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X ray Fluorescence in the IAEA and its Member States

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Activities in the IAEA XRF Laboratory

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

Proficiency test for XRF laboratories

The proficiency test (code PTXRFIAEA04) was the fourth worldwide exercise organized by the IAEA Laboratories at Seibersdorf in order to assist X-ray fluorescence laboratories in assessment and improvement of their analytical performance. This time, the test involved distribution to the participating laboratories a sample of environmental origin with established homogeneity and known target values of the analytes. The test sample was a clay material prepared and tested by an independent external laboratory. The powdered, homogenized, and dried material was distributed to 52 laboratories in sealed plastic bottles, each bottle containing 100 g of the test sample.

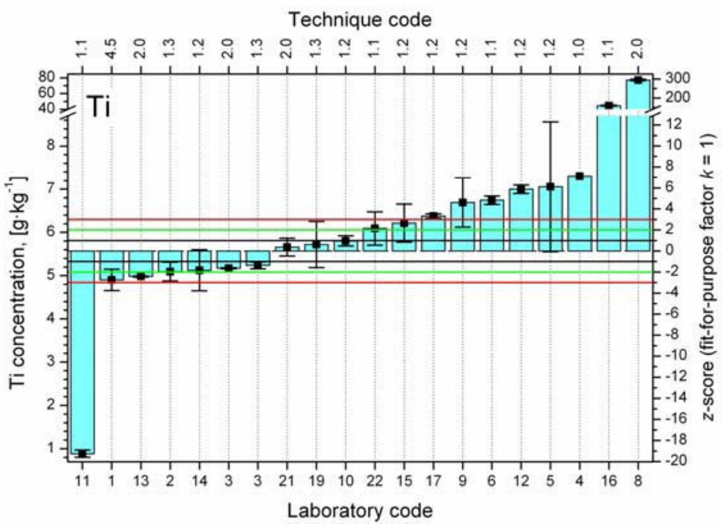

Fig. 1. Distributions of the z-scores for titanium. The bar charts show the distance between the reported and the assigned values of the analyte. The submitted results and their uncertainties, as provided by the analysts, are marked with filled squares accompanied by uncertainty bars. The horizontal lines show the admissible levels of z-score, $|z| < 2$, for three different fit-for-purpose ranges defined by factor k:

***k = 0.5 - solid black lines**, **k = 1.0 - solid green lines**, and **k = 1.5 - solid red lines**.*

The participants were requested to determine the mass fractions of chemical elements making up the sample according to their routine analytical procedures. They were also advised to determine the moisture content of the material by using a separate sample and to report the results on a dry-weight basis together with uncertainty. As usual, the laboratories were requested to analyze the sample using established techniques following their analytical procedures. The submitted results were processed, grouped versus analytes/laboratories and compared with the assigned values for the analytes. For the elements with known assigned values a set of z-scores and u-scores was calculated for each submitted result (see Fig.1 as an example). The obtained results and description of the statistical evaluation procedures were presented in the final report. Each laboratory was assigned a code to make sure that anonymity of the presented results is fully guaranteed.

Based on the results of the proficiency test each participating laboratory should be able to assess a quality of the analytical results by using standard performance criteria and, if appropriate, to identify discrepancies, and finally to correct the analytical procedures. The next proficiency test exercise will be carried out in 2008.

Further information on the proficiency test and the results obtained is available from Dariusz Wegrzynek (D.Wegrzynek@iaea.org).

Workshops and Meetings

Workshop on Non-destructive and Micro-analytical Techniques in Art and Cultural Heritage Research, Lisbon, Portugal, 25–28 April 2007

The Workshop organised by the University of Lisbon was attended by around 140 participants from the European countries and USA. The programme included invited lectures, oral presentations, poster sessions, presentations and exhibition by commercial suppliers (Bruker AXS, Horiba, Roentgenanalytik, WideColour). The following major topics were covered: (i) portable instrumentation for study of cultural heritage (CH) objects, (ii) methodology of in-situ applications for investigation of art objects, (iii) quantitative XRF analysis, (iv) micro-XRF techniques, (v) integration of various analytical techniques for characterisation of CH objects, (vi) networking in the field of study of CH objects, (vii) conservation techniques for CH artefacts, (viii) imaging techniques, and (ix) practical applications. During the Workshop an invited lecture on Portable XRF Spectrometers for In-situ Measurements – Methodology and Applications” (A. Markowicz, D. Wegrzynek, E. Chinea-Cano, S. Bamford, G. Buzanich, C. Streli, P. Wobrauschek) was presented.

The applications of the portable XRF instruments developed at the IAEA laboratories at Seibersdorf were reviewed by Ms. M. Griesser, Museum of Fine Arts, Vienna who presented a paper on Applications of a New Portable (Micro) XRF Instruments Having Low-Z Elements Determination Capability in the Field of Works of Art (M. Griesser, K. Uhlir, D. Wegrzynek, A. Markowicz, E. Chinea-Cano, G. Buzanich, P. Wobrauschek, C. Streli). The newest version of the portable XRF spectrometer with a vacuum chamber attachment was used to study bronzes, ancient Egyptian objects, old master paintings, and old paper objects. The results were used to support restoration and conservation of the objects.

The Workshop confirmed the growing interest in development and applications of nuclear and other analytical techniques in support of study of cultural heritage artefacts. Substantial number of research groups from the universities and research institutes presented home-made portable instruments based on X-rays as well as analytical methodologies for imaging and microanalysis based on synchrotron radiation sources. In view of the new developments and applications of nuclear analytical techniques it is worth mentioning that the instruments and methodologies developed in the IAEA Laboratories at Seibersdorf represent a high standard and offer unique features for in-situ measurements. A positive feedback was received from the Museum of Fine Arts in Vienna where the new version of the instrument was tested and applied.

Further information on the IAEA contributions presented at the Workshop is available from Andrzej Markowicz (A.Markowicz@iaea.org).

