IAEA International Atomic Energy Agency

XRF Newsletter

A newsletter from the IAEA Laboratories, Seibersdorf
Issue No. 23, September 2012
ISSN 1608–4632

X ray Fluorescence in the IAEA and its Member States

Activities in the IAEA XRF Laboratory

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

Preliminary results on the application of grazing incidence X ray fluorescence analysis (GI-XRF) in confocal measuring geometry for thin films characterization

Aim of the study

Grazing incidence X ray fluorescence (GIXRF) analysis is a powerful analytical tool for the characterization of thin films in terms of layer thickness and elemental composition [1-3]. In standard GIXRF measuring geometry a large area of sample, with the size of a few square millimetres, is irradiated at varying incidence angle. The analysis of the data collected in such measuring geometry can provide the average thickness and average elemental composition of layers. The problem tackled in the present work was to develop a methodology suitable for local characterization of thin film samples utilizing the depth sensitivity of incident angle variable X ray fluorescence analysis.

Experimental methodology

For the local characterization of a thin layer, with lateral resolution at the order of a few tens of micrometers, GIXRF analysis needs to be applied at confocal geometry. The in-house designed and constructed XRF spectrometer of the IAEA Nuclear Spectrometry and Applications Laboratory integrates in one set-up three measuring concepts, namely the scanning micro XRF, the confocal and transmission type of analyses (Fig. 1). It is equipped with a Mo-anode X ray tube, a monolithic polycapillary X ray lens for the exciting X ray beam focusing and three silicon drift detectors. A polycapillary conical collimator (PCCC) is attached in front of the second detector to realize a confocal geometry with an effective diameter of the confocal volume equal to about 25 micrometers (at 8.4 keV).

The motorized sample stage allows full rotational movement of the sample and all the possible translation movements (*xyz*). For the proper alignment of the incident beam with respect to the sample surface orientation, a sector angle scan was first applied rotating the sample with a step size of 0.025 degrees around the reference "zero" degree position. The reference position was found at the maximum of the transmitted beam. Measurements were performed at a certain number of incident angles in the range between 0.5 and 45 degrees, whereas at each angle a confocal (depth) scan was performed by varying the position of the sample surface versus the fixed position of the confocal probing volume. Simultaneously with the confocal measurement the micro-XRF signal was registered. Both confocal and micro-XRF signals were used for the characterization of single element bilayer thin films of Cu/Au, In/Au, Se/Au, and Au on glass surface and of a photovoltaic (CIGSe/Mo) absorber layer on glass (prepared by Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany [4]).

First results – discussion

In Fig 2 the experimental Cu-Ka and Au-La intensities obtained for analysis of a Cu/Au/glass (Cu: 199 ug/cm^2, Au: 29 ug/cm^2) thin film are plotted, as recorded by the micro and confocal detectors, respectively. The XRF intensities at variable angle have been normalized to the value at 45 degrees. It can be observed that the micro-XRF intensities exhibit a 1/sinφ1 angular dependence, whereas the confocal one (determined after integration over the depth scan positions) show a rather angle insensitive plateau (after about five degrees). This is due to the fact that in the confocal geometry the analytical signal originates from a fixed micro-volume and does not depend on the sample orientation. For the quantification of the results, the existing quantitative analytical model of confocal micro-beam XRF analysis of layered materials [5, 6], has been adapted to the measuring conditions and it was approximated by using analytical functions for the case of semi-thin film samples. The obtained results were compared with the results of combined analysis by particle induced X ray emission (PIXE) and Rutherford backscattering spectrometry (RBS) and good agreement is observed. The variable incident angle confocal XRF analysis is well suited for accurate localized depth sensitive analysis of multilayer samples. The methodology will be further developed to attain increased depth sensitivity down to the nm regime by utilizing the depth resolving power of the X ray standing wave (XSW) formed above the layer's interface during grazing incidence irradiation.

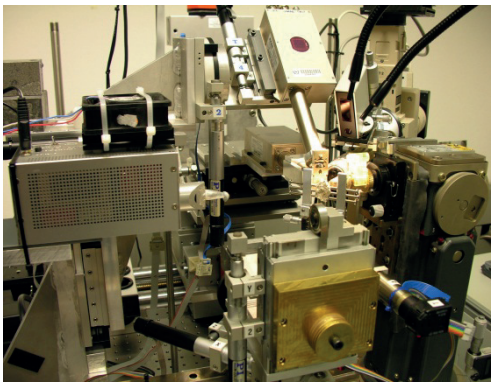


Fig. 1: *The in-house designed and constructed micro-beam scanning XRF/absorption spectrometer for comprehensive characterization of materials. Nuclear Spectrometry and Applications Laboratory, IAEA.*

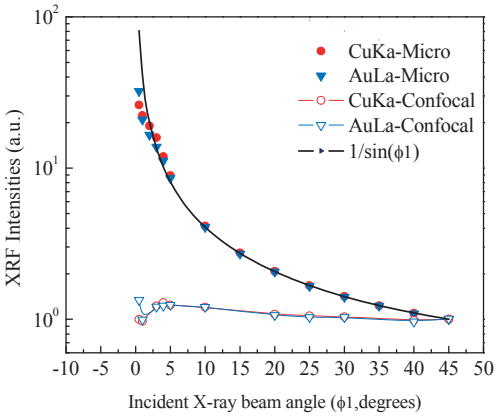


Fig. 2: *Angular dependent XRF intensities registered simultaneously in conventional micro-XRF and confocal geometry. The sample analyzed is a thin film Cu/Au/glass (Cu: 199 ug/cm^2, Au: 29 ug/cm^2). The XRF intensities are normalized with respect to their value at 45 degrees.*

References

[1] DE BOER, D.K.G., LEENAERS, A.J.G., VAN DEN HOOGENHOF, W.W., X ray Spectrometry 24, 1995, 91

[2] UNTERUMSBERGER, R., POLLAKOWSKI, B., MÜLLER, M., BECKHOFF, B., Anal. Chem., 83 (22), 2011, 8623

[3] C. STREECK, C., et al., Nucl. Instr. Meth. Phys. Res. B 268, 2010, 277-281.

[4] CABALLERO, R., et al., Prog. Photovolt: Res. Appl. (2012), in press, DOI: 10.1002/pip.1233

[5] MALZER, W., KANNGIESSER, B., Spectrochim. Acta B 60, 2005, 1334-1341.

[6] MANTOUVALOU, I., MALZER, W., SCHAUMANN, I., LUHL, L., DARGEL, R., Anal. Chem. 80, 2008, 819-826.

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

Contributors to the work:
D. Wegrzynek[1], A. G. Karydas[2,3], M. Bogovac[2,4], R. Padilla-Alvarez[2] and A. Markowicz[2]

[1]*AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, 30-059 Krakow, Poland*
[2]*Nuclear Spectrometry and Applications Laboratory, IAEA Laboratories, A-2444, Seibersdorf, Austria*
[3]*NCSR Demokritos, Institute of Nuclear Physics, 15310 Athens, Greece*
[4]*Rudjer Boskovic Inst, Zagreb 10002, Croatia*

Acknowledgement
The Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany and Cornelia Streeck for the provision of thin film samples.

Trace element concentration as a tool for predicting tolerance to salinity in rice varieties

Salinity stress, which usually occurs in arid, semi-arid regions and in coastal regions by seawater contamination or subjected to inadequate irrigation and/or draining, is a major environmental constraint to the growth and the crop plant productivity throughout the world.

The IAEA Plant Breeding and Genetics Laboratory carries out several investigations aimed at obtaining and characterizing improved varieties of different cultivars, including rice. Rice genotypes differ in their adaptation to NaCl stress and a different capability in the accumulation of various ions in plant could be used as a screening tool for selecting salt tolerant genotypes from germplasm populations.

A greenhouse hydroponic experiment was conducted to evaluate six rice genotypes (Pokkali, Nona Bokra, Bicol, STDV, Taipei309 and IR29) of known different degrees of tolerance to salinity in order to identify suitable biochemical traits as selection criteria for cultivars or mutagenic population for producing salt tolerant mutants. One month old seedlings were subjected to 0 and 10dS/m NaCl salt stress for two weeks. Growth performance parameters such as fresh weight, salt tolerance index (dry matter shoot treated / shoot non-treated) and number of tillers were measured as salt response to confirm the classification of the varieties into three groups: susceptible, medium tolerant and tolerant to salinity stress.

Shoots and roots of samples (treated and non-treated) of the six varieties were measured with an XRF spectrometer using x ray tube and secondary targets for selective excitation of different groups of elements. The weight fractions of 21 elements were determined using a modified Compton correction quantification method.

From the 21 elements determined by EDXRF, only the elements measured with a relative uncertainty better than 10% were selected for statistical interpretation. The results were rescaled to log-10 values, and the extracted by principal component analysis (PCA) components were rotated using the Varimax method, in order to provide greater agreement between axes and variable correlation, thus allowing a better interpretation of the observed differences in elemental contents due to salinity stress conditioning. The coefficients of each of the original variables (elemental concentration) in extracted principal components

(principal component loadings) provided information for the identification of correlated variables and their contribution to the variability in the data set.

The tendency in the variations of concentrations of eleven elements in the different genotypes depending on duration of salt treatment was explored. The two first components accounted for 92% of variability of the data set. The largest variability in the data set, nearly 82%, is accounted for by a group of twelve elements. The elements Na, Cl, Fe, Ca, Cu and Zn have a high loading in the first component whereas K, Mg, S have larger contributions to the second component.

The results of principal component analysis are presented in Figure 1. Each point in Figure 1 represents the results for individual samples, which are in turn labelled according to the tolerance to salinity (S – susceptible, M- moderate, T- tolerant genotypes) and duration of the salt stress treatment (T-DUR) at different days (0, 12 and 16) after starting the treatment. Continuous oval embraces the untreated samples and dashed oval the treated samples.

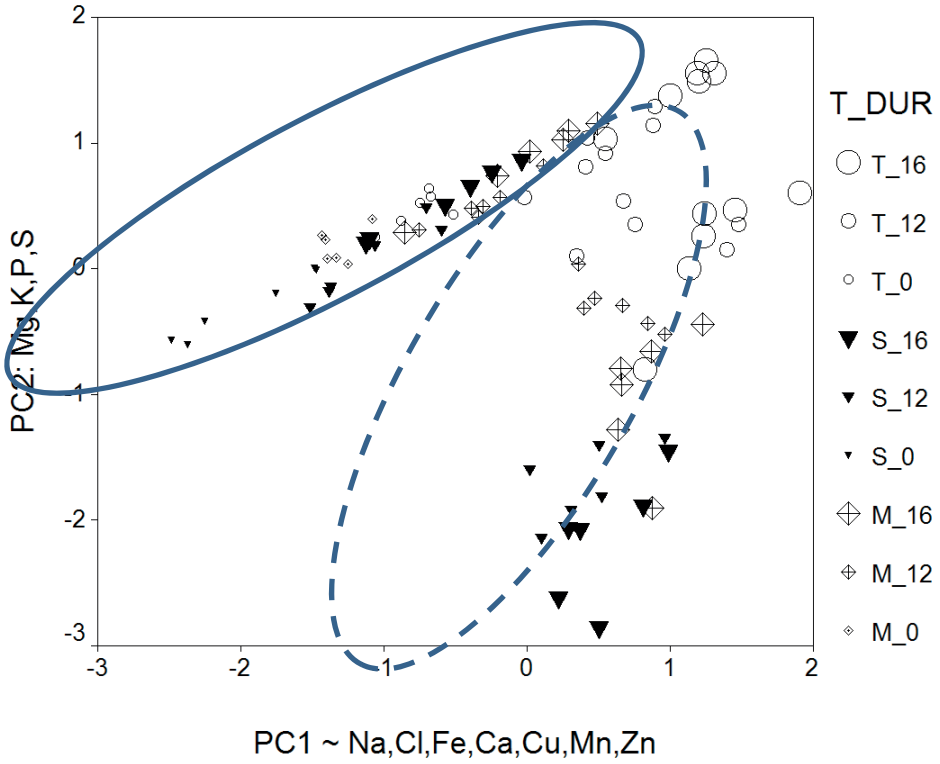


Fig. 1. Observed differences in the samples according to their scores in the PC space.

The ordination of the samples in the PC space reveals two groups corresponding to the exposure to salt levels: treated samples appear clustered in the lower right area of the graph whereas untreated appear in the upper left area.

The results obtained for the samples that underwent saline treatment show that there is a decrease in the intake of Mg, K, P and S, as compared to the non-treated samples. Such decrease is more pronounced for the susceptible varieties, whereas tolerant ones exhibit a larger intake of these elements. There are neither big differences in the contents of the elements between 12 and 16 days of treatment within a class of varieties. The inspection of the results obtained for the control samples reveal that the accumulation of the elements increases with time, and tolerant varieties have comparatively larger contents than moderate-tolerant and that susceptible ones at any the three intervals of sampling (0, 12 and 16 days). It can be assumed that tolerance to salinity can be correlated with a better capability of accumulating essential elements.

These observations suggested assessing the feasibility of classifying the varieties in three categories, based on the contents of essential elements in the shoots of one month old seedlings. Linear discriminant analysis is a method commonly used in statistics to find linear combinations of property values allowing

separating two or more classes of objects. Canonical discriminant analysis aims to find linear and uncorrelated functions defining k-1 canonical functions that allow achieving a better separation of k expected classes. CDA also allows calculating the probability of belonging to a particular class.

