XRF Newsletter

No. 27, April 2017

Contents

Editorial

Update from NSIL

Since the inception of this newsletter 17 years ago, the objective to inform and exchange views with nuclear analytical laboratories in the Member States on developments in fundamentals and applied aspects of X-ray spectrometry and nuclear instrumentation remains the same.

After 2010, the Instrumentation Unit of the former Physics, Chemistry and Instrumentation Laboratory beacme the Nuclear Science and Instrumentation Laboratory (NSIL) inside the Physics section sitting alongside programmes in Accelerator Technologies, Fusion Energy and Research Reactor technologies.

During the intervening period IAEA Seibersdorf has embarked upon the ambitious ReNuAL project aimed at significantly enhancing the capacity of the Department of Nuclear Sciences and Applications Laboratories across the full spectrum of topical areas including environment, food, agriculture and health and nuclear science.

Since 2015, NSIL has operated the IAEAXSpe X-ray Spectrometry Ultra-High Vacuum Chamber (UHVC) end station at the Elettra Synchrotron facility in Trieste, Italy. This installation provides access to state of the art equipment, supporting analytical capacity development in the field of X-ray science via a preferential beam time arrangement in a Coordinated Research Project. Through the ReNuAL project, a dedicated training and development "Mirror Facility" of the installation at Elettra has been placed at NSIL Seibersdorf.

In the coming year calls for new proposals at the IAEAXSpe will be solicited and a new experimental facility in collaboration with the Ruđer Bošković Institute in Zagreb to offer similar opportunities with particle beams will move a step forward.

Staff of the Nuclear Science and Instrumentation Laboratory (Jan'17, left-to-right): Mateusz Czyzycki, Mladen Bogovac, Janos Osan, Alessandro Migliori, Iain Darby, Sakura Gyay De Goyaz, Milan Matos, Roman Padilla Alvarez, Farhad Memarzia and Aleksander Cvetanovski.

Out in the field, the Mobile Spectrometry Team for Site Characterization, in collaboration with our colleagues from the Department of Nuclear Energy, has been active, deploying to Zambia and Nepal in 2016, with a mission to Senegal currently planned for 2017.

New materials and resources on activities at the laboratory can be found on the *Nuclear Instrumentation Forum* at:

nucleus.iaea.org/sites/nuclear-instrumentation

Join us on the new revamped site, if you're not already there!

Faces have come and gone at NSIL (see photo above) but the readiness of the team to respond to our users and community is undiminished.

I look forward to receiving your contributions to this newsletter and supporting your projects, fellowships, visits, and research needs here at NSIL.

Iain Darby
Head (a.i)
NSIL

News Round Up

IAEAXSpe Elettra

Figure 1: The IAEAXSpe positioned as the end-station of the Elettra XRF beamline.

The IAEAXSpe (shown in figure 1), an advanced X-ray spectrometry facility equipped with an ultra-high vacuum experimental environment is routinely operated at the X-ray fluorescence beamline at Elettra Synchrotron Trieste, Italy.

The IAEA, within the frame of the IAEA Coordinated Research Project G42005, provides access to the facility offering full beam-time support, dedicated preparation of the experiment and assistance with data evaluation.

In the period 2014 – 2016, sixteen research groups from fourteen IAEA Member States have conducted, in total, twenty seven experiments. In addition, direct support to Member States via the Technical Co-operation programme was provided by hosting fellows e.g. from Mongolia and Egypt. The major interests of the IAEA users are from the fields of:

- Environmental protection (37% of operating hours);
- Industrial and material science (32%);
- Fundamental science (21%);
- Life sciences (5%);
- Cultural heritage (5%).

Examples of supported experiments include: investigations into how the progress of industrialisation affects the quality of air in the regions of Indonesia and Saudi Arabia; the optimisation of an experimental protocol for trace element analysis of drinking water and its contamination with arsenic by Indian researchers; and investigators from Slovenia examined in plants and fungi the uptake and the toxicity of heavy metals (originating from an abandoned mercury mine), from the Mediterranean region.

Users participate actively in the implementation of new experimental methodology at the facility. For example Argentinian scientists performed pioneering experiments with RIXS, demonstrating that this technique can be a very successful alternative to XANES to probe element speciation.

Further information about the facility can be found at https://www.elettra.trieste.it/lightsources/elettra/elettra-beamlines/microfluorescence/iaea-end-station.html

More details of the IAEAXSpe, UHVC and the 7-axis manipulator at its heart can also be found in Issue No 24 (March 2013) of this newsletter.

NSIL Mirror Facility

NSIL has commissioned an IAEAXSpe "Mirror Facility" (shown in figure 2) at the IAEA Seibersdorf Laboratories. The facility is a training and development clone of the IAEA experimental end-station at Elettra and was provided through support of the German government.
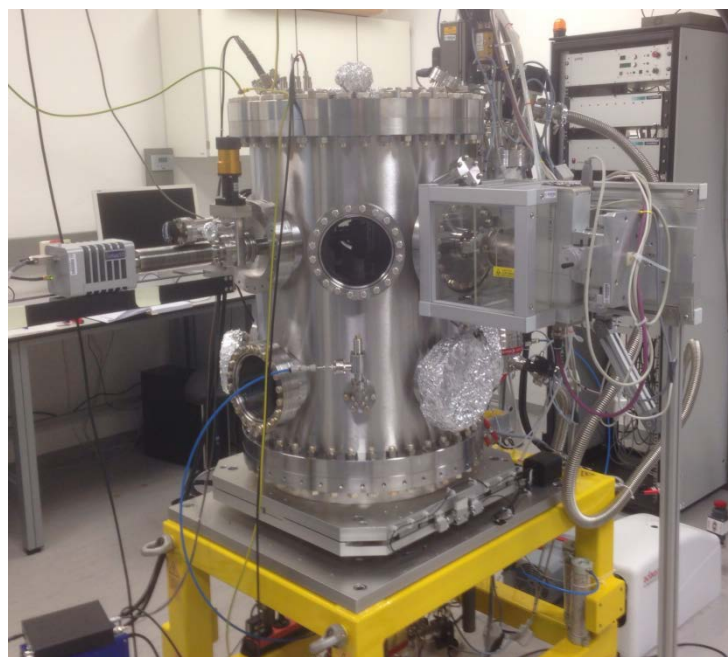

Figure 2: The IAEAXSpe "Mirror Facility" in place at NSIL.

The NSIL Mirror Facility operates with an X-ray source comprising of an air-cooled Mo-anode micro-focus X-ray tube and 2-dimensional parallel beam X-ray optics. The full assembly provides a monochromatic parallel beam with dimensions of 0.85×0.85 mm^2, and an overall intensity at 17.44 keV (Mo-Kα) of approximately 106 photons/s at tube settings of 50 kV and 0.6 mA (30 W). The fluorescence X-rays are detected by a 100 mm^2 active area silicon drift detector equipped with a 25-μm thick Dura-Beryllium

window. The energy resolution of the SDD is 136 eV (at 5.9 keV and 3 kcps).

This facility enables experimenters from synchrotron "newcomer" countries to develop their skills in experimental techniques and supports them in the drafting of synchrotron experiment proposals through a better understanding of the opportunities and capabilities of the available techniques and equipment. It is also utilised to improve hardware and software to be used on the beamline at Elettra and to commission new experimental setups without interrupting the experiments of regular users.

IAEA IBA at the Ruđer Bošković Institute in Zagreb, Croatia

Figure 3: Layout of PIXE/RBS scattering chamber attached to one of the beamlines of the 1.0 MV Tandetron accelerator.