ANKA Users Meeting, Karlsruhe, Germany, 2 October 2007

The meeting of the users of the ANKA Synchrotron Facility was held in Forschungszentrum Karlsruhe, Germany on 2 October 2007. During the meeting the IAEA's representative presented a poster on Application of X-ray Imaging Techniques for Studying the Morphology of Malaria Mosquitoes which summarized the results of collaborative work carried out in 2007 by four partners including the Instrumentation Unit, the Entomology Unit/Malaria Project, Atominstitut in Vienna and the ANKA Synchrotron Facility in Karlsruhe. The work demonstrated suitability of the X-ray phase contrast imaging techniques for examination of morphological structures of live mosquito specimens. At the time of measurements the ANKA experimental set up was still not fully commissioned therefore the high resolution imaging was not performed.

During the meeting the remaining experiments in the series related to the mosquito species was discussed. The measurements will be carried out in 2008 after commissioning of the TOPO beamline which will provide a possibility to perform high resolution imaging (0.5 micrometer) of the mosquito morphology.

Further information on the applications of synchrotron radiation sources is available from Dariusz Wegrzynek (D.Wegrzynek@iaea.org).

School on Pulsed Neutron Sources: Characterization of Materials, Trieste, Italy 15-26 October 2007

The School on Pulsed Neutron Sources: Characterization of Materials was held at the International Centre of Theoretical Physics (ICTP) in Trieste, Italy, from 15-26 October 2007. The school was organised with the cooperation of co-director Dr. Guenter Bauer, retired FZJ Juelich. The School had two main objectives. Firstly, to alert graduate and post-doctoral students to the possibilities offered by accelerator generated probes (neutrons, muons and synchrotron radiation) in the investigation of materials for practical applications and secondly, to familiarise students with the principles and technology of pulsed neutron sources and their application. It covered critical aspects of the design and optimization of pulsed neutron sources, outlining the flexibility and limitations that exist in providing customer-tailored beams for different kinds of applications. The idea was to bring together future potential source designers and users, establish contacts and facilitate networking as well as generate greater mutual understanding while encouraging the use of existing facilities.

About 35 young experts, researchers and students from 26 countries (Algeria, Argentina, Armenia, Bangladesh, Brazil, Bulgaria, China, Colombia, Cuba, Czech Republic, Egypt, France, India, Indonesia, Mongolia, Nigeria, Pakistan, Peru, Philippines, Romania, Russian Federation, South Africa, Sudan, Thailand, Turkey, and Vietnam) participated. Eighteen lecturers and directors from 7 countries (Austria, Bulgaria, Denmark, Germany, Switzerland, UK, and USA) gave 35 presentations.

The lectures during the first week of the School were related to "Sources, Source Technology and Methods", whereas the second week's lectures focused more on "Materials Science with Neutrons and Complementary Methods". Keynote lectures provided an introduction to the theme, followed by regular lectures and exercises. Specialised lectures during the second week allowed the topic to be developed and expanded. The lectures were presented by renowned scientists ensuring presentation of the highest possible quality of latest research results. The following topics attracted most interest:

- Design and Use of Neutron Sources
- Layout and Optimization of Pulsed Spallation Sources
- Data Processing and Analysis
- Accelerator Generated Complementary Probes
- Theory and Methodology of Materials Science with Neutrons
- Selected Examples of Materials Science with Neutrons and Complementary Probes

Lecture topics in the final two days of the School programme included: high resolution spectroscopy at spallation neutron sources, neutron radiography and tomography, spin echo at pulsed sources, applications of X-rays for study and preservation of cultural heritage objects, neutrons and cultural heritage, stress – strain – texture in materials, neutrons and environment. Full presentations are available at http://cdsagenda5.ictp.trieste.it/full_display.php?email=0&ida=a06221

The School on Pulsed Neutrons: Characterisation of Materials was a very successful and well organised event. The level of presentations was very high and up-to-date information was presented on applications of pulsed neutron sources for study of structure and dynamics of materials. A lecture on applications of X-rays in the study of cultural heritage objects, based on the IAEA's programme in this field, was a useful supplement to the major topics of the School, and generated positive feedback from the participants.

Further information on the School is available from Guenter Mank (G.Mank@iaea.org).