Figure 2 shows the result of such classification. With the exempt of two samples, and irrespective of the time of collection of the samples (30, 42 or 48 days of growth), for all samples the probability of belonging to its assumed category exceeded 95%. The advantage of using such a procedure is that the classification of each new variety in principle can be established by calculating the probability to belong to any of the established groups. The model can be improved by analysing more varieties.

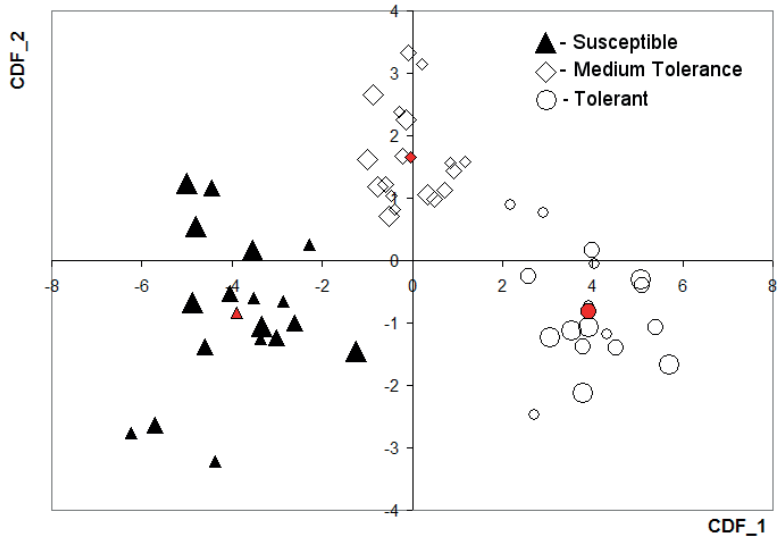


Fig. 2. Canonical discriminant classification into three groups using the weight fractions measured in the control samples.

Contributors to the work:
R. Padilla-Alvarez[1,2], S. Bado[3], A.G. Karydas[1], A. Markowicz[1], E. Chinea-Cano[1]

[1]*Nuclear Spectrometry and Applications Laboratory, NAPC, International Atomic Energy Agency*
[2]*on leave from Centro de Aplicaciones Tecnológicas y Desarrollo Nuclear, Havana, Cuba*
[3]*Plant Breeding and Genetics Laboratory, NAFA, International Atomic Energy Agency*

For more information please contact R. Padilla Alvarez (R.Padilla-Alvarez@iaea.org)

Support to Technical Cooperation projects

Regional Training Course (RTC) on Advanced Characterization of Cultural Heritage Artefacts Using Nuclear Analytical Techniques, Tirana, Albania, 14-18 May 2012

The RTC was organized under a regional Technical Cooperation project on Enhancing the Characterization, Preservation and Protection of Cultural Heritage Artefacts (RER0034) and was attended by around 40 participants from Albania, Azerbaijan, Bulgaria, Croatia, Cyprus, Greece, Hungary, Latvia, The Former Yugoslav Republic of Macedonia, Malta, Poland, Romania, Serbia, Slovenia, Tajikistan, Turkey and Ukraine. The purpose of the RTC was to provide participants with technical knowledge and practical demonstrations of the advanced nuclear techniques applied for the characterization of cultural heritage objects. The underlying principles, advantages and limitations as well as selected applications will be presented. Emphasis was on X ray fluorescence (XRF), TXRF, micro XRF, portable XRF spectrometers, in situ characterization of cultural heritage (CH) objects, Raman spectroscopy, fourier transform infrared spectroscopy (FTIR) including data analysis and data interpretation (see Fig. 1).

Fig. 1. Lecture during the Regional Training Course.

The RTC was attended by Ms. Zhulieta Harasani, National Professional Officer, UNESCO, Antenna Office in Albania who delivered a lecture on the activities of UNESCO in the context of protection of cultural heritage objects. Possible future cooperation between the IAEA and UNESCO in the field of cultural heritage with emphasis on the advantages and possible contribution of nuclear analytical techniques was also discussed.

One day of the RTC was dedicated to a technical visit to the Onufri Museum and Saint Mary Bllacherna Church in Berat. During the visit a portable XRF spectrometer was used for in situ characterization of wall pigments (see Fig. 2).

Fig. 2. In-situ characterization of wall pigments using a portable XRF spectrometer.

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

Regional Training Course (RTC) on Air Sampling and Nuclear Analytical Characterization of Atmospheric Particulate Matter (APM) Including Quality Assurance/Quality Control (AQ/QC), Zagreb, Croatia, 4-8 June 2012

The RTC was organized under a regional Technical Cooperation project on Supporting Air Quality Management (RER/1/008) and was attended by 28 participants from Albania, Bosnia and Herzegovina, Bulgaria, Croatia, Cyprus, Greece, Hungary, Kazakhstan, Lithuania, The Former Yugoslav Republic of Macedonia, Republic of Moldova, Montenegro, Poland, Serbia, Tajikistan, Turkey and Ukraine (see Fig. 1).

Fig. 1. Participants of the RTC (credit: K. Sega).

The programme of the training covered monitoring, legislation and European standards related to APM, sampling of APM, quantification of EDXRF, QA/QC in EDXRF analysis of PM10 fraction of APM, equivalence to the reference methods, EDXRF vis a vis data quality objectives of the EU Directives, sampling of APM, filter conditioning and weighing, ion beam analysis techniques for APM, characterization of individual aerosol particles by using nuclear microprobe, data handling and statistical analysis of analytical data. The lectures were supplemented by practical demonstrations of sampling and analytical equipment (see Figs 2 and 3).

Fig. 2. Demonstration of sampling equipment, Institute for Medical Research and Occupational Health, Zagreb (credit: K. Sega)

Fig. 3. Visit to the XRF Laboratory, Institute for Medical Research and Occupational Health, Zagreb (credit: K.Sega).

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

X ray Fluorescence in Member States

Australia

Accelerator Based Ion Beam Analysis techniques Contribute to a Better Understanding of Long Range Fine Particle Pollution in Asia

Contributors: D. Cohen[1], E. Stelcer[1], J. Crawford[1], V. Thu Bac[2]

[1]*Institute for Environmental Research, Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee DC, NSW, 2232, Australia.*
[2]*Institute of Nuclear Sciences and Technology, PO Box 5T-160, Hanoi, Vietnam.*

Abstract:

Fine-particle pollution in large populated Asian cities can be very high compared with internationally accepted health goals. Much of this fine-particle pollution is produced by motor vehicles, fossil-fuel combustion, industrial processes and even windblown soils from desert regions. As part of a long term project in the Asian region with support from the IAEA, ANSTO has been using nuclear techniques not only to characterize fine-particle pollution, but also to quantify their sources and origins within Vietnam.

Fine particles in ambient air are defined as those particles with aerodynamic diameters less than 2.5 µm in diameter. Particles in this size range can be directly absorbed into the blood stream from the lungs, are most efficient at absorbing and scattering visible light and can travel thousands of kilometres from their original source emission points. A full characterisation of these particles, their sources and their origins will help regulators better understand and hence control air-pollution issues in their countries.

In 2002, the International Atomic Energy Agency (IAEA) established a Regional Cooperative Agreement (RCA) with 14 member states, including Australia, Bangladesh, China, India, Indonesia, the Republic of Korea, Malaysia, Mongolia, New Zealand, Pakistan, Sri Lanka, Thailand and Vietnam, to monitor, characterize and quantify sources of fine-particle pollution in each of these countries. This is a unique study as each country uses the same stacked filter samplers and has sampled at the same times each week for at least 5 years.

The data obtained is unique for the region and will be picked up by a range of environmental agencies controlling and managing air pollution in each of the Member States as well as non-government organizations like the World Bank and the Asian Development Bank. It may be used to correlate medical conditions related to lung disease and

heart conditions with high pollution days, with sources of air pollution and with hospital admissions. Even for relatively pollution free countries like Australia and New Zealand estimates show that generally more people are dying prematurely each year from air pollution related issues than are killed on the roads. In these Asian regions the air pollution levels are often above WHO recommended guidelines much of the time and hence the health effects can be much more significant.

At ANSTO we analyse each filter using four nuclear techniques (Particle induced X ray and gamma ray emission and nuclear scattering and recoil methods) for between 20-30 different chemical species [1, 2]. This broad range of chemical species, together with the long-time series and extensive area covered by the data collection allowed a comprehensive dataset of source fingerprints and source contributions to be compiled across a very broad area of Asia [2,5-11]. The complete IAEA/ RCA dataset can be accessed at the RCA WEB site together with other fine particle datasets on the ANSTO WEB page [3].

The current IAEA database contains more than 8400 individual sampling days. The average fine particle mass for each of the 14 Member States is shown in the box and whisker plot of Fig. 1 for the study period from 2002 to 2008. The current US EPA (Environmental Protection Agency) fine-particle health goal is 15 μg/m^3 (green horizontal line) annual average and 35 μg/m^3 24 h maximum (red horizontal line). Clearly many countries exceed these two goals for both the annual and the 24 hr goals.

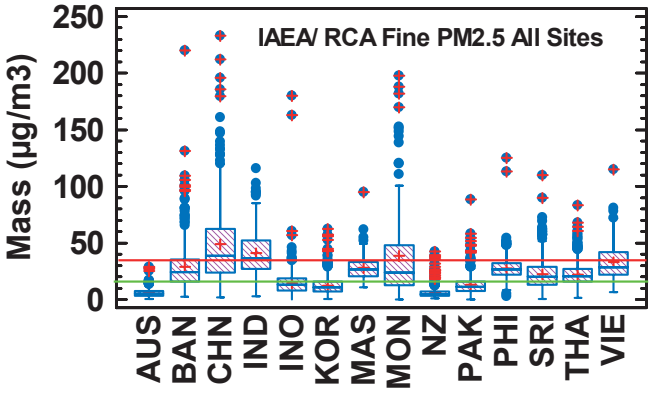


Fig 1. . Box and whisker plot of average fine particle masses for 14 Asian countries between 2002-08. (+) are means, horizontal bars are the medians. Taken from the IAEA/ RCA dataset [3].

Statistical techniques such as positive matrix factorization [6] can be applied to the database to obtain source fingerprints and their contributions to the total fine-particle mass. This has been done with the data collected at the Hanoi sampling site in Vietnam and two sources of windblown soils and sulphur emissions from coal fired power stations have been studied [8-9]. Fig. 2 shows the major desert regions and the larger coal-fired power stations in eastern China, north of Hanoi. It is well known that the Taklamakan and Gobi desert regions produced large dust storms between March and April each year which may travel across the Korean peninsula and Japan [5].

.

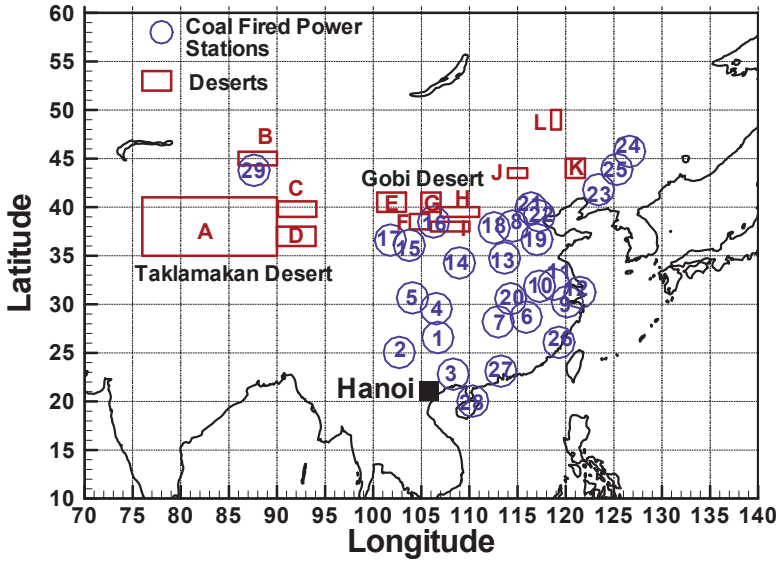


Fig. 2. Location of key desert and major coal fired power plants in eastern Asia. Coal fired power stations numbered 30 to 33 are within the black square marking the Hanoi site.

Airborne soils and desert dusts can arrive at Hanoi by wind trajectories extending back over inland areas of northern and western China and Mongolia [5]. They estimated that long range transport accounted for 50%, 34% and 33% of the fine mass in trajectories from the north over inland China, from the north-east over the east China sea and from the south-west over the Indochina peninsula, respectively.

The Taklamakan desert region is a regular known source of dust storms, especially in springtime. Resting in the Tarim Basin, between the mountain ranges of the Tien Shan in the north and the Kunlun Shan in the south, the Taklimakan desert is one of the world's largest shifting sand deserts, with dunes towering to as much as 200 meters. Dust storms also frequently arise from the Gobi Desert and other deserts regions in northern China. The Taklamakan and Gobi Desert regions are shown in Fig. 2. The boxes (labelled A to L) represent the major desert systems within these two major dust regions.

By applying standard back trajectory techniques [6] we can determine source 'fetch regions' for major soil and coal events from the Hanoi site. Figs 3 and 4 show two such seven-day back trajectories for a high soil event on 5 March 2008 and a high coal event on 10 February 2008 at the Hanoi site.

These back trajectory methods can be extended to look at all extreme events (over a long period of time) whose back trajectories intersect with known source regions such as the Taklamakan or Gobi deserts or the coal-fired power stations in eastern China.