Since 1996, the IAEA has had installed a beam line attached to the 6.0 MV Tandem Van de Graaff accelerator of the Ruđer Bošković Institute (RBI) in Zagreb, Croatia. In recent years, a new scattering chamber dedicated for ion beam analysis has substituted the original but now obsolete experimental chamber. The new chamber has been installed at one of the beam lines of the 1.0 MV Tandetron accelerator at RBI, as shown in figure 3.

This replacement enabled the opportunity for a major upgrade of the IAEA beam line. The construction of a new scattering chamber, that can accept simultaneously ion beams from both tandem accelerators, has started through the joint investment of RBI and IAEA. At present, the joint RBI-IAEA scattering chamber is equipped with PIXE and RBS detectors, sample heating apparatus and a goniometer that offers the possibility to perform channeling experiments. The beam from the Tandetron accelerator can also be focused by a quadrupole triplet microprobe configuration. The final setup of the system will include the possibility to focus the ion beam from the Tandem Van de Graaff accelerator as well, resulting in a unique dual-microbeam setup, which will be particularly interesting for irradiation of fusion materials as well as for many other interdisciplinary applications. Access to this beam

line as well as to the microbeam facility of the RBI has been secured for up to 30 days per year.

EPSILON 5 EDXRF

NSIL instrumental capabilities have been recently upgraded by the installation of an EDXRF spectrometer using secondary targets for excitation. The instrument (EPSILON 5, PANalytical, see figure 4) was acquired through support from the government of Germany within the ReNuAL project.

The excitation of the sample is made using the arrangement of an X-ray tube and suitable secondary targets/polarizers in 3-axis geometry (Polarized Energy Dispersive X-ray Fluorescence). Such an arrangement enables increasing the characteristic X-ray production in the samples, selecting a suitable target material (increase in instrument sensitivity) whilst drastically reducing the measured spectral background by reducing the intensity of the X-ray tube continuum that reaches the sample. Both effects result in achieving better detection limits.

The instrument has a 600 watt X-ray tube with a W/Sc-anode, 11 secondary targets (Al, CaF_2, Fe, Ge, KBr, Zr, Mo, Ag, Sn, CsI, CeO_2) and one Barkla polarizing device (Al_2O_3). The use of a thin entrance window high-purity Ge detector expands the efficiency from low energies to the range of K-emission lines for heavy elements.

The new spectrometer will be mainly used for the analysis of air particulate matter deposited in filters, minerals and other geological origin samples and food products, all related to IAEA fellowship training programs, regional training courses and adaptive research projects conducted with consultants and interns visiting the laboratory.

Figure 4: The Epsilon 5 EDXRF machine (right of picture) located in the main XRF Laboratory at NSIL, IAEA Seibersdorf.

Expressions of interest for performing experiments at NSIL, the IAEAXSpe at Elettra or IAEA at RBI are very welcome. For info email: NSIL.Contact-Point@iaea.org

Meetings & Conference Reports

Experiments with Synchrotron Radiation for Modern Environmental and Industrial Applications

Co-ordinated Research Project (CRP) G42005

The 2nd Research Coordination Meeting of the CRP was held at the Elettra Synchrotron, Italy from 30 May – 3 June 2016.

The CRP participants, originating from 17 countries and distributed in all continents (4 from Asia-Pacific, 2 from Middle-East, 1 from North America, 1 from Latin America and the remainder from Europe), presented research results of high quality, tackling challenging interdisciplinary applications. The CRP proposals targeted analytical applications of emerging interest in various scientific domains such as: characterization of structured novel materials for energy storage and conversion technologies; bio-sensing technologies and nano-medicine design; environmental monitoring of contaminants in air; water and biological samples; cultural heritage and preventive conservation; food products security; and study/improvement of the current level of knowledge concerning fundamental X-ray interactions and parameters.

The CRP has brought together a dynamic network of research groups who have performed experimental work at the XRF beamline of Elettra Synchrotron, bringing experience from other synchrotrons worldwide such as Indus-II in India, the Stanford Synchrotron Radiation Light source in USA, the Brazilian Synchrotron Radiation source, PETRA III in Germany, the Synchrotron Light Research Institute in Thailand and the Australian Synchrotron. The CRP is expected to increase the utilization of advanced synchrotron radiation based X-ray spectrometry techniques and enhance the competence and expertise of leading scientists from the IAEA Member States with relevant impact on future R&D activities and technology transfer from synchrotron radiation facilities to industrial applications.

At the time of the RCM, 42 peer-reviewed publications emerging from research conducted in relation to this CRP were either in-press or accepted for publication. This immense output is only possible due to the provision of access to a state-of-the-art experimental facility and the strong support of the Elettra and NSIL laboratories.

CRP G42005 remains open for proposals which will be reviewed on receipt. *Contact, prior to submission, with NSIL staff for discussion on experimental capability and proposal structure advice for applicants with no CRP or synchrotron experimental experience is strongly advised*.

Meeting Announcements

Training Workshop on Quality Assurance for Nuclear Spectrometry

Vienna, Austria 19-23 June 2017

The workshop is planned to highlight, review and discuss issues regarding the implementation of Quality Assurance and Quality Control activities relating to performing nuclear spectrometry techniques, including addressing recommendations for compliance to ISO17025 technical requirements for X-ray emission and gamma spectroscopy methods. The following topics are expected to be included in the programme:

- Method validation of nuclear analytic techniques and methods;
- Uncertainty estimation of results from nuclear spectroscopy methods;
- Internal and External Quality control activities;
- Addressing current needs of IAEA Member States for Quality Management implementation and laboratory accreditation;
- Role of the IAEA in support of the developing Member State activities to effectively implement and operate Quality Management Systems.
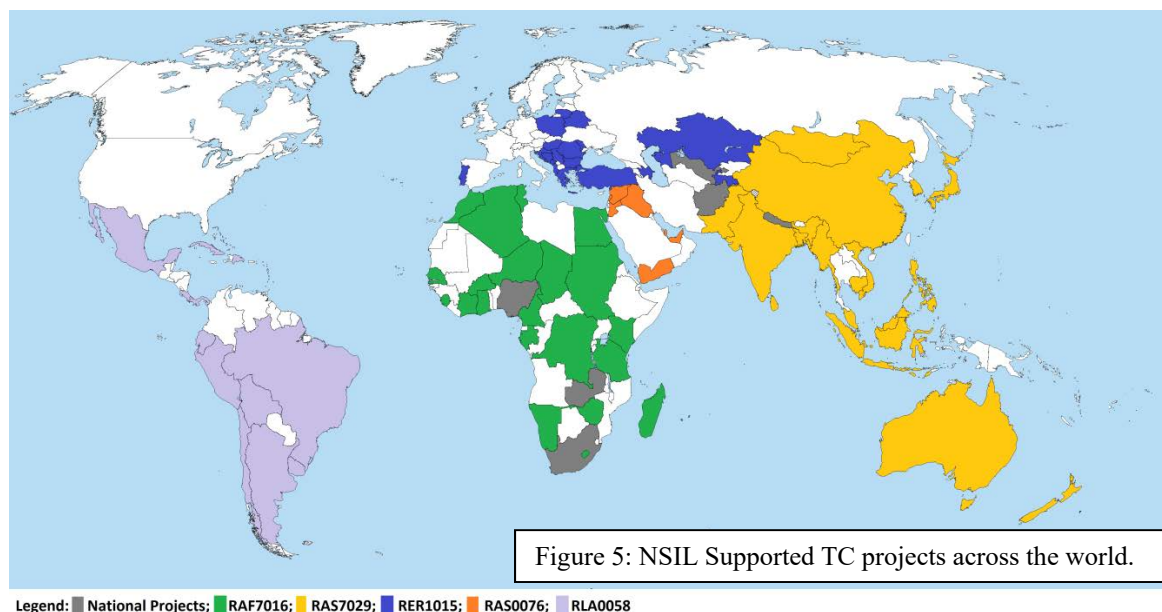
Technical Meeting on Trends in Analytical Applications and Instrumental Developments of Synchrotron Based X-Ray Spectrometry Techniques

Vienna, Austria, October 2-6, 2017

The aim of the Technical Meeting is to bring together specialists working at synchrotron radiation facilities to discuss instrumental developments and analytical applications of a number of X-ray techniques including: XAS, GIXRF, XRR, and TXRF. The meeting will also discuss the role of IAEA in facilitating the access of investigators from developing member states to synchrotron radiation facilities.