ICT-based Module on Ion Beam Analysis for Learning and Teaching

Samuel Bamford, Dariusz Wegrzynek, Ernesto Chinea-Cano, Andrzej Markowicz
Instrumentation Unit, XRF Group, IAEA Laboratories Seibersdorf, Austria
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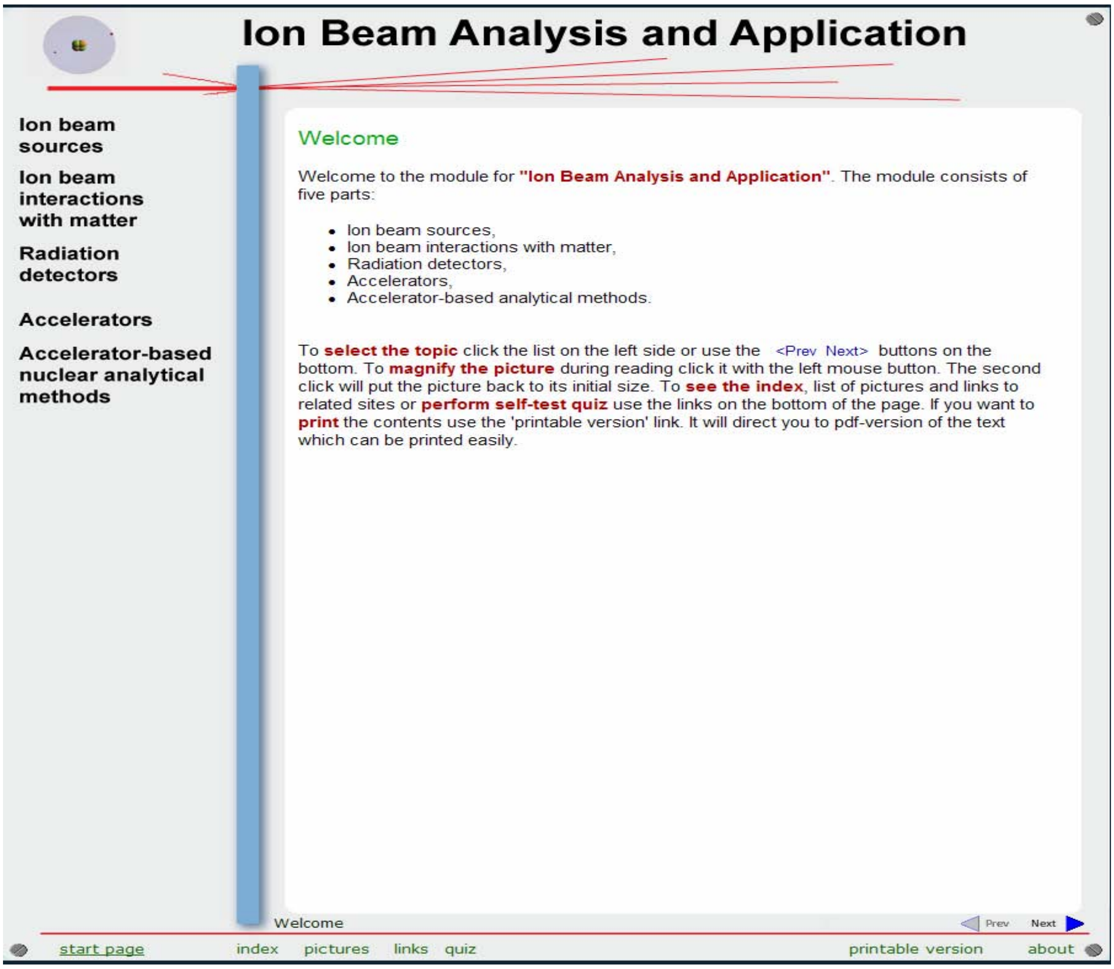
Accelerator-based analytical facilities offer the potential for applications in a wide range of fields and for different samples of interest. The International Atomic Energy Agency (IAEA), through its programmes and activities, seeks to develop and strengthen capacity in research and facility utilization in its Member States. An ICT-based module on Ion Beam Analysis and Application has therefore been developed to provide sound knowledge on the underlying scientific principles of accelerator-based facilities. This is an introductory module that precedes other modules to be developed to address specific techniques and applications. Figure 1 shows the Starting Page of the current module (under finalization). Index of the content of this module is included below. The module is being presented as a CD- and web-based interactive material. It departs from the text book format of presentation, and contains relatively more graphics, with animations of essential techniques to enhance comprehension. It is also presented in a modular form, with sequential blending of the practical approach to analysis and application. Useful web links to other relevant resources available on the internet has also been provided.

The table of contents of the module is as indicated below.

- Ion beam sources
  - The duoplasmatron
  - The negative sputter ion source
  - The radio frequency (RF) ion source
  - The radioactive ion beam sources
- Ion beam interactions with matter
  - Ionization
  - Elastic scattering
  - Nuclear reactions
  - Cross section
  - Differential cross section
- Radiation detectors
  - Introduction
  - General properties
    - Detection properties
    - Sensitivity, resolution, efficiency, dead time
  - Semiconductor detectors
    - Semiconductor properties
    - Diode detectors
    - Lithium-drifted detectors
    - High-purity germanium detector
    - Other solid-state detectors
    - Literature
- Accelerators
  - Electrostatic accelerators
    - Cockroft-Walton accelerator
    - Van de Graaff accelerators
  - Linear accelerators (LINAC)
  - Cyclic accelerators
    - Cyclotron
    - Synchrotron
- Accelerator-based nuclear analytical methods
  - Particle Induced X-ray Emission (PIXE)
    - The method
    - PIXE Instrumentation
    - micro-PIXE
  - Rutherford_Backscattering Spectrometry(RBS)
  - Particle Induced Gamma Emission (PIGE)
  - Elastic Recoil Detection Analysis (ERDA)



The module will be ready for distribution and accessible from the IAEA Laboratories website early in the year 2008.

Further information is available from Dariusz Wegrzynek (D.Wegrzynek@iaea.org).

Support to Technical Cooperation projects

The XRF Group at Seibersdorf provides assistance to a number of IAEA Technical Cooperation (TC) projects where XRF is used as one of the analytical techniques. The following events related to TC projects were supported in 2007:

Regional Training Course (RTC) on Evaluation and Interpretation of Data for Particulate Air Pollution combined with the Project Coordination Meeting under the regional TC project RLA/7/011 on Assessment of Atmospheric Pollution by Particles, Mexico City, Mexico, 7-11 May 2007

The events were organised by the National Institute for Nuclear Research (ININ), Mexico in cooperation with the IAEA under the regional TC project RLA/7/011 on Assessment of Atmospheric Pollution by Particles. The regional training course was attended by the project counterparts and representatives of the end-user institutions from Argentina, Chile, Costa Rica, Cuba, Mexico, Dominican Republic, Uruguay and Venezuela. The Project Coordination Meeting was attended by the project counterparts from 8 countries participating in RLA/7/011: Rita Plá (Argentina), Eduardo Cortés Toro (Chile), Alfonso Salazar (Costa Rica), Juana Grizel Pérez Zayas (Cuba), José Bernardino Contreras Pérez (Dominican Republic), Francisca Aldape de Flores and Javier Flores Maldonado (Mexico), Ethel Amalia Reina González (Uruguay), and Raiza del Valle Fernández Malave (Venezuela). Both events were attended by Prof. P. Hopke, USA, external lecturer; Ms. M. Zednik, IAEA expert; and IAEA Technical Officer.

The major objectives of the coordination meeting were: (i) to review the current status of the project including the achievements and problems encountered, and (ii) to discuss and agree on the work plan till the completion of the project.

Through the project all countries improved their knowledge in the implementation of procedures and analytical techniques related to study of airborne particulate matter. Due to the common interest in air pollution monitoring new cooperation was initiated between several institutions in each country.

A substantial number of professionals and technicians received general and specialized training under the project. Well trained human resources are fundamental for all participating countries to meet the objectives and ensure sustainability of the project.

Conference of Project Participants and End Users and Final Progress Assessment and Planning Meeting (RAS/7/013), Lower Hutt, New Zealand, 26-30 March 2007

The events were organised by the National Isotope Centre, GNS Science, Lower Hutt, New Zealand in co-operation with the IAEA under the regional TC project RAS/7/013 on Improved Information about Urban Air Quality Management. The objectives of the conference were to: (i) present and review the results of all activities carried out under the project from 2003-2006, (ii) collect feedback from end-users on the benefits and future directions of the project, (iii) share experience and information obtained from the project, (iv) explore further strengthening of the involvement of end-users in the project, (v) discuss common concerns and problems pertinent to air pollution, and (vi) consider actions to assure sustainability of the air pollution monitoring activities.