The symbols within the desert regions (boxes) of Fig. 3 and the coal fired power stations open circles) of Fig. 4 represent the number of trajectory intersections that impacted the Hanoi site between April 2001 and December 2008 with soil levels above 6 µg/m^3 and coal levels above 30 µg/m^3.

Clearly the Gobi and Taklamakan deserts impact the Hanoi site as do several major coal-fired power stations in eastern China. These source sites represent long range transport of fine particle pollution some hundreds and even thousands of kilometres into Hanoi.

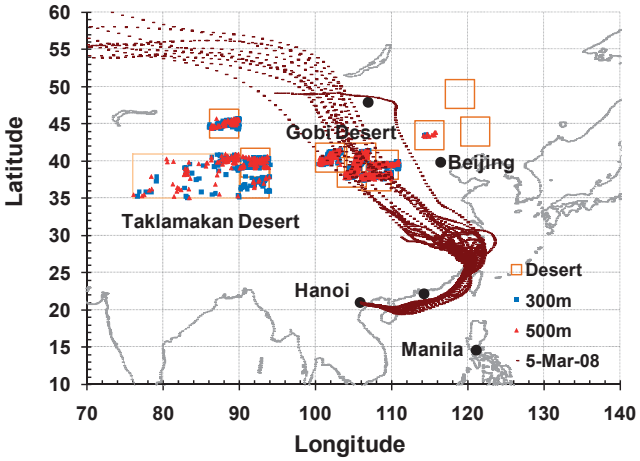


Fig. 3 Back trajectory plots and intersections for extreme Soil events between 2001-08.

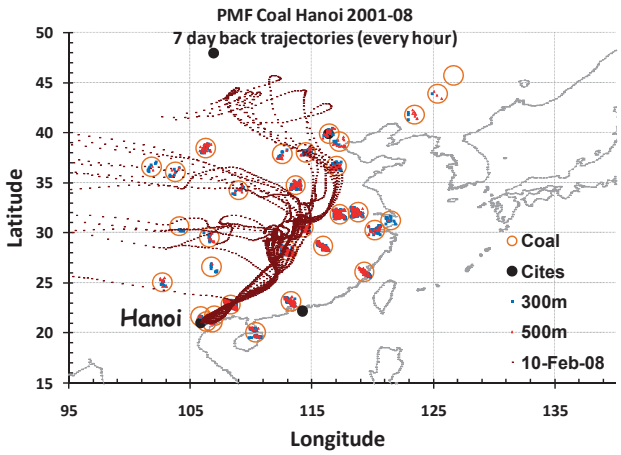


Fig. 4. Back trajectory plots and intersections for extreme Coal events between 2001-2008.

Table 1 shows the number of 7 day back trajectory intersections per cell for the top 10 contributing desert regions defined in Figs 2 and 3. No back trajectories for the study period intersected with the Horqin and Hulun Buir sandy desert regions far to the north east of Beijing (K and L boxes of Fig. 2).

TABLE 1. The top 10 desert dust sources in eastern China and their contributions to the *soil* fingerprint and their distances from the Hanoi sampling site.

#	Top 10 Soil Sources	Number of 7 Day Trajectory Intersections	*Soil* Contributions by % Trajectory Intersections	Distance from Hanoi (km)
I	Mu Us sandy	376	18.7	1,890
E	Badain Jaran	323	16.1	2,190
F	Tengger	310	15.4	1,950
H	Qubqi	291	14.5	2,080
G	UlanBuh	219	10.9	2,160
A	Takalmakan	154	7.7	2,910
C	Kumtaq	141	7.0	2,460
B	Gurban Tonggut	133	6.6	3,120
D	Qaidam	50	2.5	2,210
J	Otindaq sandy	12	0.6	2,640

The top five desert sites, shown in Table 1, contribute 76% of all hourly back trajectory intersections for extreme *soil* event days during the study period. These five sites ranged in distance from 1800 to 2200 km from Hanoi and were generally located around the central Gobi desert region some 1000 km west of Beijing.

Table 2 shows the top ten contributors to extreme *coal* source intersection events shown in Fig.4. The three closer Vietnamese coal fired power plants at Pha Lai (30), Na Duong (33) and Uong Bi (31) were in the top ten as expected but contributed less than 15% to the total number of back trajectory cell intersections. The main contributor was the closer Guangxi site (22%) only 320 km to the north-east of Hanoi, followed by more distance Hunan (13%), Hubei (8.4%), Anhui (6.4%), Jiangxi (5.5%) and Jiangsi (4.3%) sites between 1000 and 1800 km to the north-east of Hanoi contributing between 5% and 13% each. Other more distant sites also had the potential to contribute to the total *coal* factor at the Hanoi site but only at the few percent level and only on extreme event days.

TABLE 2. The top ten coal fired power station sources in eastern China and northern Vietnam contributing to the coal fingerprint and their distances from the Hanoi site.

#	Top 10 Coal Sources	Number of 7 Day Trajectory Intersections	Coal Contributions by %Trajectory Intersections	Distance from Hanoi (km)
3	Guangxi	660	22.2	320
7	Hunan	370	12.5	1,090
8	Hubei	250	8.4	1,360
10	Anhui	191	6.4	1,650
30	PhaLai	179	6.0	50
6	Jiangxi	160	5.4	1,325
33	NaDuong	159	5.4	140
9	Jiangsu	129	4.3	1,770
27	Guangdong	98	3.3	800
31	UongBi	98	3.3	100

Figure 4 also shows the twenty four hourly HYSPLIT back trajectories for 10 February 2008 and demonstrates that 8 different *coal* fired power stations in south-eastern China some 500 km to 2000 km to the north-east of Hanoi were associated with this event. This was a clear demonstration of long range transport of $PM_{2.5}$ pollution from Chinese coal fired power stations into Hanoi.

This work demonstrates that the large datasets generated by the use of nuclear techniques provide

a rich source of information on fine particle pollution, its sources and its transport over many hundreds of kilometres.

Acknowledgements

We would like to acknowledge the help of staff at the Vietnamese Institute of Nuclear Sciences and Technologies and the International Atomic Energy Agency RCA Programme for financial assistance and support throughout this work.

References

[1] COHEN, D.D., STELCER, E., HAWAS, O., GARTON, D., IBA Methods for Characterisation of Fine Particulate Atmospheric Pollution: A local, regional and global research problem. Nuclear Instruments and Methods in Physics Research, Section B 219-220, (2004) 145-152.

[2] COHEN, D.D., GARTON, D., STELCER, E., HAWAS, O., 2004b. Accelerator based studies of atmospheric pollution processes. Radiation Physics and Chemistry 71, 759-767.

[3] IAEA/ RCA WEB site is available at: http://www.rcaro.org other fine particle datssets can also be access from the ANSTO WEB page at: http://www.ansto.gov.au/research/institute_of_environmental_research/science/accelerator_science/ion_beam_analysis/publicationspostersbrochures

[4] PAATERO, P., TAPPER, U., Positive Matrix Factorisation: A non-negative factor model with optimal utilisation of error estimates of data values, Environmetrics Vol 5 (1994) 111-126.

[5] COHEN, D.D., et al., 2004a. Multielemental analysis and characterisation of fine aerosols at several key ACE Asia sites. Journal of Geophysical Research, 109 (2004) D19S12, doi:10.1029/2003JD003569.

[6] DRAXLER, R.R., ROLPH, G.D., 2003. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/ready/hysplit4.html). NOAA Air Resources Laboratory, Silver Spring, MD.

[7] COHEN, D.D., et al., 2009. Fingerprinting and source apportionment of fine particle pollution in Manila by IBA and PMF Techniques; A 7 year study. X□ray Spectrometry 38, 18□25.

[8] COHEN, D.D., CRAWFORD, J., STELCER, E., BAC, V.T., 2010a. Characterisation and source apportionment of fine particulate sources at Hanoi from 2001 to 2008. Atmospheric Environment 44, 320□328.

[9] COHEN, D. D., CRAWFORD J., STELCER E., THU BAC V., 2010b. Long Range Transport of Fine Particle Windblown Soils and Coal-fired Power Station Emissions into Hanoi between 2001 to 2008. Atmos. Environ., 44, 3761-3769.

[10] COHEN, D.D., STELCER E., GARTON D., CRAWFORD J., 2011. Fine Particle Characterisation, Source Apportionment and Long Range Dust Transport into the Sydney Basin: A long term study between 1998 and 2009. Atmospheric Pollution Research 2 (2011) 182-189.

[11] COHEN, D.D., CRAWFORD, J., STELCER, E., ATANACIO, A., 2012. A new approach to the combination of IBA techniques and wind back trajectory data to determine source contributions to long range transport of fine particle air pollution. Nucl. Instru. Methods in Physics Research B273, 186-188.

Ghana

The Use of XRF for Contaminated Site Assessment in Ghana

EDXRF has proven to be a versatile tool in assessing the levels of heavy metal contamination using surface soil samples. Over the past years the X ray laboratory has been busy with studies relating to contamination assessment. Following is a report on two such studies.

1. Identification and evaluation of Potentially Contaminated Sites in Tema, Ghana

Contributors: L. Abra-Kom Nyaaba[*1], I. J. Kwame Aboh[2], A. Bamford[1], F.G. Ofosu and S.M. Atiemo[2]
[1] *Graduate School of Nuclear and Allied Sciences, University of Ghana, Legon.*
[2] *National Nuclear Research Institute, Ghana Atomic Energy Commission*

The substantial improvement in the well-being of the world's population in the last century was largely driven by unprecedented scientific and technological progress. However, the economic processes and the scientific and technological progress that have underpinned these positive developments have been accompanied by significant negative externalities (adverse spill-over effects), which have continually posed major risks to human health, the environment and overall sustainable development. A site is generally considered contaminated when one or more contaminant concentrations exceed the regulatory criteria. Site investigation, comprising preliminary site investigation (PSI) and detailed site investigation (DSI), provides valuable information on a site, including: the nature and location of contaminants with respect to the soil and groundwater table, potential pathways for contaminant migration, the location of nearby sensitive receptors and the potential for direct human exposure to the contaminants [1]. Land degradation has become a major environmental issue in recent years because elevated concentrations of heavy metals in soils have potential long term environmental and health consequences (see Fig. 1). Heavy metals are persistent and are cumulative in the environment. Current and historic land use can provide important clues to the nature of the contamination and the types of contaminants that could be present [2].

Fig. 1. Contaminated site.

The objectives of the study were to:

- Identify potentially contaminated sites in Tema particularly, industries, playgrounds and workshops;
- Characterize heavy metal pollution in soils from selected identified contaminated sites;
- Use pollution load index (PLI) to rate the contaminated sites.

Surface soil samples were collected from the identified potentially contaminated sites. The sites are shown in Fig. 2.

The samples were placed in ziplock bags and transported to the Laboratories of Ghana Atomic Energy Commission where the elemental concentrations were evaluated. The subsoils were first sieved with 200 μm mesh size sieve to remove extraneous materials and pulverized then pelletized. The elemental evaluation was done by the use of the energy dispersive X ray florescence technique [3].

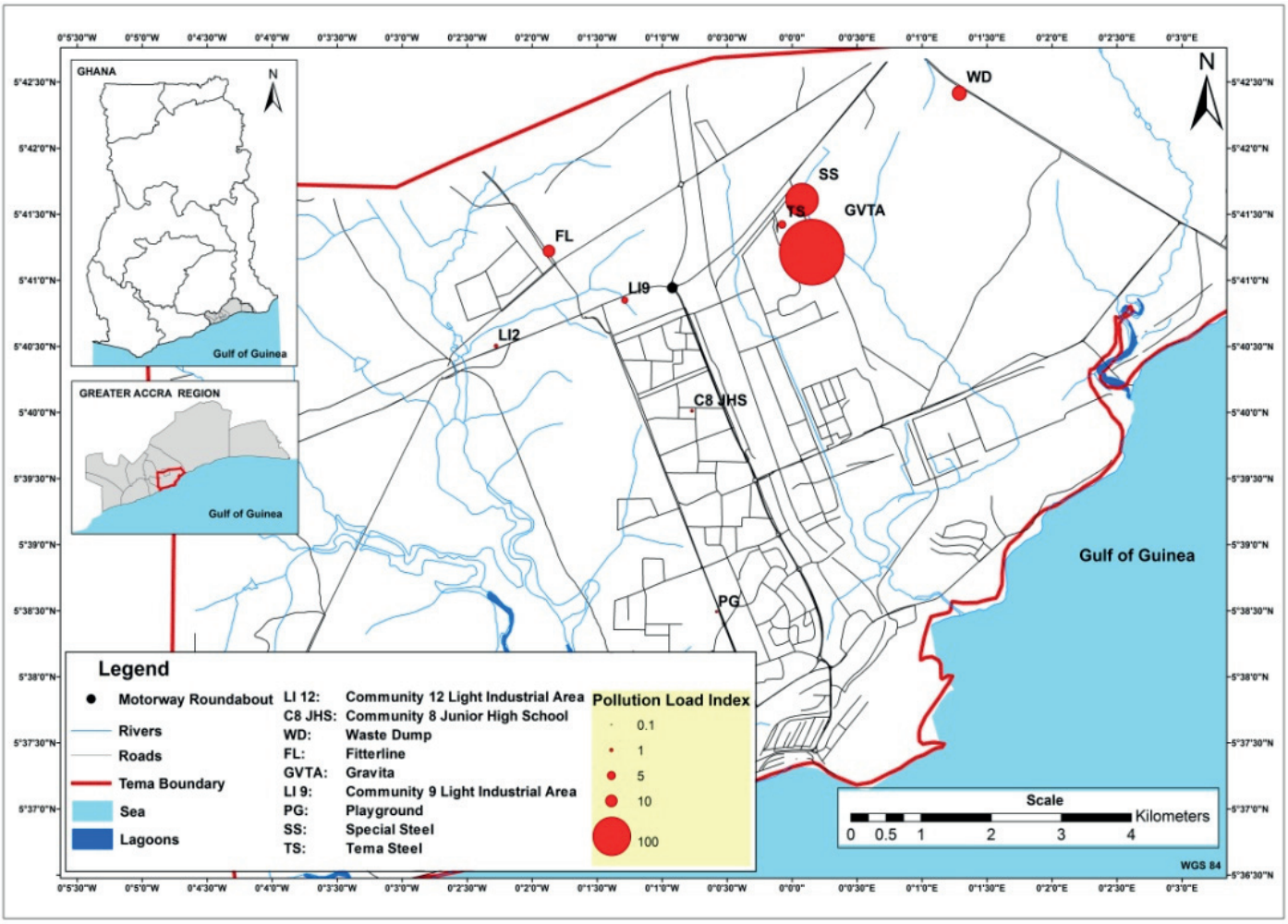


Fig. 2. Sampling sites.