Find full details of these and other meetings, including application and grant support procedures on the IAEA Meetings webpage at: http://www-pub.iaea.org/iaeameetings

Support to Technical Cooperation Projects

Figure 5: NSIL Supported TC projects across the world.

Legend: ▮ National Projects; ▮ RAF7016; ▮ RAS7029; ▮ RER1015; ▮ RAS0076; ▮ RLA0058

NSIL Technical Officers (TO's) provide technical backstopping to many TC projects (see figure 5 and table 1), particularly on the themes of "Capacity building, human resource development and knowledge management" (01), "Accelerator Technology" (32) and "Nuclear Instrumentation" (33). For the development of concepts and designs for IAEA TC projects, support can be provided informally to individuals thinking about proposing projects to their National Liaison Officers (NLOs) and more detailed project design assistance is available for Member State endorsed projects in the review, design and evaluation phase.

Table 1: Selected Examples of current (or closing) projects) across a wide range of TC Field of Activities.	
Development of Nuclear Physics Laboratory for Bachelor and Master Students	Afghanistan
Assisting the Establishment of a Laboratory for Semiconductor Detector Maintenance and Repair	Algeria
Improving and Strengthening HR in the Areas of Environment, Mining, Nuclear Reactors, Nuclear Fuel, Human Health and Agriculture	Argentina
Supporting Design and Implementation of High Sensitivity Radiation Monitoring Equipment	Egypt
Establishing Preventive Maintenance and Sustainable Management of Medical and Scientific Equipment at the Oncology Institute in Libreville	Gabon
Developing Capacity for Nuclear Physics and Nuclear Chemistry Teaching Programmes at Tribhuvan University	Nepal
Establishing a National Regulatory Infrastructure for the Proper Use of Ionizing Radiation	
Designing and Developing a National Ambient Air Quality Monitoring Network for Potential Mega Cities	Nigeria
Re-Establishing a Nuclear Science Laboratory at Fourah Bay College for the Training of All Personnel	Sierra Leone
Strengthening the Regulatory Infrastructure	South Africa
Sustaining Nuclear Instrumentation Maintenance Capabilities (Medical and Scientific Equipment)	Sudan
Improving Training Capacity in Nuclear Science at the National University of Uzbekistan (NUU) and the Samarkand State University (SSU)	Uzbekistan
Improving Nuclear Instrumentation Capability - Phase II	Yemen
Assessing Radioactive Contamination of Surface, Groundwater and other Resources in Mining Areas	Zambia
Sharing Best Practices in Preventive Maintenance of Nuclear Equipment	AFRA
Establishing and Improving Air Pollution Monitoring	
Promoting Technical Cooperation among Radio-Analytical Laboratories for the Measurement of Environmental Radioactivity	
Investigating Atmospheric Particulate Matter and Pollution Source Contributions in Urban Environments Using Nuclear Analytical Techniques	ARASIA
Apportioning Air Pollution Sources on a Regional Scale	European
Using Nuclear Techniques to Support Conservation and Preservation of Cultural Heritage Objects	Latin America & Caribbean
Assessing the Impact of Climate Change and its Effects on Soil and Water Resources on Polar and Mountainous Regions	Inter-Regional

Regional Projects

Towards improving air quality

The quality of the air is of high concern and national and regional directives describe regulations and limiting values for specific constituents of air pollution. These control measures are intended to lead to the lowering of levels of air pollution, which negatively influence human health, objects of cultural heritage and the climate. These detrimental effects are primarily due to the chemical composition of pollution, and determining the elemental/chemical profiles of observed air particulate matter (APM) serves to identify the local and regional sources of pollution. Due to the long range transport of APM, air pollution is an issue not limited to a particular area but of concern for large regions. Therefore, it is crucial to make accurate assessments of the diversity and types of sources across a given region, as required for regulatory purposes and effective monitoring of the air pollution and to address effective mitigation strategies.

Four regional TC projects aim to optimize techniques for characterization of air pollution in order to more effectively determine the number of sources and their contributions. The availability of data on a larger pool of elements and other parameters allows for the determination of more efficient methods of air pollution control and abatement in the regions.

The four projects pursue the establishment of regional networks for air monitoring and the design of remedial strategies with up-to-date data analyses where monitoring showed poor air quality and; to carry out sampling at meteorological stations for the quantitative and qualitative analysis of APM. The nuclear techniques used for elemental analyses are: X-ray Fluorescence (XRF); Particle Induced X-ray Emission (PIXE), Neutron Activation Analysis (NAA) and Synchrotron Radiation Induced X-ray techniques. Regional resource centres provide analytical services for the countries where none of these techniques are yet available. A similar project is now under design for the Latin America and Caribbean region.

The IAEA organizes workshops and technical (task force) meetings, as well as providing expert services and regional training courses during which the knowledge and experience that IAEA has in the development and applications of nuclear techniques in various fields are shared with the Member States, in order to help them optimize and use the nuclear techniques effectively. Additionally, the IAEA is expected to provide small pieces of equipment and opportunities to use specialized facilities at more advanced institutes. The support of the Nuclear Science and Instrumentation Laboratory in organizing ISO17043 compliant proficiency test exercise is also envisaged.

The Asia and Pacific Region project RAS7029 implements the fourth cycle of a project on air pollution involving 17 countries: Australia, Bangladesh, China, India, Indonesia, Japan, Cambodia, Malasya, Mongolia, Myanmar, New Zealand, Pakistan, Philippines, Palau, Korea, Sri Lanka, Vietnam.

The European project RER1015 comprises (20): Albania, Belarus, Bosnia and Herzegovina, Bulgaria, Croatia, Cyprus, Greece, Hungary, Kazakhstan, Kyrgyzstan, Lithuania, Republic of Moldova, Montenegro, Poland, Portugal, Romania, Serbia, Tajikistan, Turkey and Uzbekistan.

In Africa 21 countries participate in RAF 7016: Algeria, Burkina Faso, Cameroon, Central African Republic, Cote d'Ivoire, Democratic Rep. of the Congo, Egypt, Gabon, Ghana, Kenya, Lesotho, Madagascar, Mauritius, Morocco, Namibia, Niger, Senegal, Sierra Leone, Sudan, Tunisia and United Republic of Tanzania.

Project RAS0076 joins six countries in Middle East region: Iraq, Jordan, Lebanon, Qatar, Syrian Arab Republic and United Arab Emirates.

Supporting investigations in cultural heritage

TC regional project RLA0058 (2016-2017), aims to promote and harmonize the use of nuclear techniques in the field of cultural heritage. Preserving the rich cultural heritage of the region is of upmost importance to countries as a source of knowledge of their history, as well as for the promotion of cultural tourism, which is a key socio-economic driver in the region. Nuclear techniques are an advantageous choice to support characterization, conservation and preservation of the objects.