Fourteen National Project Counterparts from Australia, Bangladesh, China, India, Indonesia, Republic of Korea, Mongolia, Myanmar, New Zealand, Pakistan, Philippines, Sri Lanka, Thailand and Vietnam, together with six national end-users from Bangladesh, Indonesia, Mongolia, New Zealand, Philippines and Thailand as well as Prof. Philip Hopke, USA, regional data co-ordinator, participated in the conference. The end-users were mostly from governmental organizations responsible for environmental regulations and policies.

Major objectives of the Final Progress Assessment and Planning Meeting were to: (i) review and assess the progress and achievements (success stories) under the project in 2003-2006, (ii) identify major technical problems and propose remedial actions, (iii) discuss data evaluation and interpretation, (iv) review and update the work plan and needs of the participating countries for 2007-2008, (v) review functioning and contribution of Regional Resource Units, (vi) assess the role of Lead- and Assisting Lead- Country Co-ordinators, and (vii) assess the involvement and contribution of end-users. The Meeting was attended by the National Project Counterparts from fourteen countries (see above) and Prof. P. Hopke, regional data co-ordinator.

The project RAS/7/013 has generated a regional database focusing on urban, suburban, rural and industrial sampling locations in 15 Member States for the sampling period from January 2003 to December 2006. This contains more than 10,000 individual filter data analyzed by nuclear analytical techniques for up to 40 chemical species. This enables fine and coarse particulate matter compositions to be quantitatively determined for each of the sampling sites in the participating countries. The project has generated information on type and location of specific sources contributing to the air particulate matter. The analytical results were processed by advanced receptor models including PCA (principle component analysis), PMF (positive matrix factorization), CMB (chemical mass balance) and CPF (conditional probability function) for quantitative source apportionment. The likely locations of these pollution sources have been estimated using back trajectory techniques. Data produced by the project has been effective in contributing to air pollution management in a significant number of Member States, in particular to drive changes in legislation and provide effective evidence on the improvement in air quality following newly introduced legislation. End-users played a significant role in the project. The RCA helped in development of the links with the critical end-users in governmental institutions responsible for air quality management, universities, industries, health, and international development agencies.

Project Planning Meeting of the IAEA/RCA Project RAS/7/015 on Characterization and Source Identification of Particulate Air Pollution, Goa, India, 21-24 August 2007

The meeting was organised by the Bhabha Atomic Research Centre in co-operation with the IAEA, and held in Panaji, Goa. The project coordinators from Australia, China, India, Indonesia, Malaysia, Mongolia, Myanmar, New Zealand, Philippines, Singapore, Sri Lanka, Thailand and Vietnam as well as an expert form USA attended the meeting.

The project RAS/7/015 is continuation of the previous projects on air pollution monitoring with a major objective to contribute to the improvement of air quality in the RCA region by applying nuclear analytical techniques for the assessment and characterisation of air particulate matter (APM) pollution. The purpose of the project planning meeting was to discuss and identify major problems in air pollution monitoring with a special emphasis on (i) better integration of the project activities with the relevant national projects, (ii) impact of air pollution on visibility and long-range transport of pollution, (iii) establishing, maintaining and availability of regional database of high quality analytical data for APM, (iv) involvement and contribution of end-users to ensure sustainability of the project activities, and (v) updating of the work plan for 2007- 2010.

Further information on support to TC projects is available from Andrzej Markowicz (A.Markowicz@iaea.org).

X ray fluorescence in Member States

During the last months we have received contributions from Albania, Cuba and Sri Lanka on the current XRF activities. Below there are communications based on the original submissions (with only minor editorial changes).

Albania

Information about some activities at the EDXRF laboratory of the Institute of Nuclear Physics in Tirana, Albania

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Contributor: Nicolla Civici (ncivici@yahoo.com)

During the last years the EDXRF laboratory of the Institute of Nuclear Physics in Tirana, Albania has been involved in different activities and some of them are briefly presented below.

1. Monitoring of air pollution

Since some years our laboratory has been involved in the air pollution monitoring program in Albania. The laboratory is responsible for the evaluation of the level of trace toxic elements in urban air. At the beginning the program was considered as a simple survey while during the last years we are trying to approach the parameters of a monitoring process to study long term trends. For this purpose we have collected air particulate matter on filters using dichotomous sampler in Tirana and Elbasan, a city in central Albania. The filters were measured in our EDXRF system which is based on secondary target excitation and Si(Li) detector. Using a Mo secondary target we can determine 12 – 15 elements in each sample. The results allow the evaluation of trace elements level in the air and they are used to evaluate the sources of pollution by applying multivariate techniques (hierarchical cluster analysis and factor analysis). Fig. 1 presents the yearly average values together with the maximum and minimum values of Pb observed in the collected samples in Tirana.

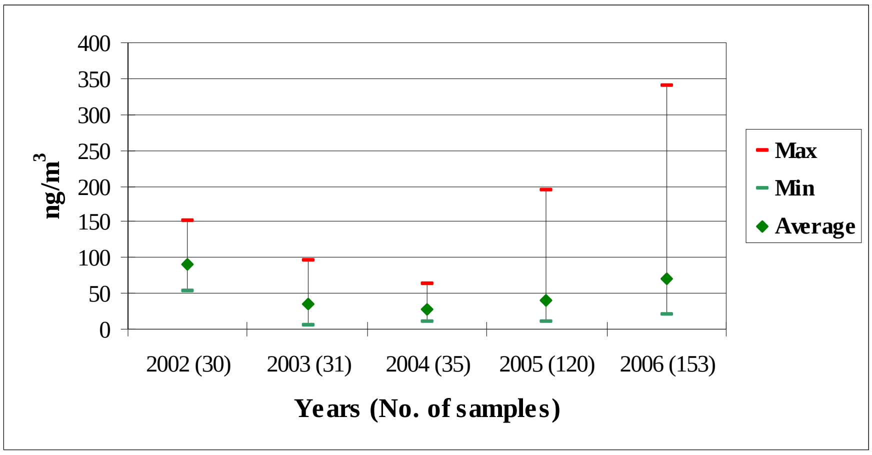

Fig.1. Measured variation of Pb at the station in Tirana center

The major pollution sources in Tirana are soil dust and car emissions, while the emissions from waste burning and small industries have a smaller contribution. In Elbasan the emissions of the metallurgical plant, situated a few kilometers from the city, together with soil dust and car emissions are the major pollution sources.