Results and discussion

The concentration of zinc ranged from 20-1290 mg/kg. Lead follows with values ranging from 8.8-4000 mg/kg. The highest concentration of 4000 mg/kg was recorded at the ULAB recycling plant. Mercury was detected at two sites; a steel processing plant and the municipal waste dump at concentrations of 9.2 mg/kg and 0.15 mg/kg respectively. At the other seven locations the mercury concentrations were below the detection limits of 0.05 mg/kg. The average value of metal concentrations are Cd=5.7 mg/kg, Cr=51.5 mg/kg, Ni=31.9 mg/kg, Pb=591.2 mg/kg, Cu=102.5 mg/kg, As =7.8, Zn=736.4 mg/kg, Hg= 4.7 mg/kg (see Fig. 3). The playgrounds recorded the lowest concentrations of the metals of interest.

The concentrations were in the following order: Pb>Zn>As>Co>Cu>Hg>Cr>Ni. The mean concentration of the heavy metals at the sites exceeded the action levels of the New Dutch List.

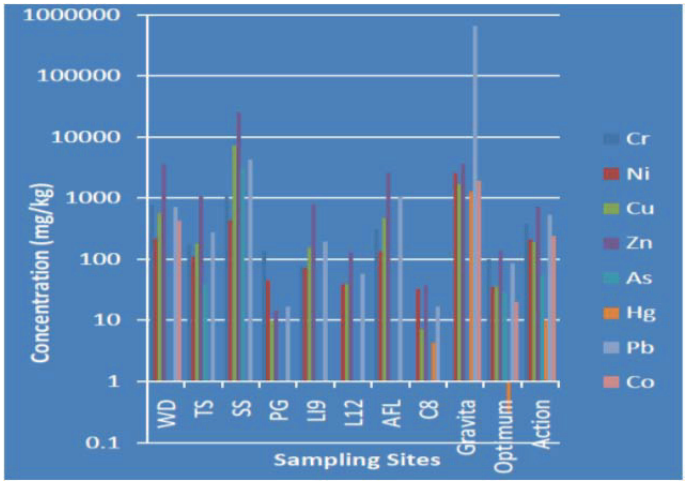


Fig. 3. Elemental concentrations at different sampling sites.

The PLI is aimed at providing a measure of the degree of overall contamination at a sampling site. The PLI ranged from 0.49-289.22. Based on the PLI the ranking of sites in terms of contamination is as follows: Gravita>SS>WD>AFL>TS>LI9>L12>C8>PG. The PLI of C8 and PG were less than 1 which denotes perfection, i.e., no contamination.

At L12 the PLI was 1.19 almost at the base line level of 1. This implies that there is contamination but the soil quality is close to the baseline level of 1. At the other sites (Gravita, SS, WD, AFL, TS, and LI9) the PLIs were greater than 1 indicating strong signs of pollution or deterioration of site quality (see Fig. 4).

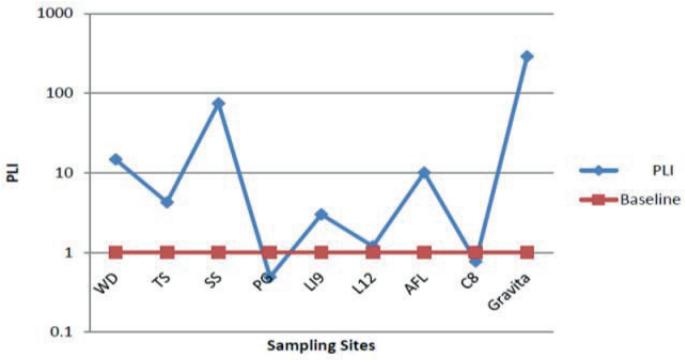


Fig.4. Pollution load index for different sampling sites.

Conclusion

Industrialization and urbanization in Tema have contributed to the contamination of soils by heavy metals known to be dangerous to the environment and human health. This study has revealed high levels of contamination in the selected sites. There is the need to conduct detailed site investigation to determine the levels of percolation of the contaminants into groundwater. Other possible contaminated sites should be investigated in order to obtain more data for possible modeling.

Acknowledgements

The authors are grateful to the National Nuclear Research Institute, Ghana Atomic Energy Commission- Accra, for providing Energy Dispersive X ray Florescence (EDXRF) facilities for this work.

References

[1] UNIDO, 2010. Persistent organic pollutants: contaminated site investigation and management toolkit (www.unido.org).

[2] NYAABA, A-K. L., 2011 Determination of heavy metal pollution in soils from selected contaminated sites in Tema, Ghana. M. Phil thesis presented to the University of Ghana.

[3] ATIEMO, S.M., OFOSU, F.G., ABOH, I.J.K. and YEBOAH P.O., 2010. Determination of Heavy Metals and Human Health Risk Assessment of Road Dust on the Tema Motorway and Tetteh Quarshie Interchange in Accra, Ghana. *Journal of Ghana Science Association*, 12. 2. 76-85.

2. Estimation of Heavy Metals Contamination at Agbogbloshie E-scrap Yard Using EDXRF Technique

Contributors: S.M. Atiemo, F.G. Ofosu, I.J. Kwame Aboh,
National Nuclear Research Institute, Ghana Atomic Energy Commission

The emergence of the digital age has underscored the important role that electrical and electronic equipment (EEE) plays in a nation's socio-economic development, including education, health delivery and communications, as well as global connectivity. In 2003 Ghana formulated its policy on information and communications technology (ICT) for accelerated development, with the understanding for instance, that Ghana's accelerated development would not be possible without an ICT-driven development agenda. The demand for EEE in Ghana grows by the day with a corresponding high rate of waste electrical and electronic (WEEE) generation. The WEEE industry in Ghana is a very vibrant one, growing at an amazing rate year after year. Ghana currently imports about 215 000 tonnes of electrical and electronic equipment per annum out of which an estimated 70% are second hand products. About 60-70% of the second hand products arrive in good working condition, 20-30% can be repaired or refurbished to get them functioning and 10-20% are junk and sent directly for the informal recycling.

The Agbogbloshie scrap market in Accra came into the limelight following the publication of the report entitled '*Poisoning the Poor*' by Greenpeace International. The report gave a damning revelation about the activities of scrap dealers and recyclers at the market. It was noted from the report that surface dust samples contained high concentrations of both heavy metals and persistent organic pollutants due to the unsafe and crude

means of retrieving metals and components from the WEEE. This project was therefore designed to determine the heavy metal concentration of surface dust using the EDXRF and estimate the degree of contamination of the dust samples. Surface dust samples were collected from various vicinities within the scrap yard using the methods described above.

Results and Discussion

The results in Table 1 reveal that the concentration of Pb were in the range 351.1 mg/kg and 5105.45 mg/kg with the highest values recorded at weighing site (WS) (where the dismantled and extracted Pb and other metals are weighed). The levels of Cd found were in the range of 2.4 mg/kg and 71.5 mg/kg. The toxicity of Cd and its adverse impact on humans and the environment cannot be overemphasized. Apart from the samples from the headquarters of ICGC the rest of the sites had concentrations which were above the guidance values for intervention. The dust from the electronic waste burning site recorded the highest concentration of Cd. This was followed closely by the weighing point. The school compound where the sampling was done recorded a Cd concentration of 12.07 mg/kg which is about 240% more than the value that can trigger an intervention. The values of Zn and Cu where found to be more than one thousand times the concentrations requiring interventions [1] which reflect the activities that are undertaken at the sites. Cr, Mn, Fe and Ni also gave very high concentrations from most of the sites.

Table 1: Heavy metal concentrations in dust sampled from the vicinity of the scrape market (mg/kg)

Element		Fe	Mn	Cu	Zn	Cd	Cr	Ni	Pb
CP	Mean	16743.1	90.7	34.4	10575.0	2.4	21.6	26.3	351.1
	StDev	193.8	10.5	5.2	347.2	0.5	2.1	4.2	30.9
DS	Mean	17495.4	294.2	16318.6	28957.9	52.1	60.0	101.9	3162.7
	StDev	321.2	9.7	531.6	900.6	22.1	5.1	49.5	688.4
WS	Mean	17920.2	293.5	16951.7	29720.7	68.5	114.5	191.4	5105.4
	StDev	279.4	8.2	641.8	442.7	2.1	19.7	33.6	895.3
BS	Mean	16644.2	145.4	16627.5	30384.4	71.6	48.7	95.5	1321.1
	StDev	394.0	43.4	622.2	612.1	60.6	17.4	27.5	223.5
CA	Mean	16493.1	189.8	11589.4	20847.2	4.4	34.6	28.7	1149.1
	StDev	54.9	22.6	3318.5	1727.7	1.0	3.9	5.4	218.2
RD	Mean	17118.0	269.7	31028.2	22256.0	5.1	72.4	49.2	1968.4
	StDev	64.8	70.1	154.2	345.9	0.4	5.2	3.5	100.9
SC	Mean	17543.6	197.4	10099.1	22052.3	12.1	105.6	29.9	1195.2
	StDev	168.2	35.5	2614.2	1216.5	4.7	10.6	4.5	179.3
	AT		1500	100	300	3	100	75	50
	IT		2500	200	600	5	300	150	100

CP: premises of ICGC headquarters, DS: dismantling site, WS: weighing site, BS: burning site, ca: commercial area, RD: road dust, AT: levels for which attention is required and IT: levels for which an intervention is required [1].

The calculated degree of contamination in the sampling sites is presented in Fig. 1. The results show that the church premises (CP) has the lowest degree of contamination. This is because the church premises is located upwind, thereby preventing the thick smoke from the burning site to the premises.

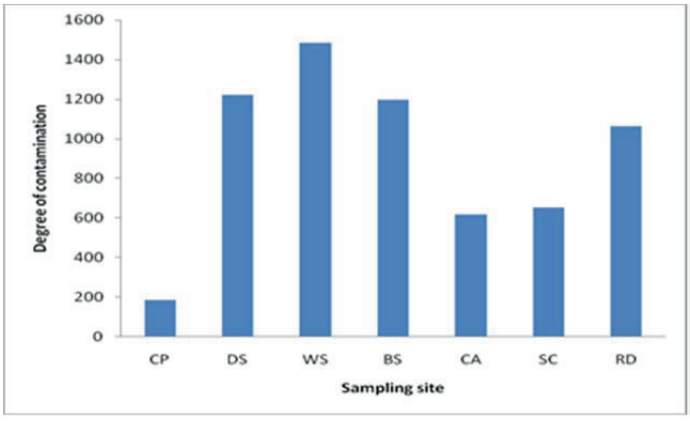


Fig. 1. Degree of Contamination of various sites.

However, there is a thoroughfare from the burning site to the church which is used by many people going in the direction of the church. Hence contaminants are carried to the premises. The site labeled CA (commercial area) showed extremely high degrees of contamination. The thick cloud of smoke from the burning site blows in the direction of these buildings. The school compound (SC) serves as a place of rest to some of the people engaged in the scrap business during the night. This practice is likely to have resulted in the transport of contaminants from the adjacent scrap market to the school compound. Road dust is known to reflect the level of pollution of a particular site. The contaminants in road dust may come from exhaust or non-exhaust sources [2]. It is therefore possible that the combination of vehicular emission and activities of the scrap dealers, some of which are carried out close to the road side are responsible for the high degree of contamination. The weighing site (WS), dismantling site (DS) and the burning site (BS) respectively recorded the highest degree of contamination. These are sites with intense scrap activities within the yard where unscientific methods are used for dismantling, burning and weighing. All these activities release high levels of toxic substances into the environment, leading to the exceptionally high degree of contamination.

Conclusion

This study has shown that EDXRF can be an effective tool in understanding the e-waste problem from contamination assessment viewpoint. Further detailed study must be contacted for the assessment of critical metals such gold in order to evaluate precious metal loss during informal processing of e-scrap.

References

[1] LACATUSU, R. CITU, G, ASTON, J. LUNGU, M. LACATUSU, A.R. 2009. Heavy metals soil pollution state in relation to potential future mining activities in the Roşia Montana area, *Carpathian Journal of Earth and Environmental Sciences*, 4, 39–50.