Regional cooperation in terms of knowledge exchange, sharing of specialized facilities among Member States and the creation of a data base are among the key targets of the project. A national and regional collaborative network of scientists, conservation scientists and conservators has been established, enhancing synergism between facilities with nuclear techniques experts and cultural heritage organizations at national and regional levels. The project offers training and capacity building in the utilization of nuclear techniques, as well as transnational access to analytical infrastructures. The project will be instrumental in providing further support to the harmonization of procedures and best practices, thereby improving the quality assurance of nuclear techniques.

Argentina, Bolivia, Brazil, Chile, Costa Rica, Cuba, Dominican Republic, Ecuador, Mexico, Panama, Peru and Uruguay participate in the project, involving both research and conservation institutes. The capabilities and techniques built with the IAEA assistance through previous research and technical cooperation projects will be used for characterization and conservation practices. NSIL provides technical backstopping to this project in the field of using nuclear analytic techniques for comprehensive characterization of art and archaeological objects.

Activities in the IAEA NSIL Laboratory

Prediction of salt tolerance in rice genotypes based on elemental contents

Introduction

Soil salinity is prevalent in arid, semi-arid, and in coastal regions subject to inadequate irrigation and/or drainage. It is a major environmental constraint to crop productivity throughout the world [1] and especially problematic in irrigated agricultural systems. In general, salt tolerance in plants is associated with maintenance of growth and the ability to complete the life cycle. Salinity stress reduces growth and productivity [1] and susceptible plants may die before reproduction. For crop plants salt tolerance may be generally defined as the ability to produce a yield in saline conditions.

Rice is the most important cereal crop after maize in the world in terms of production. Irrigated rice accounts for 55 percent of the global harvested area and contributes to 75 percent of global rice production [2]. Rice is classified as a salt sensitive crop [3] and is particularly sensitive to salt stress at the seedling stage. Among rice genotypes there is a range of tolerance; three classes have been identified (tolerant, moderate and susceptible) according to their response to salt stress [4].

Following the evidence of associations between some ion contents (Na^+, K^+, Ca^{2+}, K^+/ Na^+ and Na^+/Ca^{2+} selectivity) in plant tissues and growth performance of plants with respect to genotypic differences [5] a preliminary study was conducted to explore some variability in elemental contents measured by XRF.

In the current study 62 rice genotypes of documented salt tolerance were analysed by Particle Induced X-ray Emnission (PIXE) and XRF to validate the finding that element up-take in control conditions reflected responses in salt stress conditions.

Experimental

a)   Samples

Sixty-two rice genotypes with known responses to salinity were used as plant materials, including 23 tolerant, 13 moderately tolerant and 26 susceptible genotypes. These genotypes were sourced mainly from the International Rice Research Institute (IRRI, Philippines) and in addition to salt tolerance criteria the rice genotypes were selected from a range of countries and include contemporary as well as traditional cultivars. Growth parameters such as shoot biomass (fresh and dry weights), height and tiller number were used as a basis for determining genotype performance under salinity.

Hydroponic experiments were carried out in a glasshouse (temperature approx. day/night of: 30/20°C ($\pm$ 2°C) with 50-70% relative humidity provided by misting). Seeds were pre-germinated in Petri dishes on filter paper with distilled water. Germinated seeds were transferred to mesh supports in contact with the surface of a hydroponic solution. After 2 weeks the seedlings were removed carefully and wrapped in sponge strips and transferred to test hydroponic tanks. A modified Yoshida nutrient solution was used in the hydroponic system [6]. Two treatments were set up, a control (no added NaCl) and a salt treatment (NaCl, 10 dS/m or approximately 6.4 mg/l NaCl). These were applied after seedling establishment in hydroponics to four weeks old seedlings. Hydroponic solutions were replenished every 2-3 days. Details of the hydroponics protocol can be found at: http://www-naweb.iaea.org/nafa/pbg/public/manuals-pbg.html. Plant distribution was set up as a completely randomized design in the glasshouse with three replications per treatment and ten plants per replication. Samples were collected 16 days after the start of the treatment (DAT).

For dry weight determination, shoots and roots were oven-dried at 70ºC for four days and weighed. Then the shoots samples were grinded to fine powder for element contents analysis.

b)   Measurements

In order to obtain results of the best possible accuracy , the performance of PIXE and XRF was compared for the analysis of Na, Mg, P, S, Cl, K, Ca, Mn, Fe, Cu, Zn, Br, Rb and Sr. Figure 6 shows the measurement of low energy characteristic emission by both XRF and PIXE, and illustrates the gain in sensitivity attained by PIXE for the analysis of Na, Mg, P and S.

PIXE measurements were made at the PIXE/RBS end station, connected to the 1 MV electrostatic Tandem particle accelerator (HVE Tandetron) of the Division of Experimental Physics (DEP) at the Ruder Boskovic Institute (RBI), Zagreb, Croatia. Two MeV protons from a direct extraction duo-plasmatron source were used for excitation. For selective detection of more energetic X-rays a 360 μm Mylar film was positioned in front a Si (Li) detector placed at 145º respective to the excitation beam, while for low energy X-rays a Silicon Drift Detector (SDD) was placed at 150º with a deflector made of permanent magnets attached to the front to avoid being reached by backscattered protons. RBS spectra were collected simultaneously with an Ion implanted silicon detector in order to determine the charge deposited in the samples accurately. The measured X-ray emission and RBS spectra were processed with the Windows version of GUPIX [7] and SIMNRA [8] respectively.

XRF measurements were made following a procedure similar to that described in [9]. Three measurement conditions were
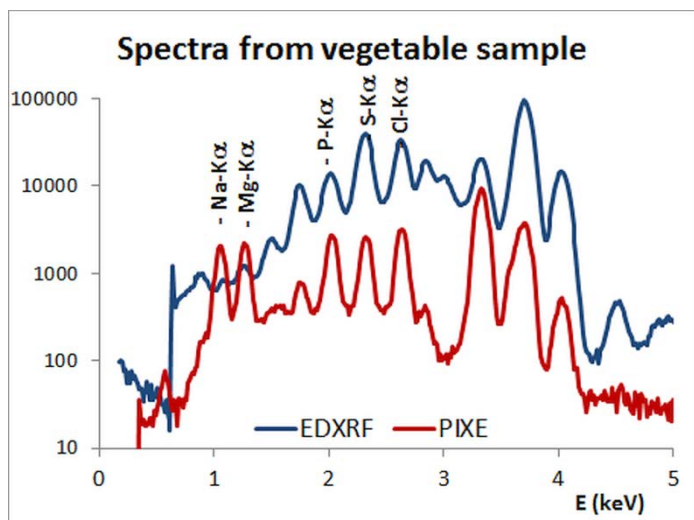
Figure 6: Comparison of sensitivity for low atomic number elements: XRF (Pd tube, HOPG scattered, SiLi detector) PIXE (2MeV protons, SDD detector).

set as to improve the excitation of different groups of elements using a Pd-anode tube and different ST: a molybdenum ST for the analysis of Fe, Cu, Zn, Br, Rb, Sr; a cobalt ST for K, Ca, Mn and; a Highly Oriented Pyrolytic Graphite (HOPG) scattering element for Na, Mg, P, S and Cl. The measurements were made with a Si (Li) detector in a vacuum chamber with automatic change of samples and secondary targets.