2. Evaluation of hyper accumulator plant species grown in metalliferous sites in Albania

A small number of plant species can grow in soils containing high levels of heavy metals, and can also accumulate these metals to high concentrations in the shoot. During the research project we aimed to study the response of plant root system to the presence of metals, the available pools of metals to plants, photosynthetic pigment metabolism and chlorophyll fluorescence signature of leaves which allow to characterize hyper accumulator properties, and to detect the differences between selected ecotypes due to heavy metal accumulation. Alyssum murale, a plant that grows in areas covered with serpentine soil in Albania, was studied as a model system for Ni hyper accumulation. Alyssum murale plants were collected in four different areas and representative samples from the native soils and those from the roots, shoots, leaves and flowers of the plants were studied with different techniques.

The elemental compositions of the samples were determined by EDXRF spectrometry. The results were obtained by the measurement of intermediate thickness samples using a program based on the emission-transmission method. Standard reference materials were used for quality control of the results.

Parameters that allow to evaluate the photosynthetic activity of the plants like the photosynthetic pigments (chlorophylls a and b and total carotenoids x+c) and the chlorophyll fluorescence induction kinetics (Kautsky effect) of pre-darkened leaves of the samples were also determined.

High concentrations of Ni were found especially in the leaves and flowers of the plants that were grown in soils with high concentrations of Ni (Fig. 2). This element is transported from soil through the roots and is accumulated in the leaves of the analyzed plants. Differences in Ni accumulation were observed between the four selected areas demonstrating higher contents in station 4. Iron, despite its higher concentrations in the soils, is not accumulated to the same degree as Ni.

The photosynthetic activity of the plants, as indicated by the measured parameters, demonstrates differences between ecotypes of the different stations and generally an inverse relationship with Ni content.

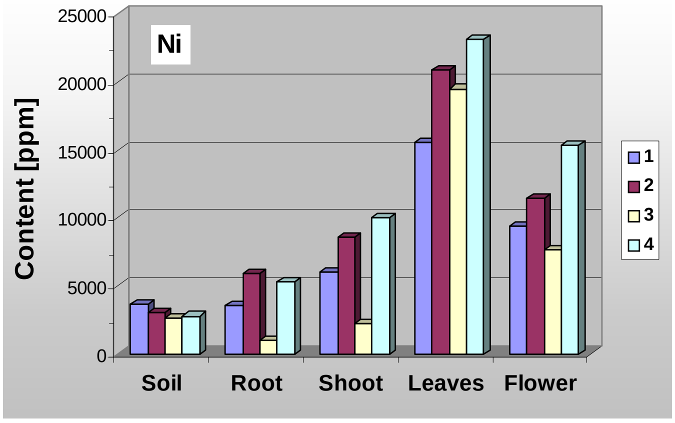

Fig. 2. Ni variation in soils and different parts of the plants collected in four stations.

3. Study of cultural heritage artifacts

The work of our laboratory in this field is steadily increasing as a result of the increased awareness of the conservators and restorers of the possibilities and advantages that the nuclear techniques offer in this field. This has been the result of our initial efforts and of the participation of the Albanian team, composed of nuclear scientists and conservators, in the regional IAEA Technical Cooperation project on Nuclear techniques for the protection of cultural heritage artefacts in the Mediterranean region (RER/1/006).

The first activity was the study of a group of Illyrian terracotta figurines of Aphrodite and related ceramics that belong to IIIrd century BC. The objects were found under water close to the bank of Seferan Lake which is situated about 2 km from the ancient Illyrian settlement of Belsh (central Albania). Most of the figurines were covered with a black layer of not uniform thickness. X-ray fluorescence was used for the determination of the elemental composition of small samples taken from the objects.

The data obtained by EDXRF analysis of the ceramic objects from Seferan Lake allowed us to determine the type of raw materials used for their manufacture which was important in support of technological studies. By comparing these data with those obtained from other ceramic samples of the same period and raw clays coming from different locations it was possible to demonstrate their local origin. This constitutes a scientific proof in support of the archaeologists’ thesis about the existence of an extensive ceramic manufacture activity in the area of Belsh.

The examination of the black layer that covers some of the figurines, which is not very frequent in this kind of artifacts, was very interesting. It was found that it is made of an iron rich material but the discussion regarding its origin is still open. It is not clear if the black layer was intentionally prepared during the manufacture of the figurines or created due to the weathering of the objects under water.

Another important activity is related to the application of X-ray techniques available in our laboratory for the identification of inorganic pigments in old icons and wall paintings. At the beginning small samples taken from the paintings were analyzed by EDXRF in our lab. Later it was possible to analyze micro samples, collected with a Q-tip, by TXRF while now we are mostly using our portable XRF instrument for in-situ analysis of the paintings.

During the last years we have studied three collections of icons (about 25 icons) that belong to a period from 14th to the beginning of 19th century, wall paintings from about 12 monuments (churches and mosques) of the same period and several other artifacts like painted iconostasis, painted ceiling, etc. Although the main objective of these studies was the collection of data that can help the restorers and conservators, a careful examination of the data can also lead to conclusions of more general character.

For example, we have observed a decrease in the usage of the yellow pigment ‘orpiment’ (As_2S_3) from 14th - 18th century (it is the main yellow pigment in a 14th century icon while it is rarely detected in the next centuries). The reduced use of orpiment was the consequence of its toxic properties and this trend was observed everywhere.

Another interesting observation is related to the blue pigment ‘smalt’. We have detected it in a 16th century wall painting, two icons of the 17th century and another wall painting from 18th century. In all cases the pigment’s key element, Co, is associated with the same trace elements (As, Ni, Bi) and furthermore the ratio of As/Co is rather constant. This can be an indication that through all these centuries the pigment has come from the same producer which according to literature data should had been in Saxony (these trace elements are referred as impurities of the smaltite ore produced in Saxony).