[2] ATIEMO, S.M., OFOSU, F.G., ABOH, I.J.K. and YEBOAH, P.O. 2010. Determination of heavy metals and human health risk assessment of road dust on the Tema motorway and Tetteh Quarshie interchange in Accra, Ghana. *Journal of Ghana Science Association, Vol. 12 No. 2. pp 76-85*

South Africa

Selected activities in the Materials Research Department of iThemba LABS in South Africa

Contributor: W.J. Przybylowicz
Materials Research Department, iThemba LABS, P.O. Box 722, Somerset West 7129, South Africa;
e-mail: przybylowicz@tlabs.ac.za

The iThemba Laboratory for Accelerator-Based Sciences (iThemba LABS) is a group of multi-disciplinary research laboratories administered by the South African National Research Foundation. Based at two sites in the Western Cape (see Fig. 1) and Gauteng provinces, these provide facilities for: (1) basic and applied research using particle beams; (2) particle radiotherapy for the treatment of cancer; (3) the supply of accelerator-produced radioactive isotopes for nuclear medicine and research [1].

Scientific themes realized at the Materials Research Department, located at the Western Cape campus, can be divided into four categories: (1) nanotechnology and thin film physics using material characterization and modification with radiation and scanning probe microscopy; (2) biotechnology – trace element distribution and mobilization in biological systems; (3) environmental and geological studies using ion beams; and (4) innovation in methodology, instrumentation and electronics [2]. The core competency of the Department is based on ion beam techniques, such as particle induced X ray emission (PIXE), particle induced gamma-ray emission (PIGE), Rutherford backscattering spectrometry (RBS) or elastic backscattering spectrometry (EBS) also in channelling mode, nuclear reaction analysis (NRA), elastic recoil detection (ERD) and other, less used techniques. The main research instrument is a 6 MV single-

ended Van de Graff type CN vertical accelerator, commissioned in 1964, one of the oldest fully utilized accelerators of this type in the world. Five experimental beam lines are available for the specialized experiments.

Fig. 1. Aerial view of the Western Cape campus of iThemba LABS in South Africa. The tall white tower is the location of the 6 MV single-ended Van de Graff accelerator, with the adjoining buildings of the Materials Research Department.

Fig. 2. Nuclear microprobe at the Materials Research Department of iThemba LABS, with visible experimental chamber and focusing lenses (Oxford triplet OM150).

Materials characterized by accelerator techniques are either produced on-site using specialized equipment (e.g. pulsed laser deposition, e-beam deposition, sputtering, growth chambers) or are adequately prepared before measurements. Some instruments and techniques can be used independently from accelerator-based techniques (X ray diffractometers, atomic force microscope, Mössbauer spectrometer, electron transport measurement facility, optical and fluorescence microscopes) and their location in the Department is advantageous for a more complete characterization of materials. Commissioning of the nuclear microprobe in 1991 reflected recognised need for microanalyses in a variety of studies, undertaken in collaboration with South African universities and research centres (see Fig. 2). In addition to initial studies related to geology and materials science there has been a steady increase of interest in analyses of microstructures of biological origin [3, 4]. This

prompted on-site development of a specialized cryo-preparation laboratory, with some state-of-the-art equipment for cryo-fixation, freeze-drying and freeze substitution. It is worth noting that the available high pressure freezer was the first such equipment installed on the African continent.

Information on the concentration and distribution of elements at trace levels in living matter plays an important role in a variety of biological research programmes. For example, studies of iron distribution in blood-feeding organisms are part of research aiming at the fight with malaria, bilharzia as well as Dengue and yellow fever. In pharmacokinetic studies, the observation of pharmaceutical compounds diffusing within cells and through the various tissue compartments remains a difficult task. For some therapeutic agents, there are no fluorescent or radioactive markers, and the detection of some metallic or halogen complexes at the trace level is necessary. In cancer research, some studies on the development of cellular resistance to the drug can be performed by detection of the amount of elements such as platinum, iodine or iron accumulated in cells from a human tumour cell line. In plant physiology, fundamental processes are affected or regulated by mineral nutrients; hence understanding the mechanisms of nutrient uptake and their functions in plant metabolism is of fundamental importance. It is known that, depending on their concentrations, elements can play different roles in plant life. Studies related to elemental deficiency and toxicity, as well as environmental pollution, require accurate, fully quantitative methods with good spatial resolution.

Elemental microanalysis of soft biological material is only biologically relevant when the location and concentration of elements reflects the natural hydrated state of the tissues and cells. The best way to achieve this goal is by very quick freezing of specimens to liquid nitrogen temperature, and further analysis in frozen-hydrated state. Hydrated structures of cells and tissues cannot shrink and soluble compounds are trapped in their position as in the living state. Special cryotransfer systems have been developed for work using electron microscopes, and are commercially available. However, the sensitivity of these facilities is not sufficient for studies of trace elements and more sensitive microanalytical techniques, such as micro-PIXE (microanalysis using protons is typically 100 to 1000 times more sensitive than with electrons) must be used. In 2006 the nuclear microprobe at Materials Research Department of iThemba LABS became the first such facility in the world with proven capabilities of PIXE microanalysis of biological material in the frozen-hydrated state. One of the commercially available cryotransfer systems has been coupled to the experimental chamber of the microprobe after necessary modifications (see Fig. 3). Thorough testing using thick sections of selected plant and animal material have been performed and satisfactory quantitative results were obtained [5]. After further improvements cryo-micro-PIXE measurements of frozen-hydrated semi-thick biological specimens are now possible.

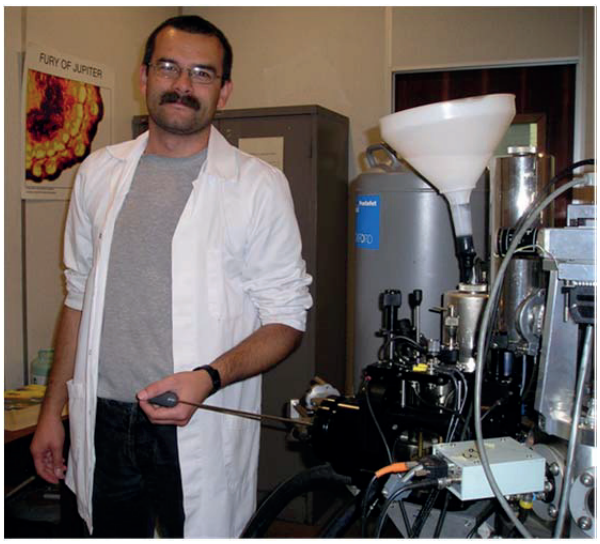


Fig. 3. Dr Grzegorz Tylko operates the cryotransfer system during the first successful micro-PIXE measurements of biological specimens in frozen hydrated state.

Quantitative results are obtained by standardless method using GeoPIXE II software package (see Fig. 4) [6]. Elemental mapping is performed using the dynamic analysis method. This method generates elemental images which are (i) overlap-resolved, (ii) with subtracted background and (iii) quantitative, i.e. accumulated in mg kg-1 dry weight units. Maps are typically complemented by PIXE and EBS data extracted from arbitrarily selected micro-areas. Matrix corrections done on the basis of EBS spectrometry results are essential due to the (often) highly variable thickness of analyzed specimens.

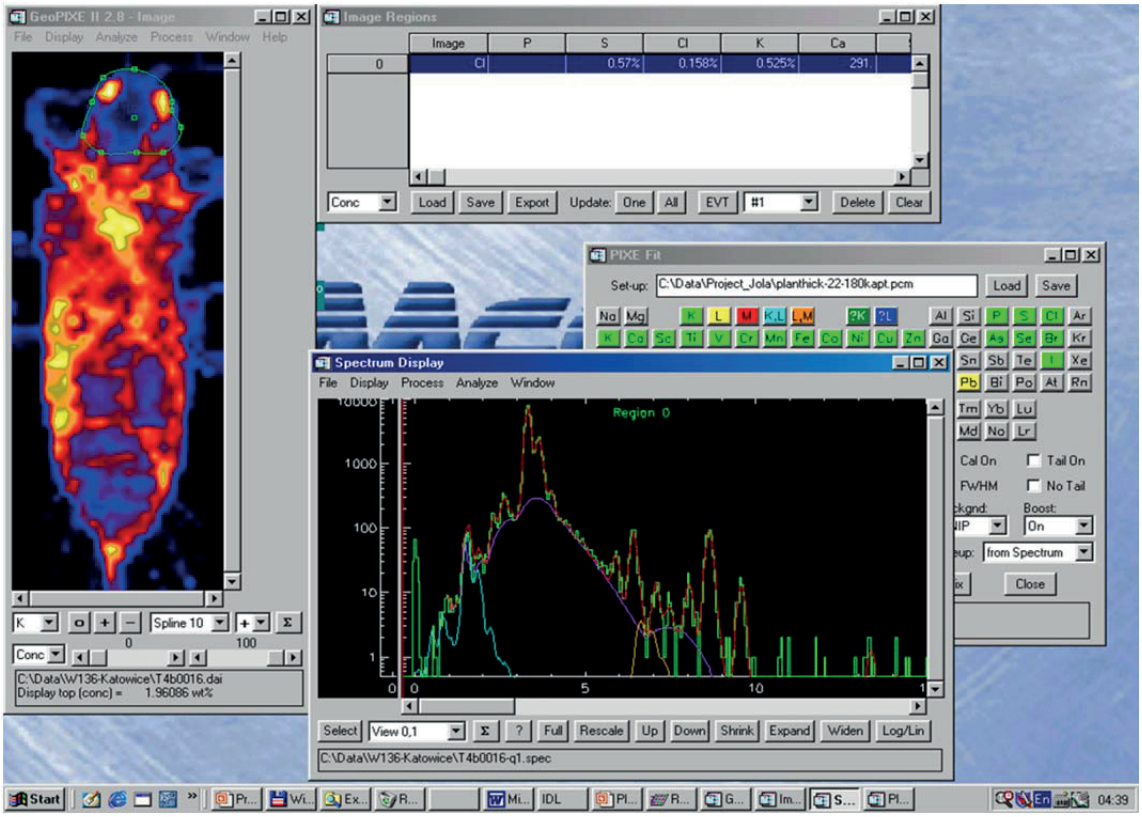


Fig. 4. An example of data processing using GeoPIXE software. The PIXE spectrum has been extracted from an area selected on the potassium map of an insect body.

Conclusions

Success in biological applications of the ion beam techniques is subject to close collaboration between biologists and physicists in terms of addressing problems of specimen preparation, refinement of analytical protocols such as quantitative elemental mapping and the interpretation of results.

References

[1] http://www.tlabs.ac.za

[2] Five Year Research Plan – Materials Research Group, iThemba LABS, October 2007 (internal document).

[3] MESJASZ-PRZYBYLOWICZ, J., and PRZYBYLOWICZ, W.J., Micro-PIXE in plant sciences: present status and perspectives. Nucl. Instr. and Meth. B189 (2002) 470.

[4] PRZYBYŁOWICZ, W.J., MESJASZ-PRZYBYŁOWICZ, J., MIGULA, P., TURNAU, K., NAKONIECZNY, M., AUGUSTYNIAK, M., GŁOWACKA, E., Elemental microanalysis in ecophysiology using ion microbeam. Nucl. Instr. and Meth. B219-220 (2004) 57.

[5] TYLKO, G., MESJASZ-PRZYBYŁOWICZ, J., and PRZYBYŁOWICZ, W.J., X ray microanalysis of biological material in the frozen-hydrated state by PIXE. Micros. Res. Tech. 70 (2007) 55.

[6] RYAN, C., Quantitative trace element imaging using PIXE and the nuclear microprobe. Int. J. Imaging Systems and Technol. 11 (2000) 219.

United Arab Emirates

Recent Activities at the National X ray Fluorescence Laboratory (NXFL), United Arab Emirates

Contributors: N.M. Hamdan[1,2*], H. Alahawadhi[2,3] and N. Jisrawi[2,3]

[1]*American University of Sharjah;*
[2]*NXFL*
[3]*University of Sharjah, Sharjah, United Arab Emirates.*

Abstract

The NXFL was established in early 2010 with support from the IAEA through a National framework Project. The lab consists of a HORIBA XGT7200 energy dispersive micro X ray fluorescence system, supporting equipment such as material preparation devices, a hand held XRF device, a portable RAMAN spectrometer and particle impactors. During the last two years, several projects of various natures have been performed at the laboratory, mainly related to environmental and cultural heritage applications, in addition to several educational projects. In this review, we present a few examples of these projects, such as aerosol particulate investigations in the UAE and, studies of colour pigments in old Islamic manuscripts. Finally, we will present our recent experience in introducing an interdisciplinary introductory course in physics and cultural heritage where students from various academic disciplines were involved in a cooperative teaching utilizing the XRF laboratory.

Introduction

Several small projects had been performed at the NXFL during the last two years for the purpose of introducing the laboratory and its capabilities to the UAE communities (e.g., museums, environmental protection agencies, municipalities, and universities). These projects included examples of old paintings, ancient Quran pages, several archaeological artefacts belonging to various museums, in addition to several graduate and undergraduate senior projects for students at both the American University of Sharjah and the University of Sharjah. During the same period, the NXFL team has initiated three major projects:

(i) investigation of archaeological pottery collected from UAE sites; (ii) study of colour pigments in old Islamic and Arabic manuscripts; (iii) study of aerosol particles using the micro X ray fluorescence (XRF) technique.

In this review, we present results from the second and third projects mentioned above in addition to a brief presentation to an interdisciplinary educational experience and training.