All XRF spectra were processed with the software package QXAS, freely distributed by IAEA. The calibrations were made by linear regression of measured count rates versus concentration using twelve Certified Reference Materials (CRM) of biological origin. Normalization of characteristic emission intensities to the intensity of scattered excitation radiation was used as a means to account for the differences in sample self-attenuation.

c) Statistical interpretation

The main steps followed for the multivariate statistical interpretation of the measured elemental concentrations were the following: (a) multiplying the concentration values by the dry mass of the samples, in order to obtain the total amount of nutrients intake by the plant; b) transforming the resulting data to log 10 values, to avoid that uneven concentration ranges of the elements might impose different weights in subsequent analyses; (c) reducing of the dimensionality of the data space using Principal Component Analysis (PCA) to ease the interpretation, and in the search for some ordination; (d) establishing a classification criterion based on using two Canonical Discriminant Functions to differentiate three classes in the data set (tolerant, medium tolerance and susceptible varieties) and evaluation of group membership probabilities using Canonical Discriminant Analysis (CDA). The statistical interpretation was performed using the procedures included in the software SPSS 11.5.
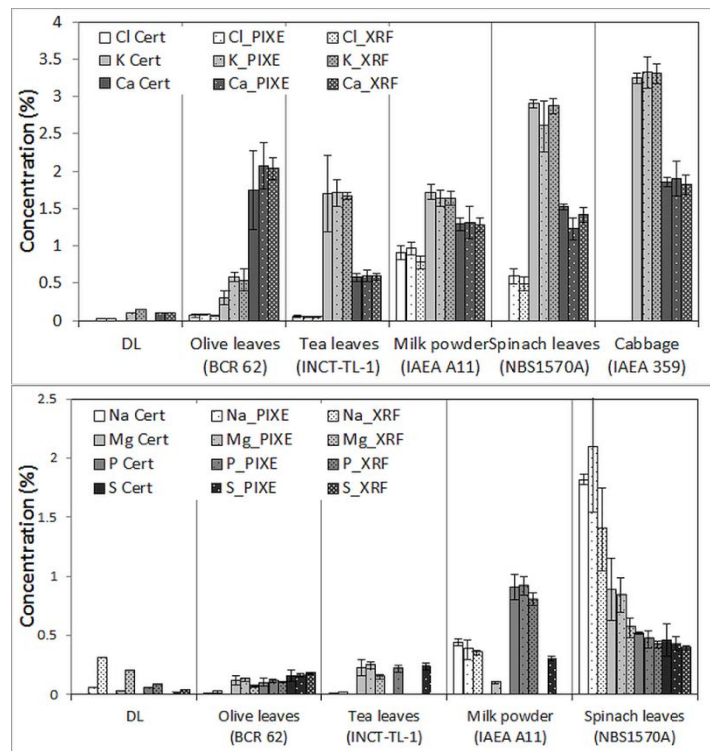

Figure 7: Validation of the results using CRMs.

Results

a) Comparison of performance of PIXE vs XRF

The quality of the results - in terms of accuracy, associated uncertainty and correlation between the two methods - was evaluated with regard to their usability for compositional classification of different rice genotypes with known tolerance levels to salinity stress [10]. The results from the analysis of a set of certified reference materials and associated uncertainties are presented in figure 7.

It was decided that the best accuracy for Na, Mg, P, S and Cl is obtained by PIXE, whereas the analysis of K, Ca, Mn, Fe, Cu, Zn, Br, Rb and Sr is more accurate by XRF.

b) Interpretation of the results

The tendency in the variations of concentrations of the elements in the different genotypes was explored for the two data sets containing the control and exposed to salinity stress samples, respectively. The results of the PCA revealed that the two first components accounted for 65% and 23% of variability of the data set, respectively. The largest variability in the data set, nearly 65 % is accounted for by the nutrient elements, even larger than the contribution to variability due to the elements related to the salinity stress (Na, Cl and Br). The tendency in variations of the elemental mass fractions with salt status and treatment can be observed from figure 8.

The results obtained for the samples that underwent saline treatment show that there is a decrease in the intake of nutrients Mg, P, S, K, Ca, Mn, Fe, Cu and Zn compared to the control (non-salt treated) samples. The decrease is more pronounced for the susceptible genotypes, whereas tolerant ones exhibit a larger intake of these elements. All these
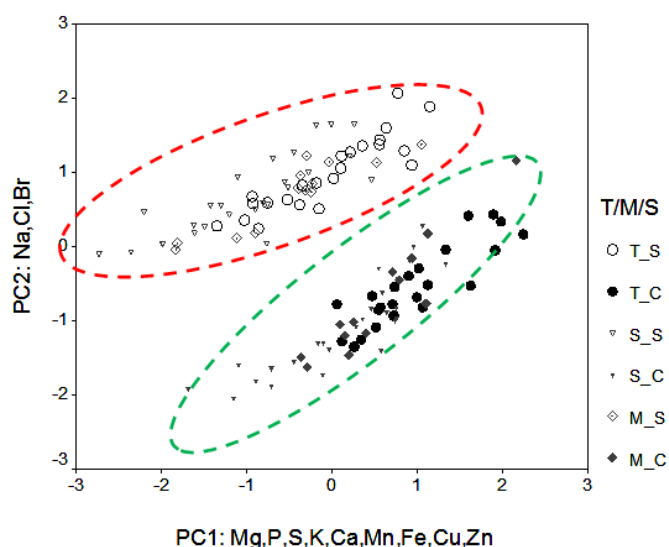
Figure 8: Ordination of the samples according to their scores in the PC-space. Each point represents the results for individual genotype samples, which is in turn labeled according to the tolerance to salt (S - susceptible, M- Moderate, T- tolerant genotypes) and to the group C- Control, S - Salt treated. Red ellipse: samples grown in salt stress, Green ellipse: Control samples. Note that the pattern for control genotype (closed symbols) shows a strong similarity to the pattern of salt treatment data (open symbols).
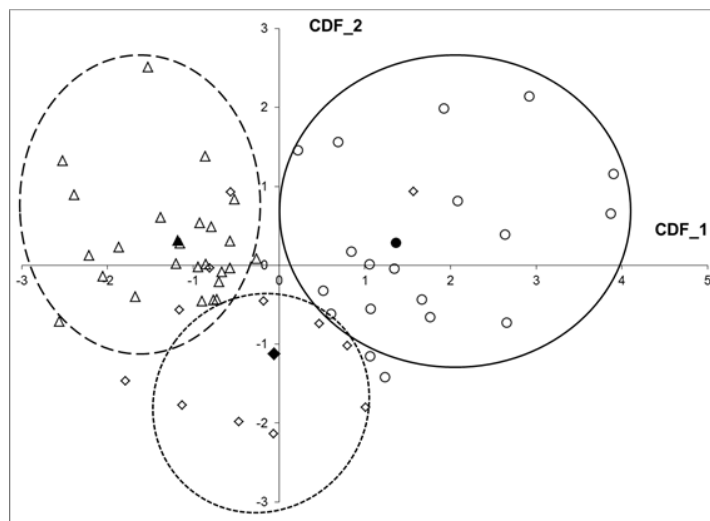

Figure 9: Clustering of rice genotypes with known salt tolerance into the three salt tolerant classes based on conical discrimination analysis of 16 DAT shoot element content. The mid-point for each cluster is indicated by a solid symbol. Each open symbol represents the mean of three replications of ten plants per individual genotype samples, which is in turn labeled according to the tolerance to salt. Triangle symbol: susceptible, square symbol: moderate, round symbol: tolerant genotypes).

elements showed a decrease under salt stress, whilst Na, Cl and Br accumulated in the shoots.