Recent publications

1. **N. Civici,** O. Demko, R. J. H. Clark, *“Identification of pigments used on late 17th century Albanian icons by Total reflection X-ray fluorescence and Raman microscopy”*, **Journal of Cultural Heritage, 6, 157-164, 2005**

2. E. Pavlidou, M. Arapi, T. Zorba, M. Anastasiou**, N. Civici,** F. Stamati, K.M. Paraskevopoulos *“Onoufrios, the famous XVI’s Century Iconographer, creator of the “Berati School”: Studying the Technique and Materials used in Wall Paintings of Inscribed Churches”*, **Applied Physics, A 83, 709-717, 2006**

3. T.Dilo**, N.Civici,** F. Stamati, Sh. Gjongecaj, I. Prifti, O. Bilani, N. Pistofidis, G. Vourlias, E. Pavlidou, G. Stergioudis, E.K. Polychroniadis, *“On the comparative study of three silver coins of the IIIrd cantury BC minted in Korkyra, Dyrrachion and by the Illyrian king Monounios”*, **Applied Physics, A 83, 632-642, 2006**

4. **N. Civici** “*Analysis of geochemical samples using a field-portable x-ray fluorescence instrument: assessment of analytical performance*”, **Albanian Journal of Natural and Technical Sciences, No. 19/20, 29-39, 2006**

5. **N. Civici** “*Non-desctructive identification of inorganic pigments used in 16 – 17th century albanian icons by total reflection x-ray fluorescence analysis*“, **Journal of Cultural Heritage, 7, 4, 339-343, 2006**

6. F. Babani, **N. Civici**, A. Mullaj, E. Kongjika and A. Ylli *“Evaluation of hyperaccumulator plant species grown in metalliferous sites in Albania”*, **Proc. of the 6th International Conference of the Balkan Physical Union, 22 – 26 August 2006, Istanbul, Turkey**

7. **N. Civici** *“Analysis of Illyrian terracotta figurines of Aphrodite and other ceramic objects using EDXRF spectrometry“*, **X-Ray Spectrometry, 36, 92-98, 2007**

8. **N. Civici**, SH. GJongecaj, F. Stamati, T. Dilo, E. Pavlidou, E. K. Polychroniadis, Z. Smit, *“Compositional study of IIIrd century BC silver coins from Kreshpan hoard (Albania) using EDXRF spectrometry”*, **Nuclear Instruments & Methods in Physics research B, 258, 414-420, 2007**

Cuba

Activities in Centre for Technological Applications & Nuclear Development (CEADEN)

Centre for Technological Applications & Nuclear Development, CEADEN, Havana, Cuba
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Introduction

The CEADEN Laboratory of Analytical Chemistry has a two-fold mission: providing analytical services to the industry, health care and environmental control institutions, and carrying out research projects aimed to introduce the use of nuclear and related analytical techniques in different type of investigations. The laboratory works on a self-sustained financial basis and has held accreditation by the Cuban QA/QC authority according to the ISO regulations since 1992. In 2004 the Laboratory upgraded its Quality Management System to fulfil the requirements of the ISO 17025 standard.

XRF constitutes one of the more used analytical techniques, and the analytical work is carried out following validated analytical instructions. The laboratory applies three different XRF spectrometers, allowing the applications of XRF technique to the study of samples of diverse nature:

- A spectrometer based on ^{241}Am and ^{109}Cd annular radioisotope excitation sources is employed for the analysis of metal alloys and raw materials, thus allowing determination of minor and major constituents in a prompt way.
- A TXRF spectrometer using a cut-off reflector to modify the excitation spectrum is applied to the analysis of metals in liquid samples and for the identification of pigments in minute samples of paintings.
- A third spectrometer is based on the principle of polarized excitation using X ray tube and secondary targets (EDPXRF). By choosing suitable secondary targets the excitation energy can be selected as close as possible to the absorption edge of the elements of interest, thus improving the efficiency of X ray production. Whilst the flux intensity of the characteristic radiation of the secondary target element is only two orders of magnitude lower than that of the direct X ray tube anode emission, the intensity of the Bremstrahlung radiation reaching the sample decreases by a factor of about thousand. The latter allows to reduce the detected continuum background and to improve the detection limits.

The development of a compact design holder for secondary target excitation (X-PRISM) and its combination with a digital signal processing spectrometer (DSP) allowed achieving a significant improvement in the instrumental sensitivity. This configuration has been successfully implemented in three laboratories of the IAEA Member States: CNEA-Paraguay, OBIMAR (Puerto Quetzal, Guatemala) and CEAC (Cienfuegos, Cuba) in frame of various IAEA technical co-operation projects.

Research projects involving XRF studies during the last three years

- Bio-monitoring studies based on lichen analysis (IAEA RLA 7010-ARCAL LX, 2002-2004).

This research allowed evaluation of suitability of using some lichen species to assess the state of pollution with several metals. The obtained results served to identify the main sources contributing to the pollution in Havana city. The work is expected to be continued as part of a forthcoming ARCAL project that aims to contribute to improvement of the life quality and the sanitary conditions of the population in the region. The main objective of this ARCAL project is to reveal correlations between the observed alterations in metal contents and some of the health problems identified in these territories.

- Metal speciation in environmental studies in coastal ecosystems (as part of IAEA CUB/7/006, 2004-2006).

The laboratory participated in this project by developing a group of preparative techniques allowing to isolate different chemical species of Cr, As and Se in samples of environmental origin. The further pre-concentration with APDC co-precipitation served to ease the determination by EDXRF analysis. The obtained results were of great value for assessing the toxicity risks of environmental pollution with these metals in the Cienfuegos bay.

- Non-destructive EDXRF archaeological pottery composition analysis (IAEA Research Contract CUB/13051, 2005-2007).

