X-Ray Fluorescence (TXRF) spectrometry for Se determination using sorption processes on volcanic ashes as a geochemical application. Kinetic adsorption experiments using direct TXRF with as little as 10 µL solution (LOD 0.4-8 µg/L depending on the sample characteristics) showed that the anions present play a key role in the selenite adsorption on volcanic ash by competitive behaviour and/or changes in the pH conditions promoted by glass dissolution processes (see Figure 4).

Our experiments show the high potential of TXRF in such applications. Similarly, TXRF can be used as an analytical tool to study the mobility of trace elements in other geochemical studies [11].

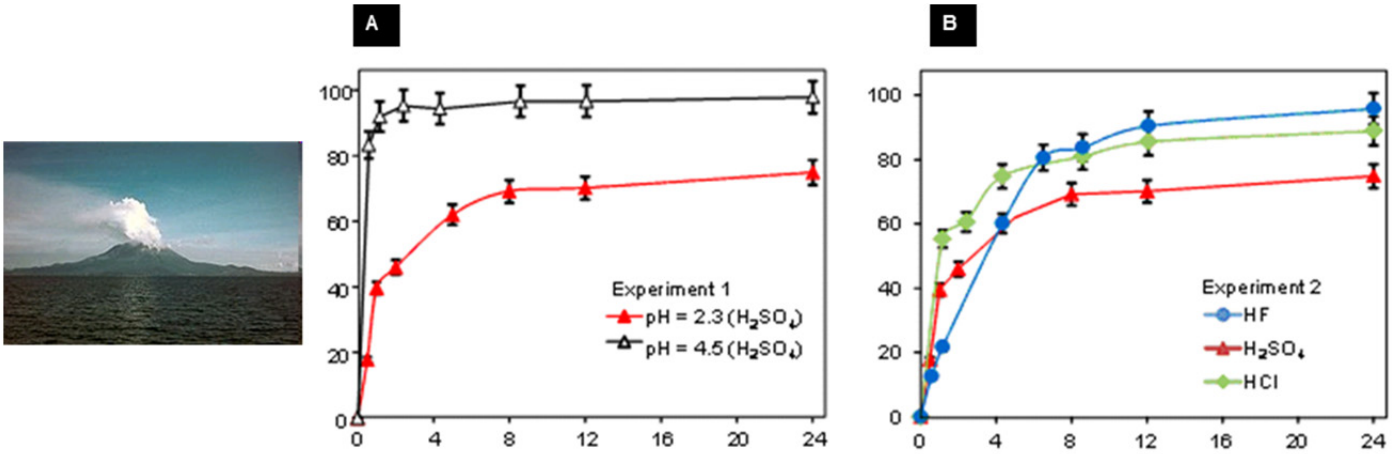

Fig. 4. Kinetics of selenite adsorption on volcanic ash from Sakura-jima volcano. (A) Experiment 1: The influence of rainwater pH on selenite adsorption. Synthetic acid rain: H_2SO_4 at pH = 2.3 and 4.5. (B) Experiment 2: The influence of competitive anions on selenite adsorption. Synthetic acid rain: diluted HF, HCl and H_2SO_4 at pH = 2.3 – 2.5.

C. *Determination of trace metals and essential elements in commercial edible clams by XRF*

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Bivalves have been widely used as bioindicators to assess coastal aquatic environments, since they can accumulate trace metals and other substances. For instance, it has been demonstrated that shellfish can accumulate trace elements up to 100 times higher than the concentration levels found in the water they live in. Iron, copper and zinc are considered important nutritional trace elements which must be part of the human daily diet to ensure normal biological functions but other elements such as Cr, Pb, As and Cd can be toxic even at low concentration levels. For this reason some organizations and agencies such as the Food and Agricultural Organization (FAO) of the United Nations stablished legal limits for metals and other contaminants in fishery products.

In a recent study, we evaluated the analytical capabilities of total reflection X-ray spectrometry (TXRF) for the determination of trace and essential elements in commercial edible clams in a simpler and economic way. We compared the direct analyisis of powdered suspensions with the analysis of the digested samples for trace determination. As it is shown in Figure 5, acceptable results were in general obtained when using the simpler sample preparation procedure (sample suspension). Moreover, the digestion procedure of the reference material did not lead to a noteworthy improvement of the accuracy of the results except for some specific elements (Zn, Se and Fe). The calculated detection limits for most elements (from 0.5 to 5 mg/kg) were also similar using both analytical methodologies. Therefore, TXRF using a suspension of the biological powdered sample can be an interesting approach for minor and trace elements determination in bivalves in a simple, fast and economic way [12].