PCA analysis (see figure 8) showed differentiation between the treatments and genotype tolerance to salinity. These clusterings were less pronounced for root data in the analysis of standard genotypes. As a consequence the untreated shoot data set from validation experiment was explored for differentiation under control condition in a CDA.

Linear discriminant analysis is a method commonly used in statistics to find linear combination of property values allowing separating two or more classes of objects. Canonical discriminant analysis aims to find linear and uncorrelated functions defining a k-1 canonical functions that allow achieving a better separation of k expected classes. CDA also allows calculating the probability of be-longing to a particular class.

The results of such interpretation of the results obtained for the entire population of control shoot samples are represented in figure 9. The probability of belonging to its assumed class was found to be more than 75% for the majority of tolerant and susceptible genotypes, over 80% of all samples. The canonical discriminant analysis allowed the three salt tolerant classes (tolerant, moderate tolerant and susceptible) to be separated.

Conclusions

The concentration of elements in rice shoots can serve as a basis for predicting the response to salinity stress. The most effective measurements are the ones made on shoot dried weight and elemental composition, particularly the ratio K:Na and Mg:Na under salt stress taken at 16 DAT. That may be

assessed from leaf biopsies and plants possessing element compositions indicative of salt tolerance selected.

Testing for salt tolerance in benign conditions offers a simple, non-destructive pre-screening tool for plant breeders and since the tests may be conducted in fertile areas large amounts of seed may be harvested for subsequent testing, e.g. in saline fields.

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Results of the IAEA Proficiency Test PTXRFIAEA11: TXRF determination of minor and trace elements in water samples

Introduction

The IAEA assists its Member States Laboratories to maintain their readiness by producing reference materials, by developing standardized analytical methods and by conducting inter-laboratory comparisons and proficiency tests as tools for quality control. To achieve this aim and ensure a reliable worldwide, rapid and consistent response, the IAEA NSIL organizes proficiency tests annually for X-ray spectrometry laboratories.

The proficiency test PTXRFIAEA11 on the determination of minor and trace elements in three different water samples was organized in 2014 and supported a petition from the ISO TC WG3. The exercise aimed at gathering enough results to support the evaluation of a guideline and a standard method-ology proposed for water analysis.

The exercise supported the project "Inter-laboratory comparison of Total-Reflection X-ray Fluorescence Spectroscopy for Environmental Analysis" initiated in the frame of VAMAS (Versailles Project on Advanced Materials and Standards [1]) Technical Working Area 2, related to surface chemical analysis. The project aim is the development of guidelines and standard methodologies for analysis of biological and environmental samples by means of TXRF [2]. The evaluation of the results will allow assessing a standard for water analysis to be submitted to ISO TC201.

The type of sample and the concentration levels of the analytes were designed to enable identification of potential analytical problems, to support IAEA Member States laboratories to improve the quality of their analytical results and to provide a regular forum for discussion and technology transfer in this topic.

Thirty-one (31) laboratories from seventeen (17) countries submitted their results.

Samples

Two samples were prepared from a certified reference solution by the coordinators as to obtain two different concentration levels of the analytes (~ 10 mg/L for sample "1" and 0.1 mg/L for sample "2"). A third sample ("3") was prepared from a commercial drinking water.

The three samples were loaded in sterile plastic tubes, sealed and distributed to 37 laboratories, each tube containing around 5 mL of the test solutions.

The participants were explicitly asked to analyse the samples "1" and "2" without any sample preparation procedure. The participants were asked to consider gallium as internal standard for quantification. Gallium was already present in samples "1" and "2", and its concentration was given: 10.0 mg/L in sample "1" and 0.100 mg/L in sample "2".

To harmonize the expression of standard deviation reported by the participants, it was instructed to prepare five independent measurement replicates for samples "1" and "2", each one corresponding to dry residue of depositing 10 μL (in one drop) on the sample carrier.

For the analysis of sample "3" the participants were asked to follow the instructions established by the coordinators for sample dilution, and to use Ga (from a 1000 mg/l certified solution) as internal standard for quantification. The resulting measured sample should be a final solution with a gallium concentration of 1 mg/L. The participants were asked to prepare five independent measurement replicates also for this sample, as described before.

Methodology and Evaluation of Results

The three water samples were distributed to 37 laboratories for chemical composition analysis; out of the 37 laboratories, 31 participated in the test. The exercise followed the methodology described in previous IAEA PTXRF exercises [3].

The reference value supplied by the provider of the initial standard solution used for the preparation of sample "1" was then considered as the assigned values of the analytes. For sample "2" the consensus values were used for comparison with respect to the experimental values provided by the participants instead of the assigned analyte values. It was evidenced that the concentration of the internal standard (Ga) was lower than the expected value of 0.1 mg/L, resulting to systematic errors in the measured concentrations by the most
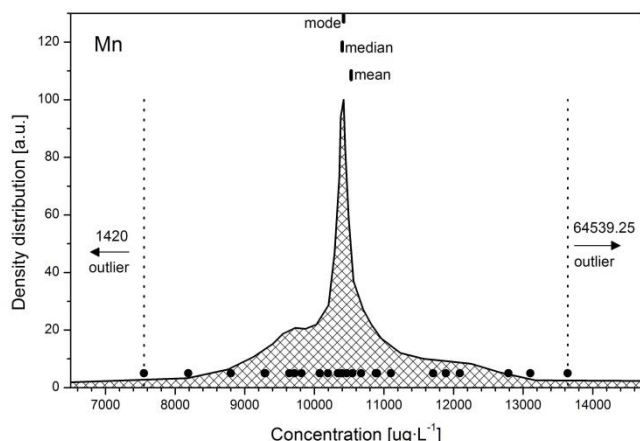
Figure 10: The density distribution function for the analyte Mn in case of sample "1".

Figure 11: Distributions of z-scores for analyte Mn in case of sample "1".

Of the participants. In the case of sample "3", being commercial water without certified elemental concentrations, the consensus values arising from this exercise were used for the evaluation.

As an example of the density distribution function of the proficiency test results, figure 10 shows data obtained by the participating laboratories on Manganese for Sample "1". The individual results are marked with filled circles. The dotted lines show the range of the accepted results (the results within these lines were used to calculate the consensus values). The outliers are marked with arrows. Also shown are the estimated parameters of the distribution (after outlier rejection): mode, median and the mean value.

Figure 11 shows the bar chart distributions of the z-scores for the analyte Mn. The results are sorted in ascending order versus laboratory code. The bar charts show the distance between the reported and the assigned/consensus values of the analyte. The submitted results and their uncertainties are marked with filled squares accompanied by uncertainty bars. The horizontal lines show the admissible levels of z-score, $|z| < 2$, for three different ranges [4]: $k = 0.5$ (solid black lines), $k = 1.0$ (solid green lines) and $k = 1.5$ (solid red lines). The decision levels of satisfactory results, $|z| < 2$, for different fit-for-purpose targets have also been marked.