EDXRF has been extensively used for qualitative inspection of art works. The main causes hampering the performance of quantitative analysis are the usually complex structure of art objects (heterogeneity in composition, layered structures, among others), the lack of theoretical models to describe and account for such complexity, and the lack of suitable reference materials or well-analyzed standards allowing straightforward comparison with unknown samples. In the particular case of archaeological pottery, EDXRF can be successfully applied for compositional profiling. Ceramic objects are much simpler in structure, and both ceramic fabric and many cases of decoration layers can be considered as of 'infinite' thickness in regard to EDXRF fluorescence production volume.

A reliable EDXRF analytical procedure allowing the quantitative analysis and compositional classification of archaeological pottery was implemented. Besides its non-destructive and multi-elemental capabilities, the main features of the implemented methods are the use of standard-less quantitative approaches for quantification and the improvement in instrumental sensitivity by using selective secondary target excitation. Different types of pre-Columbian Cuban aborigine ceramics and colonial period pottery are under study to assist museum curators and archaeologists in classification and contextualization tasks. The results of the determined elemental mass fractions will also serve as input data for a database on art objects that is expected to be created as part of the activities of an RLA project in execution (IAEA RLA 8043: Use of nuclear analytical techniques and development of databases for the characterization and preservation of national cultural heritage objects)

- Integrated EDXRS - XRD characterization of materials (IAEA Research Contract CUB/13861, 2007-2009).

The limited capabilities of most of the conventional EDXRF spectrometers for determination of light elements lead to incomplete information about matrix composition which hampers the accuracy of the quantitative results due to wrong estimation of the X ray attenuation properties of the matrix of the sample. Quantitative phase analysis in powder XRD allows obtaining information on the major compounds in a relatively fast way. The combined use of both techniques thus complements the information required for a more accurate and adequate characterization of materials.

The present research is aimed to achieve a characterization of aluminous-silicate samples based on the combined use of XRD and EDXRF analysis. The main objective is to improve the analytical performance of EDXRF standard-less procedures for quantitative analysis by performing the attenuation correction based on the preliminary estimation of matrix composition by XRD technique.

- Evaluation of the degree of marine intrusion in the coastal aquiferous system at the south of Havana by using chemical and isotopic analysis (IAEA RLA 8041: Development of tools for integral management of coastal aquiferous resources, 2007-2009).

The Project will implement analytical tools supporting the integral management of the aquiferous system at the southern coast of Havana province. The study of the metal contents, in combination with the application of isotopic techniques will contribute to a better management of the water resources, minimizing the environmental impact of the works related to the potable water supply.

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Sri Lanka

Use of X ray fluorescence method combined with APDC co-precipitation technique in water monitoring programmes in Sri Lanka

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Introduction

Life style of Sri Lankan people was mainly based on agriculture until 1940-1950. At that time there were only few industries based on main economic plantations like tea, rubber, coconut etc. People did not use artificial fertilizers and pesticides for cultivation. Therefore there was a little risk to contaminate the agricultural and livestock products as well as drinking water. However, due to the recent socio-economic development programmes, the eco system of the country has been influenced by industries, in particular in Free Trade Zones (FTZ). Because of above reasons, the probability of contamination of the environment with harmful elements has considerably been increased.

The *Kelani River* from which *Ambatale* water treatment plant takes water, is one of the major water resources used to supply 343 million m^3/day of treated water to 4.7 million of population in Colombo city. *Ambatale* water treatment plant is situated about 4 km downstream from the *Rakgahawatta* canal through which the effluents from industries at FTZ are discharged to the river. Therefore Cr, Cu, Zn, Mn, Pb, Fe and Cd may contaminate the river water a tendency to accumulate those metals in living species has been observed. It is thus important to know the levels of heavy metals in consuming water in order to apply a proper treatment to get rid of harmful elements.

Use of XRF technique in pollution monitoring programmes

Dissolved heavy metals in water are normally present in the µg/Ll to ng/L range and their determination requires reliable and fast trace element analysis techniques in support of water monitoring programmes. They are usually based on atomic absorption spectrometry or stripping voltametry, and allow either single element determination or simultaneous determination of a very few elements. Owing to the growing need for information for a large number of samples produced in monitoring programmes and also because of favorable cost-benefit ratios, there is a need for efficient analytical procedures which allow simultaneous and multi-element determination. In this respect the X ray fluorescence method combined with co-precipitation technique used in this study has an advantage over other analytical techniques and therefore was used in water monitoring programmes in Sri Lanka.

Good performance, in terms of detection limits, accuracy, and precision is achieved by this method. The procedure has been used to determine contents of trace element such as Fe, Ni, Cu, Zn, As, Hg and Pb in water supplied to the water treatment plant, *Ambathale*. It was found from the analysis that Fe, Cu and Zn are the dominant trace metals dissolved in waters concerned. The obtained values are in the ranges of 20 to 1000 µg/L, 3 to 17 µg/L and 2.7 to 30 µg/L, respectively. Other heavy metals such as As, Pb, Hg and Ni were present below the detection limits for all sampling sites. The detection limits of the method were 4.0, 2.0, 2.0, 14.0 and 5.0 µg/L for Pb, Cu, Zn, Fe and Ni, respectively.