XRF study of ancient Islamic manuscripts

Identification of pigments in old Islamic manuscripts is important for conservation and restoration purposes, as is the detailed study of compounds used in the inks. In a preliminary investigation of a set of fragments from old Islamic manuscripts, two complementary techniques were utilized. XRF and micro XRF were used for elemental analysis. However, since the various XRF techniques can only identify elements heavier than Na, and can't identify the chemical structure, we used RAMAN, a compound-specific technique, in an attempt to determine the chemical composition of various colour pigments. The integration of the two techniques provides comprehensive information about the chemical composition of various pigments and the structure and manufacturing processes of ancient paper. In addition, such investigation may also provide information about the degradation of metallic-based pigments in ink used in ancient manuscripts [1-5].

In this review, we present measurements on two fragments from ancient Islamic manuscripts obtained from Juma Al Majid Center for Culture and Heritage in Dubai. The first fragment is a page from an unknown old Arabic poem (the poet and date of writing are also unknown), while the second is a page from a manuscript by Sirajudiin Omar Bin Ali known as 'Qari' Al-Hidaya', a religious scholar who died in the year 826 A.H. in Baghdad. The manuscript contains answers to questions on various religious matters by the scholar. The manuscript is known as 'FATAW's of Qari' Al-Hidaya'. It is believed that the manuscript was written by Al-Hammam Bin Abdel-Wahid in 861 A.H. It is also thought that the same manuscript was rewritten in 990 A.H., in a version available at King Saud University Library in Riyadh, Saudi Arabia.

Manuscript 1

Figure 1 shows both sides of the fragment identified here as Manuscript 1.

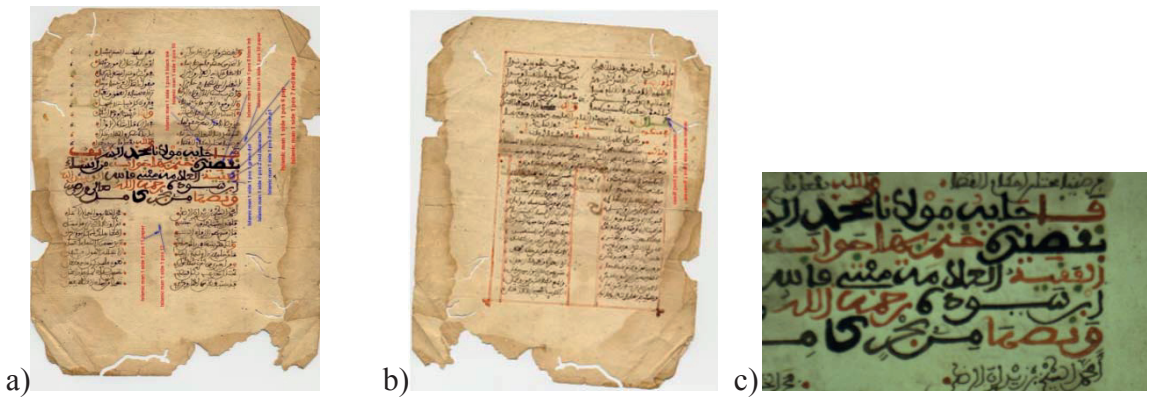


Fig. 1. Manuscript 1: (a) side 1; (b) side 2; (c) mapping area of side 1.

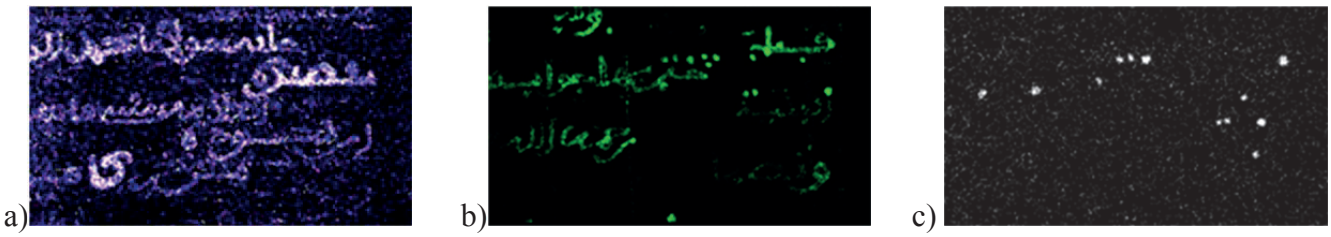
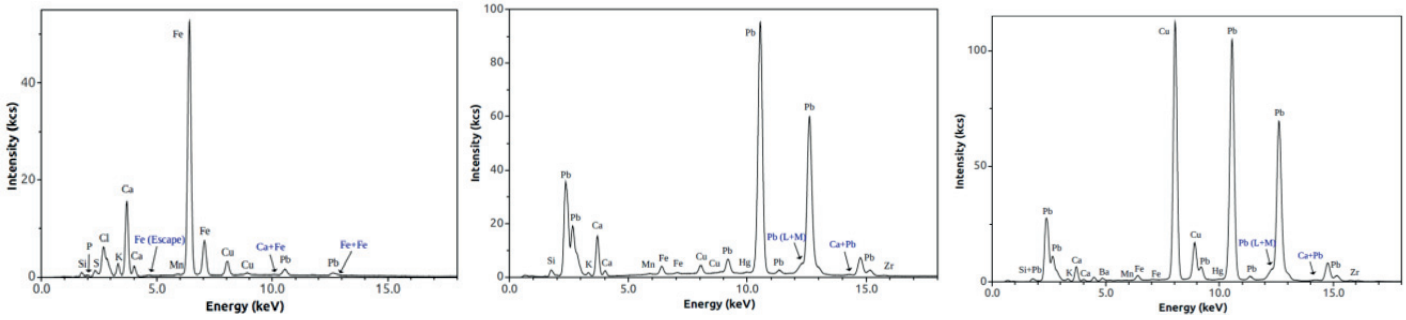


Fig. 2. Elemental maps of manuscript 1 side 1: for (a) Fe; (b) Pb and (c) Cu.

Figure 2 shows the elemental map for the three colours used in the manuscript: (a) the Fe map corresponding to black ink, (b) Pb map corresponding to the red ink and (c) Cu map corresponding to the green color ink. The maps were produced at 10 μm beam size and 50 kV X ray energy. These results were also confirmed using spot analysis for various points, as shown in Figure 3. When analyzing the black writing, the main components are found to be iron and calcium, where the Ca is believed to come from the paper. Smaller amounts of Cu could be attributed either to contamination, as inks used to be stored in copper pots, or it could in some cases be attributed to the green colour on the back of the manuscript. The trace amounts of Pb and Hg are also attributed to contamination.

Figure 3 (b) is a scan of the red writing. The figure shows that the main element in this pigment is Pb. The green ink on the other hand (Figure 3 (c)) shows the existence of two major elements which are Cu and Pb. It is obvious that the main component of the green pigment scan is Cu, and lead is most probably due to fluorescence of the red pigment on the backside of the page.



(a) (b) (c)

Fig. 3: XRF spectra for spot measurements of (a) black, (b) red and (c) green colour.

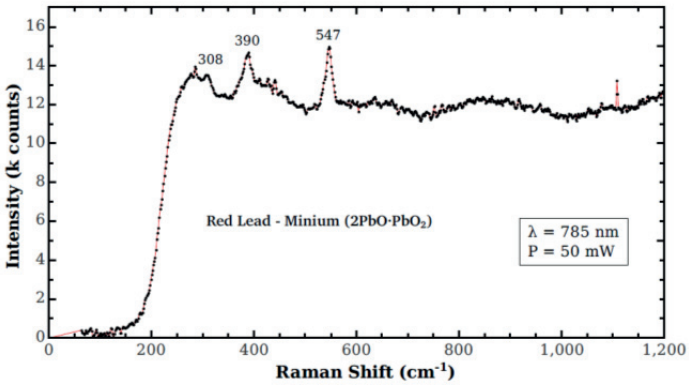


Fig. 4. RAMAN spectra of red color pigment.

Figure 4 shows the RAMAN spectrum of the red pigment used in this manuscript. The spectrum shows peaks of RAMAN shifts at 308, 390 and 547 cm^{-1}. The results of RAMAN combined with those of XRF (mapping and spot analysis) confirm that the red pigment used in this manuscript is Red Lead, also known as Minium (Pb_30_4 sometimes written as 2PbO PbO_2) [3]. Similar RAMAN measurements were performed on the black and green inks (to be published elsewhere), showing that the Cu-based green pigment in this manuscripts is malachite ($CuCO_3$. $CuO(H)_2$) [3-7], while the black color is iron gall ink, consisting of vitriol ($FeSO_4$), tannic acid (from gall nuts), Arabic gum and water [5]. These results were also confirmed by observing the iron gall RAMAN bands.

Manuscript 2

The second document is a fragment from a manuscript known as 'Fatwas of Qari' Al-Hidaya'. Figure 5 shows scans for the two sides of the fragment. The μ-XRF mapping area is shown in Figure 5(c).

Fig. 5. (a,b) The two sides of manuscript 2; and (c) mapping area of side 2.

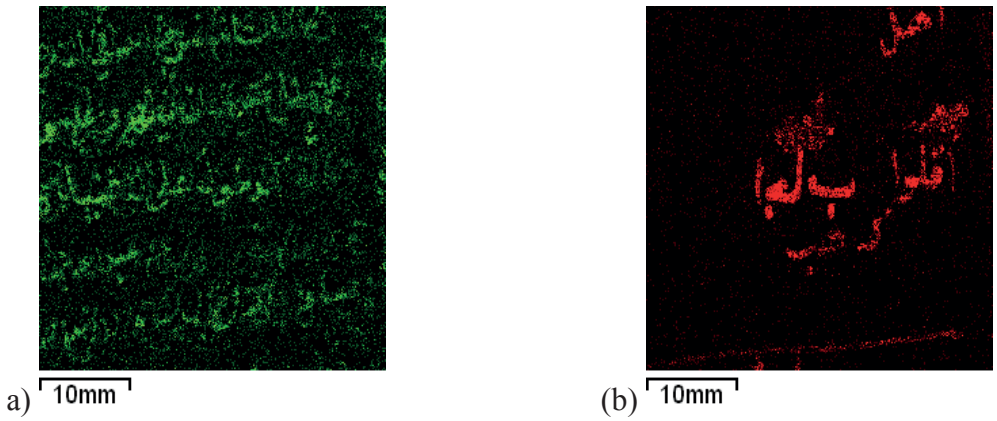


Fig. 6.Elemental maps of (a) Fe and (b) Hg.

Figure 6 shows elemental maps of side 2 of manuscript 2. The maps show that black color is Fe-based while the red color is Hg based pigment. RAMAN results (to be published later) confirm that iron gall ink was used as a black pigment, while HgS, known as Vermillion or Cinnabar, was used for the red colour. Cinnabar was a common pigment used for red colour after the 16th century [1, 3-5].

Figure 7 shows XRF scans for the red and black colours, respectively. As in the previous scans (Fig. 3), the X ray beam energy was 50 keV. The main peaks of Figure 7(a) are identified as Hg and S, with Fe, Ca and others as trace elements coming from the paper. Small amounts of Pb were also observed as impurities associated with the Hg. The XRF results provide a strong indication that the red pigment in this manuscript is basically HgS (Cinnabar) [3-7]. Figure 7(b) shows the XRF scan for the black writing. The figure shows that the main component of this pigment is Fe, while other lines in the spectra come from the paper (Ca) and from impurities (Cu, Pb, K, S and Zn). These results also provide a strong indication that the black ink is iron gall.

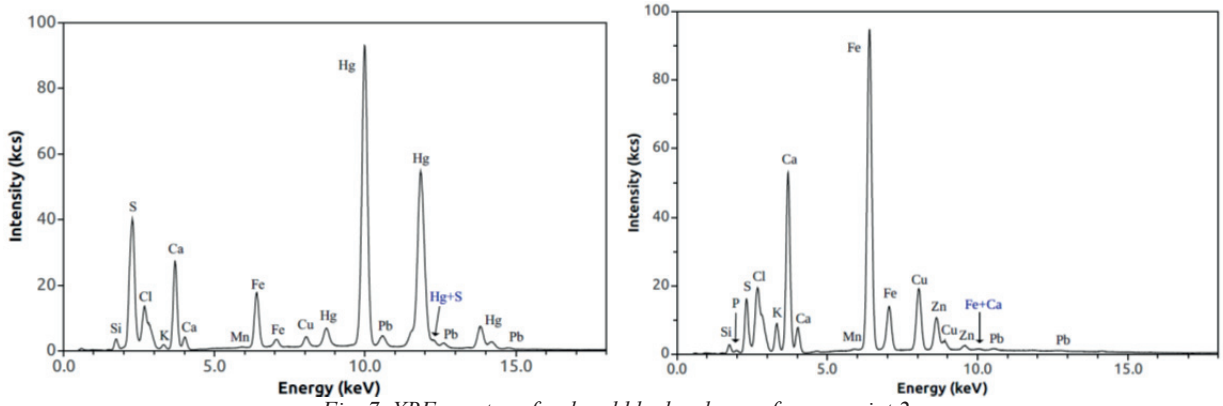


Fig. 7. XRF spectra of red and black colours of manuscript 2.

Study of the aerosol pollution in Dubai using the Micro X ray Technique

The scientific scope of this study is to investigate air pollutants, with special attention to heavy metal elements that may be present, and to the distribution of other metallic particulates. In a previous investigation, we have found, using 0.8 µm-pore MCE filters and utilizing 'macro' XRF techniques, that the major air pollutants are Ca, Si, and Fe. In the this study, we have found both spatial and size distribution of various particulates that consist of several elements like Na, Si, S, Al, Ca, Cu, Fe, Ti, Zn, Sr, Zr and even Ba in one case. We will attempt to relate these distributions to possible sources in the region. One important aspect is to highlight elements with particulate sizes corresponding to $PM_{2.5}$ or smaller.