Figure 12 shows the overall performance of one participating laboratory concerning the analysis of samples "1". The plots presented in these figures relate all the u-scores and z-scores calculated for a given laboratory. The hollow symbols denote the values calculated for specific fit-for-purpose levels [4] with factor k, namely: $k = 0.5$ (black triangles), $k = 1.0$ (green circles), and $k = 1.5$ (red squares). The decision limits of unsatisfactory results were marked with black lines ($|z| > 3$, $u > 3.29$). They divide the plot area in four quadrants. The smaller the laboratory estimate of the uncertainty the closer the related point to the $u = |z|$ line. Points in the immediate proximity of the dashed diagonal line ($u = |z|$) have underestimated uncertainty values. The well performing laboratories would have more points located in the lower-left quadrant of the plot. If there are many points located in the upper-right quadrant it suggests that these results do not fall
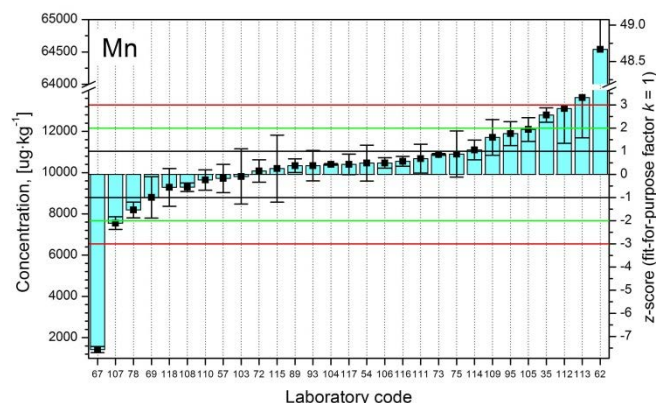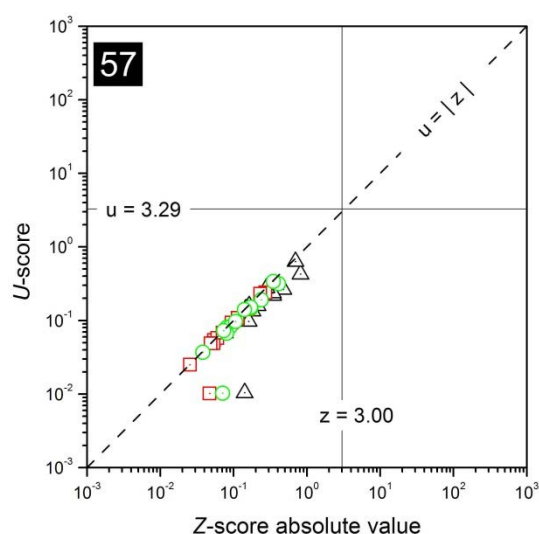

Figure 12: Combined plots of z- and u-scores for one participating laboratory in case of sample "1".

within the defined "fit-for-purpose" targets and that the laboratory provided too "narrow" an uncertainty estimate.

Further information on the results of the test can be obtained by contacting *NSIL.Contact-Point@iaea.org* with subject: *XRF PT*.

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XRF in Member States

Autonomous University of Madrid: SIdI-TXRF laboratory   *Laboratory Portrait*

The TXRF laboratory of the Autonomous University of Madrid (UAM) began its work in 1989, in the hall of the first floor of the Applied Chemistry and Physics department (C-II) of the Science Faculty. In this "particular" place, the TXRF spectrometer EXTRA-II, from Rich & Seifert (Germany), was the first TXRF instrument installed in Spain. In this way, the TXRF in Spain began 28 years ago due to the vision of future of Prof. Jesús Tornero Gómez and Prof. Lucas Hernandez, helped by a young assistant named Ramón Fernández Ruiz. Two years later in 1992, the TXRF laboratory was moved to its present location and so, it was one of the founder labs of the new Interdepartmental Research Service (SIdI) created in the Autonomous University of Madrid (UAM). Some years later, in 2005, and bearing in mind the objectives of analytical quality and excellence, the TXRF lab obtained, with other SIdI labs, the ISO 9001 quality assurance certification, which is still maintained. In 2006, the TXRF laboratory was also one of the first to be incorporated into the RedLab/Madri+d Laboratories Network. Finally, from end of 2012 TXRF lab acts as coordinator laboratory of the collaborative social network initiative named "TXRF Workgroup" created mainly around the Facebook and LinkedIn environment and open to all X-Ray Spectrometry professionals [1].

Nowadays, the Inter-departamental Research Service (SIdI) of the Autonomous University of Madrid is an open centre whose first mission is to give scientific, technical and analytical support to researchers of our own university, however SIdI-UAM also actively collaborates with other public and private institutions and companies at national and international level. Other main activities of the SIdI labs include the development of new analytical methods to solve diverse research questions continuously proposed by users. Additionally, SIdI labs are open to provide specialized scientific and technical training to everyone upon demand. Up to now, most popular are the laboratories of TXRF, ICP-MS, chromatography, and electron microscopy. Currently, SIdI is constituted by 21 different laboratories (CHNS, ICP-MS, TXRF, Thermal Analysis, Citometry, Cromatography, IC, IRMS, EM, FTIR, NMR, MAS-NMR, SEM, HR-SEM, TEM, Confocal, HR-XRD, Single Crystal-XRD, Polycrystalline-XRD, NMR-Self-service, Fluorimeter-Self-service) with more than 50 principal analytical instruments, and a staff of around 46 people grouped in eight units. In particular, TXRF lab is located inside the unit of Elemental Analysis next to the laboratories of organic elemental analysis (CHNS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Additional information about SIdI-UAM activities and policies can be found in http://www.uam.es/sidi.
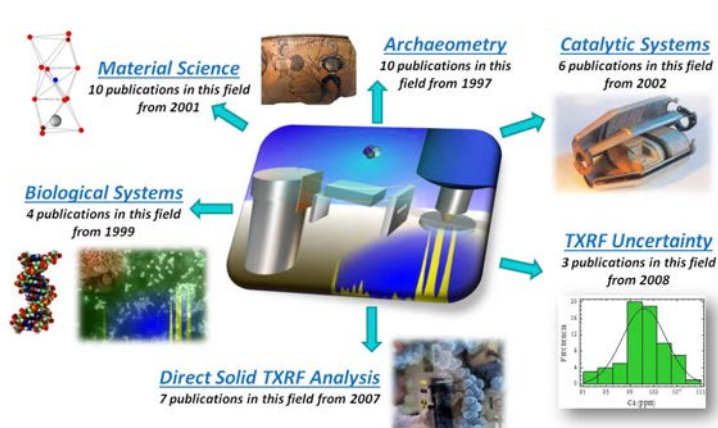

Figure 13: Main scientific fields boarded by SIdI-UAM TXRF Lab.

The main activity of the SIdI-UAM TXRF Lab is to give support to users from an analytical point of view. In this regard, a brief resume of its activity can be obtained from some significant statistics associated with the running of the Laboratory in the last five years. The number of analytical applications carried out by the laboratory was 998. These applications were performed by 106 different principal researchers associated to the same number of research projects, mainly from our own university (UAM) and other public and private institutions around Spain. To solve this number of analytical applications it has been necessary to perform the evaluation of approximately 4,748 samples, performing around 17,960 analyses by means of TXRF. This indicates that the average number of samples per application was only 4.7 samples per analytical application, i.e. our TXRF laboratory is sought by researchers to investigate small numbers of extremely complex samples which very often are redirected from other analytical laboratories which have not been able to resolve the specific problem properly. We like to call our laboratory as the "Laboratory of Last Resource" with the good and bad that it entails.

Research in the SIdI-UAM TXRF Lab

As a foundational lab of SIdI, the work philosophy of the SIdI-UAM TXRF lab follows the same basic directives of all other SIdI labs but, additionally, it has developed an intense research profile during the last 25 years, centered mainly on the methodological and conceptual development of TXRF spectroscopy.