D. *Possibilities and drawbacks of TXRF for the determination of metal residues in active pharmaceutical ingredients*

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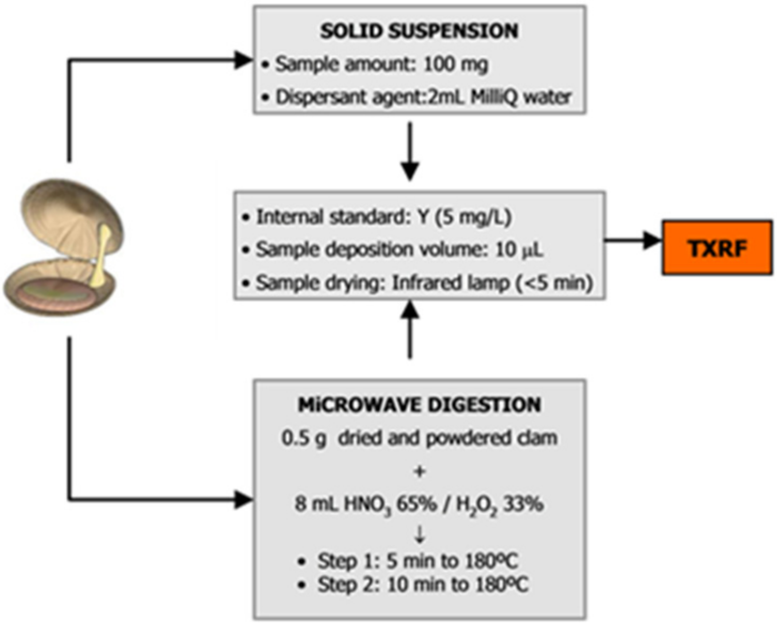
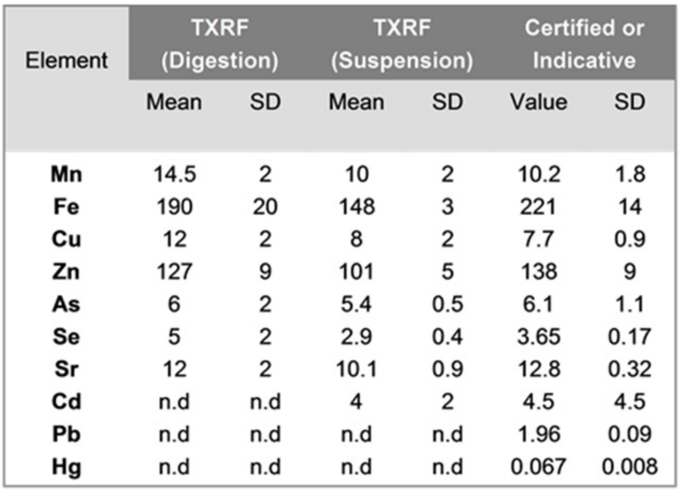
The control of metal catalysts residues (i.e., platinum group metals (PGMs)) in different stages of the manufacturing processes of the active pharmaceutical ingredients (APIs) and, especially, in the final product is crucial. For API specimens, there are strict guidelines to limit the levels of metal residues based on their individual levels of safety concern. For PGMs, the concentration limit has been established at 10 mg/kg in the API. Therefore great effort is currently being devoted to the development of new and simple procedures to control metals in pharmaceuticals.

Recently, an analytical methodology based on benchtop total reflection X-ray fluorescence spectrometry (TXRF) has been developed by our research group for the rapid and simple determination of some PGMs catalyst impurities (Rh, Pd, Ir and Pt) in different types of API samples.