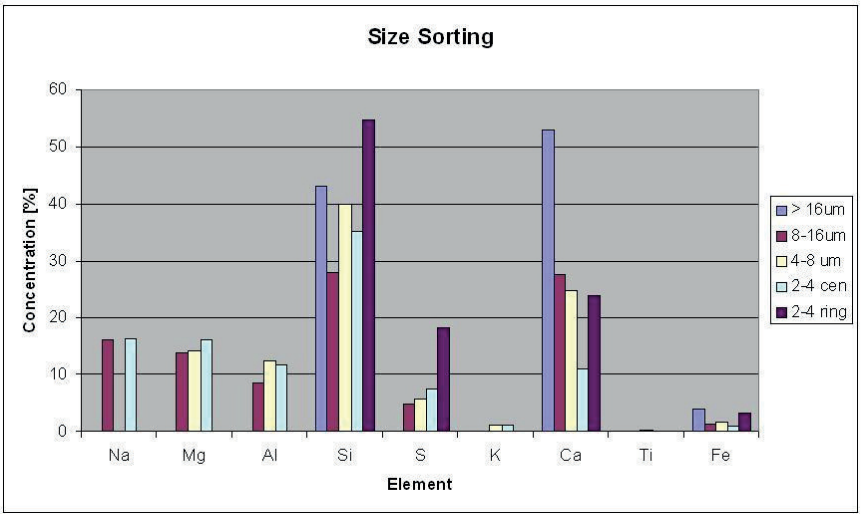
We present samples collected from three different locations in Dubai: one sample was collected near a major highway, the second one was collected from the rooftop of a building in downtown Dubai (Deira) and the third one from a sidewalk of a major road in Dubai and close to the shore. The major highway cuts through the desert and is prone

to sand storms; the shore road is less exposed to desert pollution, while the urban downtown location is closer to large construction sites. All three locations are congested with traffic at times. X ray measurements were done using 50 kV, 1 mA, and 1.2 mm beam-spot for 100 s.

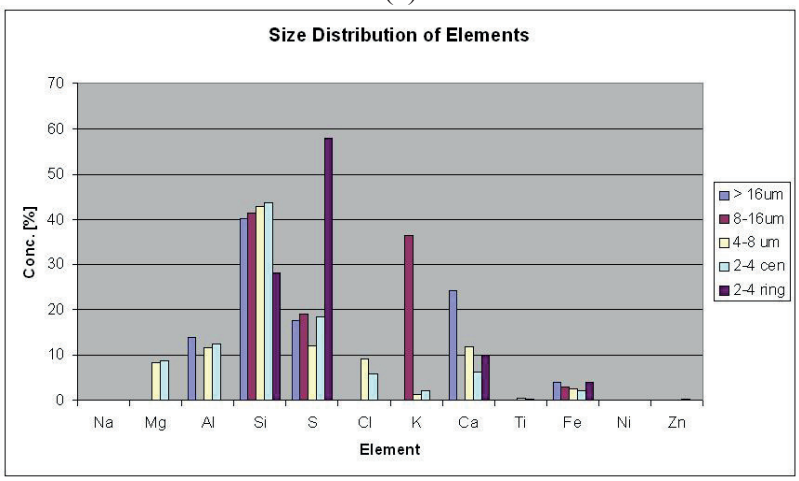
In general, we observed that the filters with coarse pore size had less particulate matter than those with fine pore size. We also observed that the spatial and elemental distribution of particulate matter depended on the filter pore size.

Figure 8(a-c) shows the elements present on the four filters with diameters in the ranges: >16, 16-8, 8-4, 4-2 (center), 4-2 (ring) µm collected from the three different locations. The figures show that filters with smaller particles contained more elements than those with larger particles. We note that for the sample in Fig. 8(c) that was collected closer to the sea, elements that originate from sea salts such as Na, Mg are present. For the filter with coarse pores (>16 µm), the main elements are Ca, Si, Fe and some Al in two locations out of three.

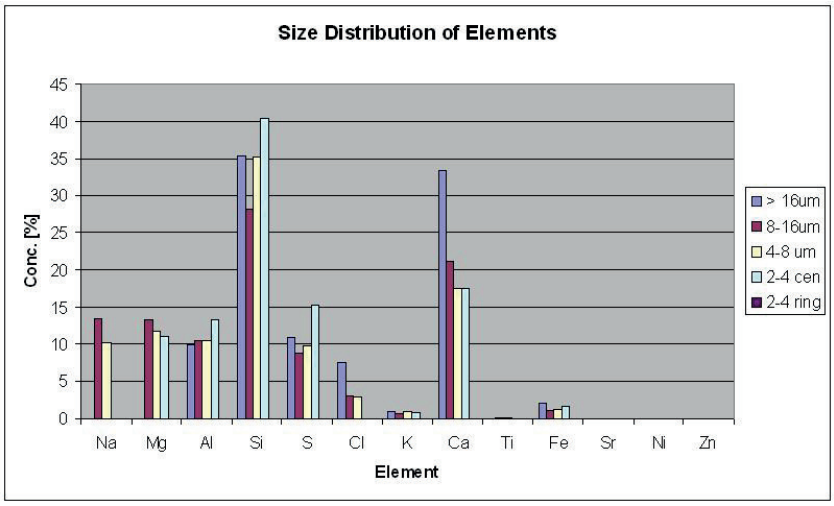
The UAE experiences frequent desert sand storms that make air pollution a problem on top of environmental and health concerns in the country [9, 15]. For this reason, we have collected fine desert sand that is believed to be a major source of particulate pollutants and investigated the elements present in these samples using XRF. We used the same experimental parameters as those for the filters discussed above. One sample was used without processing and contains large and small grains while the others were sieved using 75 and 63µm sieves. Fig. 9 shows the size and elemental distribution of various particulates found in the sand. The figure clearly shows the presence of traces of Cr, Ti, and Mn in the particles < 63 µm. The concentration of these elements increases as the particulate's size decreases.



(a)



(b)



(c)

Fig. 8. Size distribution of elements for the three locations. (a) near the highway, (b) downtown Duba and (c) near a shore road.

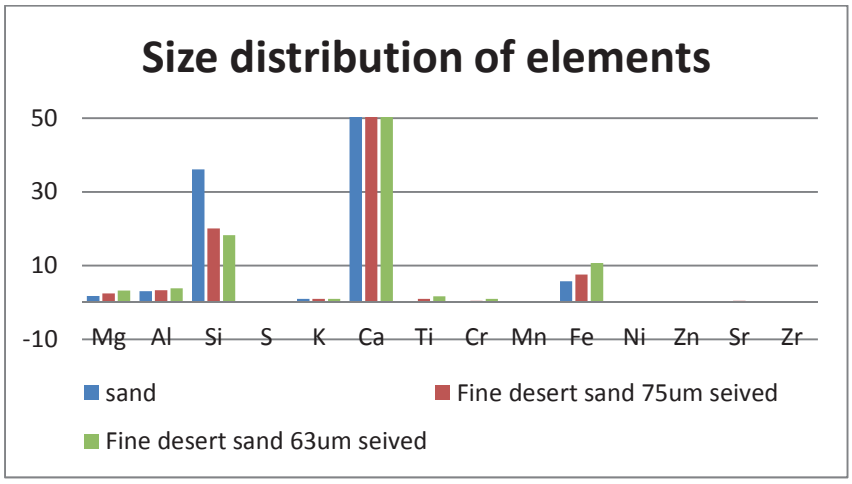


Fig. 9. Elemental distribution of sand, as a function the particle size.

Educational activities

Among several education related activities such as graduate and senior undergraduate projects, we present in this report an interdisciplinary course introduced at the American University of Sharjah. The course identified as IDS 194, was proposed by the author of this report in collaboration with an archaeologist. The course was open to all undergraduate students from various academic disciplines and it was entitled 'Uncovering Cultures through Physics'. Eighteen students registered for the course. Several introductory lectures were delivered about the importance of science in cultural heritage from both science and cultural heritage point of views. The students were given a set of articles on the use of XRF and related techniques in cultural heritage and each group of three was asked to choose one article to analyze, write a summary report and make an oral presentation. This provided students with an introductory experience on practical applications of scientific techniques in cultural heritage and prepared them for the next stage: to perform their own XRF measurements.

Several ancient archaeological artefacts that were recently discovered in Sharjah were borrowed from the Department of Antiquities, Sharjah Department of Culture and information.

Each group was provided with one or two artefacts and was asked to perform a research project that included the use of XRF technique at the NXFL in addition to any other available method that could provide some useful information. The students were asked to submit a comprehensive report and make an oral presentation about their investigation

including the use of XRF for elemental analysis and how to relate their data to the humanistic and cultural aspect of the artefacts, i.e. if these research measurements can reveal any information about the way of living of the people at those times, trade routes, manufacturing techniques, etc. The reports and the presentations were of high quality.

This interdisciplinary course provided a rich experience for both professors and for all the students. Two independent on-line student opinion surveys were performed: one a couple of weeks before the final exam and the other one week after the final grades were announced. The outcome of these two questionnaires were very positive and all responding students answered with 'yes' when they were asked if they would take another course on the same topic. They also responded with 'yes' when they were asked if they would recommend the course to a friend.

Workshops, meetings and training courses

In the period of 7-8 of December 2011, the NXFL co-organized the International Conference of X rays in Arts and Cultural Heritage at the American University of Sharjah (Figure 10). In the period of 3-8 of December 2011, it also hosted a regional training course on the use of nuclear techniques in cultural heritage (Fig. 11). The training course was organized in collaboration with the American University of Sharjah as part of the activities of the TC-RAS1011 project: Using Ion Beam Analysis and Complementary Nuclear Techniques for Material Characterization in ARASIA State Parties.

Fig.. 10: Participants of the XTACH11 conference organized by AUS in collaboration with the NXFL and the IAEA at the Gala dinner at Sharjah Maritime Museum.

Participants of the course were trained on the use of physical and analytical techniques in cultural heritage. In addition to lectures from the NXFL (Fig. 12) and from the IAEA, the NXFL team provided the opportunity for trainees to undertake projects on ancient pottery samples, metal artefacts and Islamic manuscripts. The practical part of the course included experiments on XRF (portable and micro XRF), Raman measurements, as well as other sample preparation techniques. The training course concluded by a series of presentations of the results by the participants, attended by the NXFL team, Dr. Andrzej Markowicz and Aliz Simon from the IAEA. The course was attended by participants from Iraq, Jordan, Lebanon, Qatar, the Syrian Arab Republic, the United Arab Emirates and Yemen.

Fig. 11. Participants of a regional training course during one of the presentation by Dr. N.M. Hamdan.

Fig. 12. NXFL team during the installation of the XGT7200 system on December 2009, from left: Dr. A. G. Attaelmanan, Dr. Hussain Alawadhi, Horiba representative, Dr. Nasser Hamdan and Dr. Najeh Jisrawi.

References

[1] DURAN, A., et al. , *Anal BioanalChem*(2009) **395**:1997–2004.

[2] BURGIO, L., CLARK, R.J.H. and HARK, R.R., *PNAS*, March 30, 2010,vol. **107**, no. 13, 5726–5731

[3] ACETO, M., AGOSTINO, A., BOCCALERI, E., CRIVELLO, F., *J. Raman Spectrosc*. 2010, **41**, 1434–1440

[4] BURGIO, L., et al. „*Applied Spectroscopy*, **63**, Number 6, 2009, 611-620.

[5] VAN DER SNICKT, G., et al., *Appl. Phys*. **A 92**, 59–68 (2008).

[6] EREMIN, K., et al., *J. Raman Spectrosc*. 2008; **39**: 1057–1065.

[7] SAWCZAK, M., et al., *Applied Surface Science* 255 (2009) 5542–5545

[8] The National Strategy and Action Plan for Environmental Health for the UAE, 2010.

[9] Science Plan, United Arab Emirates Unified Aerosol Experiment (UAE), DWRS, NASA, NRL, ONR, 2004.

[10] LI, Y., et al, *Science of the Total Environment* 408 (2010) 5784–5793.

[11] SIVERSTEN, B.J., Dust Storms Dominate the Air Pollution in the Emirates Norwegian Institute for Air Research, *NILU annual magazine*, (2009) page 20,

[12] HANDLER, M., et al., *Atmospheric Environment* 42 (2008) 2173–2186.