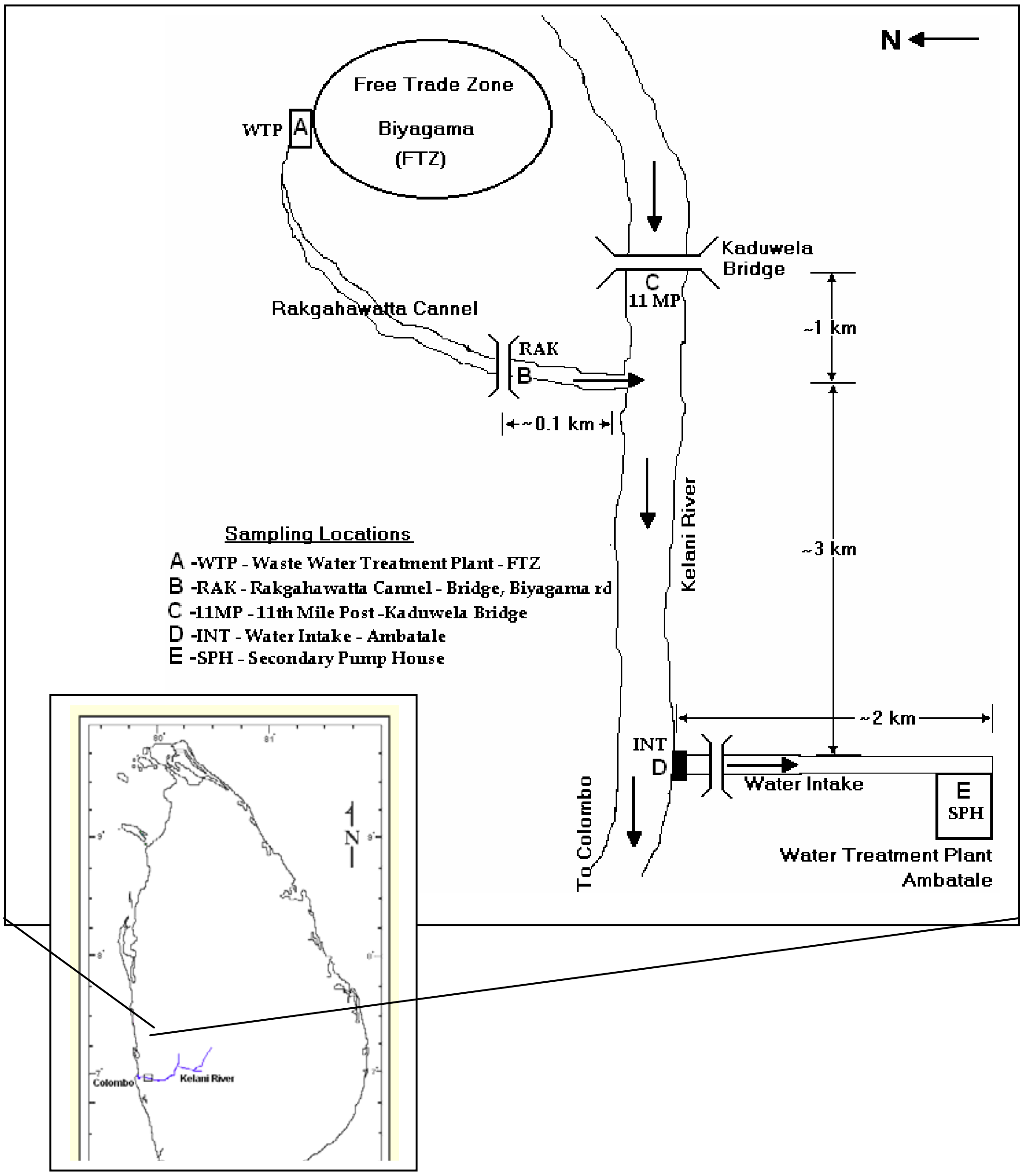
The concentration levels of Fe, Cu and Zn in Secondary Pump House (SPH) at *Ambatale* water treatment plant were within the acceptable levels for drinking water and lower than the concentrations of the elements in other sampling locations. Therefore it is concluded that the treatment for above three elements was appropriate.

Sampling and sample preparation

Water samples (1L) were collected from sampling locations A, B, C, D, and E shown in the figure below during the time period from July - November 2004.

All calibration standards were prepared using 10 ppm stock solutions previously prepared from 1000 ppm spectroscopy grade single element standards. Freshly prepared double distilled de-ionized water was used in final cleaning of the glassware and plasticware before starting the preparation of calibration standards. A 100.0 ml of the NIST-SRM 1640 (trace elements in water) was used as a reference water sample to validate the method.

A 100.0 mL of water sample was taken in properly cleaned polythene beakers. Then 100 µL of 1000 ppm Cd solution was added into each beaker as the carrier. Then the solutions were thoroughly mixed using a plastic rod and pH of the solution was checked. The pH of the solution was brought in the range between 3-4 by adding *Analar* grade *dil.* HNO_3 acid drops. If pH of the solution exceeded the desired range *Analar* grade ammonia solution was used for adjustment. The solutions were thoroughly mixed by stirring with a plastic rod for a minute. Then 1 mL of 1% APDC solution was added to each solution while stirring. The solutions were then allowed for precipitation for about 60 minutes. Then the suspensions in beakers were filtered through 25 mm diameter 0.45 µm pore size cellulose acetate membrane filters. The precipitate was carefully washed with double distilled de-ionized water by rinsing. The filters with precipitates were carefully removed from the filtering unit and placed securely in the clean air bench for one day for drying. After drying, flat precipitates on filters were measured by XRF technique.



Conclusion

The experimental results show that XRF analysis combined with APDC-based sample preparation is well suited for the routine monitoring of river water quality. In view of the sample preparation technique, it is simple and free from many difficulties as compared to other analytical procedures adopted in water analysis. The analytical method enables many trace elements to be determined simultaneously. As such, this method may help to improve the laboratory performance and increase efficiency in support of environmental monitoring programmes. Because of the relatively simple sample preparation procedure, a risk of trace element loss or contamination can be controlled.

The obtained results for “Fe” are in the ranges of 20 to 1000 µg/L and relatively high values (>650 µg/l) are always detected in *Rakgahawatta* cannel (RAK). Distribution among two locations *Kaduwela Bridg*e (11MP) and *Ambatale* intake (INT) which are both in *Kelani* river, was also studied and no direct effect of dissolved “Fe” in *Rakgahawatta* cannel on intake water to *Ambatale* water treatment plant was observed. The relatively high “Fe” concentrations were observed in RAK, 11MP and INT sampling stations with increase of water level after heavy rains. It can be concluded that the “Fe” from soil is always introduced into the river and other water streams after the rain. However, the dissolved “Fe” levels (<100 µg/L) in treated water were within acceptable limits. The results obtained for dissolved "Cu" and "Zn" in selected water bodies were in the ranges of 3 to 17 µg/l and 2.7 to 30 µg/l, respectively. The levels of dissolved "Cu" and "Zn" in treated water from *Ambatale* treatment plant were in the acceptable range. Other heavy metals such as As, Pb, Hg and Ni were not in the detectable levels at any sampling site. The method can also be used to analyse other water samples including rainwater, well water and bottled water.

Acknowledgement

Technical assistance provided by the IAEA to establish XRF laboratory in Sri Lanka and the fellowship training provided to local staff in XRF techniques are highly acknowledged.

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