Element	TXRF (Digestion)		TXRF (Suspension)		Certified or Indicative	
	Mean	SD	Mean	SD	Value	SD
Mn	14.5	2	10	2	10.2	1.8
Fe	190	20	148	3	221	14
Cu	12	2	8	2	7.7	0.9
Zn	127	9	101	5	138	9
As	6	2	5.4	0.5	6.1	1.1
Se	5	2	2.9	0.4	3.65	0.17
Sr	12	2	10.1	0.9	12.8	0.32
Cd	n.d	n.d	4	2	4.5	4.5
Pb	n.d	n.d	n.d	n.d	1.96	0.09
Hg	n.d	n.d	n.d	n.d	0.067	0.008

Fig. 5. Schematic setup for analytical methodologies used for edible clam analysis. Element concentrations (mg/kg) for the certified reference material CBW08571 (Mussel muscle tissue) after different sample treatment procedures and subsequent TXRF analysis (sample volume: 10 μL, measuring time: 1000 s, n=2).

An evaluation of different sample treatments (dissolution and digestion of the solid pharmaceutical samples) was carried out and the developed methodologies were validated according to the analytical parameters to be considered and acceptance criteria for PGMs determination according to the United States Pharmacopoeia (USP). Limits of quantification obtained for PGMs metals were in the range of 2-4 mg/kg, which is satisfactory according to current legislation. As an example, in Figure 6, TXRF spectra obtained for the direct analyses of an API dissolution (150mg/2mL MilliQ water) containing increasing amounts of PGMs is displayed.

From the obtained results it is shown that the developed TXRF method can be implemented in the pharmaceutical industries to increase productivity of the laboratory; offering an interesting and complementary analytical tool to other atomic spectroscopic methods [13].

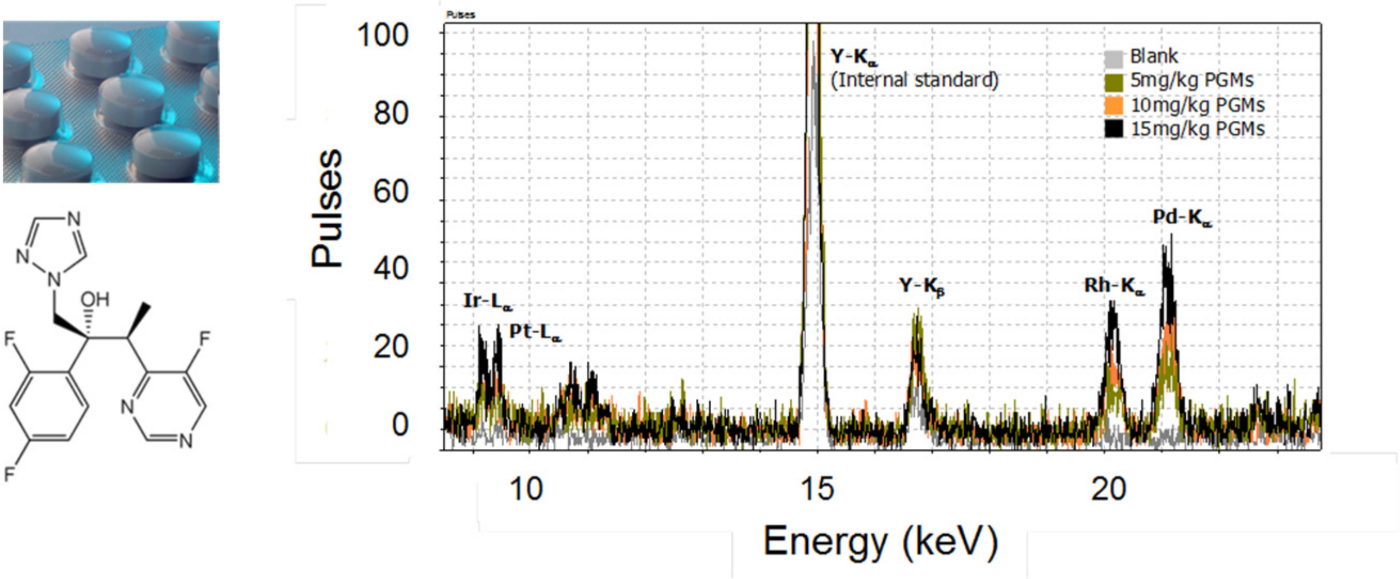


Fig. 6. TXRF spectra obtained for the direct analyses of API dissolutions (150mg/2mL MilliQ water) containing increasing amounts of PGMs.

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