[13] HOCHSTETLER, H.A., et al., *Atmospheric Environment* 45 (2011) 1444e1453

[14] BUKOWIECKI, N., *Environ. Sci. Technol.*, 2005, 39 (15), 5754-5762

[15] BUSEK, P.R., *Proc. Natl. Acad. Sci. USA,* Vol. 96, pp. 3372–3379, March 1999

Uruguay

Elemental composition of airborne PM2.5 and PM10 during volcanic ash intrusion in Montevideo, Uruguay

Contributors: M. del Rosario Odino[1], A.M. Gabrielli[1], L.A. Piuma[1], E.A. Reina[2], R. Suárez Antola[1,3]

[1]*Ministerio de Industria, Energía y Minería – Laboratorio de Tecnogestión, Hervidero 2861, Montevideo, Uruguay*

[2]*Dirección Nacional de Minería y Geología – Laboratorio de Tecnogestión, Hervidero 2861, Montevideo, Uruguay*

[3]*Centro de Investigación y Desarrollo, Universidad Católica del Uruguay, 8 de Octubre 2801, Montevideo, Uruguay*

Abstract

Principal component analysis was performed on the results of the elemental concentrations obtained for 126 PM10 and PM2.5 samples collected daily from an area of Montevideo, capital city of Uruguay during eight months in 2011. Results reveal compositional variation attributable to different mixtures of natural and anthropogenic sources, mainly soil and crustal, petrochemical refinery and thermoelectric central emissions, metallurgical activities and traffic. The chemical elements Al, Si, S, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn As, Sr, Ba, Pb were determined with different levels of accuracy and precision using energy dispersive X ray fluorescence (EDXRF) and black carbon was estimated in PM2,5 fraction by reflectometry. A dichotomous sampler Andersen and polycarbonate membranes were used and the sampling time was established between 6 and 24 hours depending on the atmospheric conditions. During the study period episodes of volcano's ash incursions appeared due to the emission of Puyehue -Cordon- Caulle Volcano. When the events were detected the concentrations of Al, Si, K, Ca, Ti, V, Mn, Fe, Cu, Zn and Pb in PM2,5 and Si, Al, S, Cl, K, Ti, V, Mn, Fe, Cu and Pb in PM10 differed significantly from the concentrations determined before the interference. Sedimented particulate matter was also collected and analyzed with EDXRF.

Introduction

There is reasonable epidemiological evidence that inhaled particulate matter in the outdoor air is associated with adverse health effects. This evidence comes from epidemiological studies of acute and chronic health effects from both short term and long term exposure to air pollution [1].

In the present study the interference of ash's volcano emissions is analyzed in the monitoring of particulate matter of air. The study was conducted from February to September 2011 in Montevideo, Uruguay. The city is the capital of the country; it is located in 34º S 56º W and is extended on the left of Rio de la Plata. It has been developed from a natural seaport. The number of inhabitants are about of 1 900 000 and it represents more than a half of total population of the country.

This work shows the chemical characterization of airborne PM2.5 and PM10 [2]. The sampling site used for this study is located near highways of access to the city, a thermoelectric station, a

petrochemical complex and the most important seaport of the country.

The objectives of this research are the identification and quantification of the chemical elements which are tracers of sources related to natural events and anthropogenic activities. Principal component analysis is also applied to obtain the emission sources.

From June of 2011, the volcano's ash emissions appears in Montevideo. This fact causes interferences in the monitoring of particulate matter of local sources.

The volcanic ash appeared as sedimented dust which was collected and analyzed using the energy dispersive X ray fluorescence method.

The comparison of the characteristics of samples (chemical composition, mass) with and without volcano's interference was performed.

Methodology

Particulate matter of air was collected using a dichotomous sampler [1] (16 L/min) equipped with PM10 and PM2.5 inlets and polycarbonate membranes (Nucleopore®). Since the sampler operates at low flow there is a disadvantage that an increase of the aerodynamic resistance interrupts the operation of sampling. Because of this, the maximum time of operation and the total volume of air that passes through the filters differ significantly depending on atmospheric conditions. For this reason the sampling time was established between 6 to 24 h.

The sampler was situated at a distance of 2 meters of sea level to avoid interference from the surrounding buildings. The distance to the nearest streets was more than 50 meters. The sampling involves an area in the surroundings of access highways to the city, a thermoelectric station, a petrochemical complex and a seaport (Fig. 1).

Fig. 1. Area of Study: Access Highways to the city
1. Petro-chemical complex; 2. Collection Site; 3.Thermoelectric Station; 4. Seaport.

A total of 126 membranes (PM10 = 63, PM2.5 = 63) were collected from February to September 2011 for gravimetric and chemical characterization.

Following the procedure described by the Agency of Environmental Protection (EPA -Method IO-2.2), the membranes were conditioned and maintained at 40±5ºC during 24 hours before and after to be exposed. They were weighted using a microbalance[2]. Black smoke was determined in PM2.5 fraction using the reflectometry technique following the procedure described by ISO 9832 [3]; the reflectometer[3] was previously calibrated using standards with the same type of filter that was used for collecting the samples. The filters were also analyzed using energy dispersive X ray fluorescence (EDXRF)[4] [4]. The following elements were determined: Al, Si, S, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn As, Sr, Ba, Pb with different grade of precision and accuracy in PM10 and PM2.5 .

Sedimented dust was collected 9 of June and 17 of October, and next analyzed by EDXRF. For quality control, reference material NIST 2783 was analyzed to check the accuracy of the analysis of EDXRF.

Data analysis

In order to determine if the appearance of the volcano ash causes a significant difference in the

[1] Andersen Dichotomous Sampler Serie 240.

[2] Sartorious filter microbalance M5P-00V001.
[3] EEL smoke stain reflectometer model 43D.
[4] Spectro Xepos.

parameters analyzed, the Mann-Whitney Test was applied [5].

Principal component analysis (PCA) with varimax rotation was also performed by applying SPSS software in order to identify main sources affecting the PM composition in the sampling site. Two analyses were realized. The first one considering all data obtained in the sampling period and the second one considering only the data when there is no evidence of volcano ash's intrusion.

Results

The results of the Mann Whitney Test show a significant increase of Al, Si, Ti, V, Mn, Fe, Cu, Pb in both PM2.5 and PM10 fractions. On the other hand Ca shows a significant increase only in PM2.5. It can be seen that Al, Si, Ca, Ti, Mn and Fe are more associated to PM10 while S, K, V, Cu, Zn and Pb are more associated to PM2.5. And this fact is observed before and when the event happens. The ratio of PM2.5 / PM10 increases for S, Cl, Ca, Fe. However the ratio of PM2.5 / PM10 for Al, Si, K, Ti, Mn and Cu remains constant during entire study period. Furthermore the ratio of PM2.5 / PM10 for gravimetric concentrations doesn't show variation in the same period.

During the occurrence of the interference event a remarkable increase of V and Pb in PM10 was observed due to decreasing of relationship PM2.5 / PM10 for these elements.

PCA of PM2.5. Taking out data that shows the presence of volcanic ash accounted at least for 77.7% of the variance dataset. In this case there are 4 sources (factors). Factor 1 is linked to rock forming minerals (Si, Cl, K, Ca and Fe). Factor 2 (Mn, Fe, Cu and Pb) is related to metallurgical activity. Factor 3 (S and V) is associated to fuel oil produced by petrochemical complex; thermoelectric station operation and vehicles. Factor 4 (black carbon and Zn) is related to the high traffic in the study area.

Considering data that shows the presence of volcanic ash PCA of PM2.5 accounted at least for 72.3% of the variance dataset. In this case there are 3 sources (factors). Factor 1 (Ca, Ti, V, Mn, Fe, Cu and Pb). These elements show a significant increase in concentrations during the volcanic ash intrusion. Therefore this factor could be linked with volcanic ash.

Factor 2 (Al, Si, Cl, K, Ca, black carbon) is likely a mixture of sources: crustal (resuspension of soil), volcanic ash and biomass burning.

Factor 3 (S, V, Zn and BC) is linked with fossil fuel combustion related to heavy transport, thermoelectric station and petrochemical complex operation situated nearby of the monitoring site. The results of PM10 fractions calculated by PCA show 3 components in both cases (including and extracting the dataset that show interference events). The components account for at least 86% and 83% of the variance, respectively. Factor 1 links the elements related with crust in both analyses. Factor 2 (Mn, Cu and Pb) changes the percentage in the total variance according to the dataset considered.

A third factor associates S, Cl and Zn and no explanation for a possible source was found.

The results of the analysis of sedimented dust performed by EDXRF. There is good agreement between these results and the elements that have a significant difference in PM2.5 and PM10 fractions (Si, Al, Ca, Fe, K, Ti, Mn, Pb, V and Cu). Enrichment factors calculated in volcanic ash will indicate an enrichment of Cl, S, Zn, Br and Pb and to a lesser extent for As (Fig. 2).

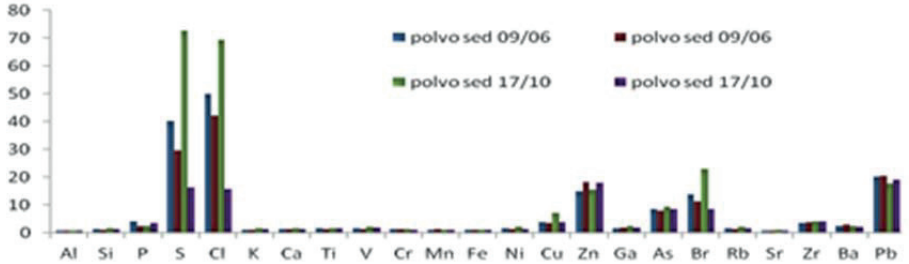


Fig. 2. Enrichment Factors of volcanic ash collected 9 of June and 17 of October 2011.

Conclusions

The determination of elemental composition in PM10 and PM2.5 fractions by EDXRF and the application of PCA allowed identification of the elements concentrations and their alterations during the intrusion of volcanic ash. The occurrence of this event introduces the interference in the determination of main emission sources of local origin.

References

[1] ATKINSON, R.W., FULLER, G.W., ANDERSON, H.R., Links Between Urban Ambient Particulate Matter and Health – A time Series Analysis Of Particle Metrics LINKS BETWEEN URBAN AMBIENT, Airborne Particles: Origins, Composition and effects, *RSC Avancing Chemical. Science*, UK. 2008

[2] EPA, 1999, Compendium Method IO-2.2, Sampling of Air for PM 10 Using an Andersen Dichotomous Sampler

[3] Internacional Estándar ISO 9835, 1993, Ambient Air- Determination of a Black Smoke Index, Reference Number ISO 9835:1993(E)

[4] Center for Environmental Research Information Office of Research and Development U.S. Environmental Protection Agency, 1999, Determination of Metals in Ambient Particulate Matter using X- Ray Fluorescence (XRF) Spectroscopy

[5] http://es.wikipedia.org/wiki/Prueba_U_de_Mann-Whitney

Publications of potential interest to the XRF community

1. Handbook of Green Analytical Chemistry, Miguel de la Guardia, Salvador Garrigues, John Wiley & Sons, Inc., 2012
2. E. Desimoni, B. Brunetti, Uncertainty of measurement and conformity assessment: a review, Anal Bioanal Chem, 400, 1729-1741,2011
3. Total Reflection X ray Fluorescence Analysis, Training Course Series (CD-ROM) 51, IAEA Training Course Series No.51, 2011

IAEA
International Atomic Energy Agency
Atoms for Peace

50th Anniversary of the Agency's Nuclear Sciences and Applications Laboratories in Seibersdorf

Believe it or not: the Agency's Nuclear Sciences and Applications (NA) Laboratories in Seibersdorf have just completed half a century of dedicated support to Member States in their efforts to optimally exploit 'atoms for peace'. It seems to be an appropriate time to celebrate the completion of these five decades in a fitting manner.

Throughout these many years, the activities of the NA Laboratories in Seibersdorf have continuously evolved, also through their partnership with FAO, in response to the ever changing landscape of nuclear technologies and applications, and to the multitude of expectations of national and international organizations for cooperation in nuclear research and technology transfer. In this process, the Laboratories have consistently remained at the forefront of assisting Member States in fostering the use of nuclear science and technology wherever these offer unique opportunities or provide added value.

The Laboratories have indeed come a long way. Starting with a mere 1736 m^2 of combined laboratory, office and corridor space in 1962, the original U-shaped building housed 14 professional and 24 general service staff. Today, it covers an area of more than 13 000 m^2 and is a dynamic hub for nearly one hundred scientists, technicians, fellows, visitors, interns and students from all over the world that are engaged in a wide range of activities dedicated to supporting global development and cooperation. These dedicated and concerted efforts have led to a myriad of success stories in the many areas of work in the Laboratories, which is both satisfying and enthusing.

Many of you have, at some stage in your career, interacted with the NA Laboratories in Seibersdorf and contributed to these successful projects and programmes, which are glowing examples of success stories that fully justify the mandate of these Laboratories. We are very grateful to all of you for seamlessly working with us, as we realize that it is only through the dedication, the enthusiasm and the numerous ideas of our many internal and external stakeholders, that it has been possible for the Laboratories to consistently remain at the forefront in our numerous and very diverse endeavours.

Nonetheless, this is not the time to lay back in satisfaction but a time to look forward to further enhance the performance of the Laboratories and to improve our outreach. While the NA Laboratories in Seibersdorf have served the Member States well over the last half century, they need to be modernized and upgraded to cater to growing demands and to keep pace with increasingly rapid technological developments. The planned 50 year anniversary celebration of the Laboratories is an apt time to look back and feel proud of the numerous achievements, as well as to plan the future road map that will enable the Laboratories to retain the high level and quality of service that Member States have come to expect.

So, when we celebrate the 50th anniversary of the NA Laboratories in Seibersdorf, it is really you we are celebrating. We sincerely hope to see as many of you as possible during this year of celebration or maybe even at the actual event in late November 2012 at the Laboratories.

Daud Mohamad

Deputy Director General
Department of Nuclear Sciences and Applications

Impressum

XRF Newsletter, No. 23, September 2012
The XRF Newsletter is prepared twice a year by the IAEA Laboratories in Seibersdorf. Correspondance and materials to be considered for publishing should be sent to:

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

International Atomic Energy Agency
Vienna International Centre, PO Box 100, 1400 Vienna, Austria
Printed by the IAEA in Austria, September 2012