This scientific labour has been only partially showed with around 45 international and 6 national scientific publications over the years. The main scientific fields where some relevant contribution has been carried out in our lab are as follows; archaeometry, material science, real catalytic systems, biological science, direct solid analysis and uncertainty theory
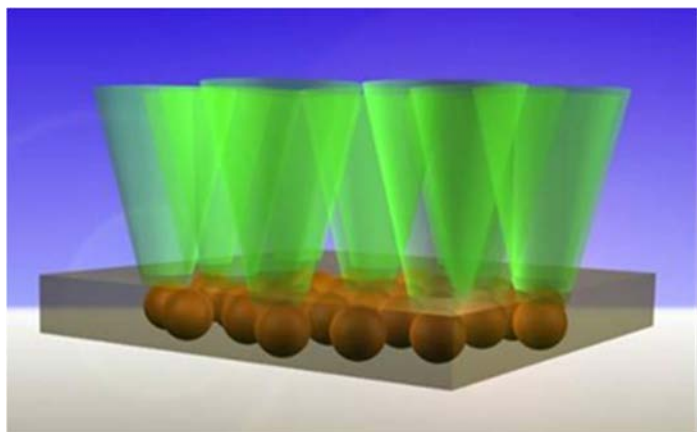
Figure 14: First approximation for the Direct Solid Analysis by TXRF (DSA-TXRF).

in TXRF. Figure 13 shows a graphical resume of this scientific activity where these fields and the approximate number of scientific contributions for each one are displayed.

In the field of archaeometry, our contribution to the TXRF community was the development of some of the first approximations to the study of archaeological ceramics by means of TXRF technique by inter-comparison with Instrumental Neutron Activation Analysis (INAA) [2,3] from a semi-quantitative [4] and quantitative [5] approach. The methodologies developed were applied to the study of ceramics from different origins but mainly Numantine from Soria in Spain. This analytical problem was very complex due to the strong diversity of elements and crystalline phases presents in a clay and/or a ceramic. In this way, to analyze solids constituted by microparticles with very different densities and suspension properties, was not an easy challenge but unlocked the basic knowledge for the direct analysis of solids by mean of the suspension method. The key lines for this were found by means of the best approach to the ideal TXRF thin film criteria for a solid particle deposition. In this sense three fundamental requirements should be fulfilled for a correct TXRF approximation: (1) chemical homogeneity of the solid particles, (2) average particle sizes around 1 μm and lower than 10 μm, and (3) homogeneous spatial distribution of the deposited particles on the sample carrier (figure 14).

In a parallel way, also very diverse "New Materials" have been extensively analyzed in the SIdI-UAM TXRF lab. One of the more relevant systems were solid solutions of Cu:In:Se (CIS), due to its photovoltaic relevance and to the analytical problems associated with the low vapour pressure of some of the elements in the digestion process, in particular with indium. The development of a direct solid analysis by means of TXRF was the solution for the correct evaluation of the atomic molar ratios of the CIS materials synthesized with different stoichiometries [6]. In this line, the optoelectronic materials based in lithium niobate (LN) doped with different rare earths as Nd, Yb, Er or Ho, were accessible via the developed CIS methodology. So, the quantity of rare earth incorporated to the LN crystalline lattice could be evaluated

Figure 15: Single-crystal of LiNb$_{1-x}$Ta$_x$O$_3$ analyzed by DSA-TXRF.

easily [7] by TXRF. Also the mixed phases of niobate and tantalate could be easily quantified with the aim of correlating its composition with the structural and optical properties [8] (figure 15).

Additionally, due to an intense scientific collaboration initiated with researchers of the Institute of Catalysis and Petrochemistry (ICP-CSIC) a study of real Three Way Catalysts (TWC) by mean of TXRF was developed. Thus, pioneer analytical TXRF methodological approximations were developed from a semi-quantitative [9] and quantitative approach [10]. The systems under study were the catalytic monoliths from a used (59,000 km) and fresh (0 km) catalyst of a Ford Focus 1.6i (see figure 16). In general lines, the study was centered in the evaluation of the axial and radial compositional distribution of the catalytic (Zr, Rh, Pd) and contaminant (P, Pb, Zn, Pt, Ca and Ni) elements along the cordierite bricks.

Two main and relevant scientific discoveries were obtained; first the existence of a strong interface effect between both monoliths which affected all the evaluated elements and second the confirmation of the elimination of Pb and Zn to the environment due to the axial elemental profiles obtained

Figure 16: Catalytic block from a Ford Focus 1.6i.

Figure 17: DNA molecular model with a simulation of Pt atoms intercalated.

Figure 18: Graph resume of the study carried out for the gold nano-rods (GNRs) bioaccumulation process by several mammalian tissues.

for these elements. Additional studies related to the poisoning by P of TWC were very well considered by the catalytic community [11] and also the study of the effect of mileage on the deactivation of vehicle-aged three-way catalysts [12] were relevant contributions in this area.

It is well-known that "Biological Systems" are, in a first approximation, ideal systems for TXRF spectrometry due mainly to the presence of light elements which allows the easiest detection and quantification of heavy metals. In this way, the number of applications developed in this area in the SIdI-UAM TXRF lab is substantial [13]. One of the more important works was the pioneer study of the novel antitumor drug Pt-berenil by TXRF. Analyzing very small quantities of DNA samples (100-500 nanograms) thanks to the use of TXRF spectrometry, allows the study of the kinetic of binding of this drug "in vitro" and "in vivo" in DNA of HeLa cells [14] (see figure 17). This achievement allowed the comparison of the behavior of this new anti-tumor drug, Pt-berenil, versus other well know drugs such as CIS-Pt, in an easy way, quick, very sensitive and with very low quantities of DNA.

Recently, we have published other pioneer work where TXRF has been applied for first time to evaluation of the bioaccumulation kinetics of gold nanorods (GNRs) in various mammalian tissues upon intravenous administration in mice (see figure 18). This work presents TXRF as a new and powerful alternative analytical method in this field of knowledge showing that TXRF spectrometry can help to solve these complex scientific problems in a more global way than other more conventional analytical techniques [15].

The field of the "Direct Solid Analysis by TXRF" (DSA-TXRF) has been, and currently is, a main research question in our laboratory. In the analytical field, the possibility of being able to analyze directly a solid sample in a quantitative and lineal way, without any previous chemical digestion, has been the most sought after of spectroscopic techniques. Classical XRF was initially the technique ideally to get this success but the lack of linearity, due to second and higher order interact-
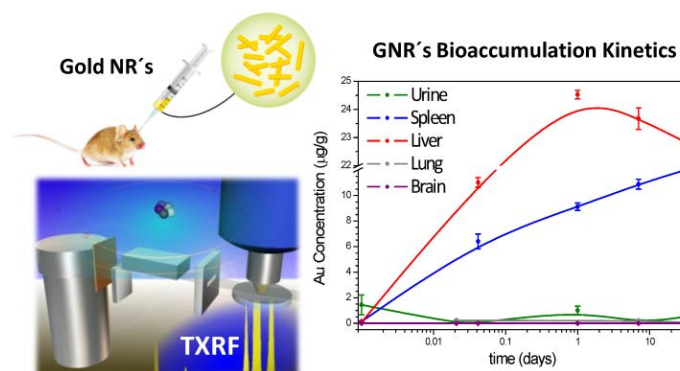
ions, next to the strong dependence of the matrix composition were a deception from an analytical point of view. But from the beginning of TXRF this goal could be achieved again with more possibilities of success. In our laboratory, the use of TXRF spectrometry taking advantage of the analytical versatility; the use of one or more internal standard for quantification; the physical modulation of the particle size distribution of the samples by mechanical systems or high power ultrasound probes; the optimization of the suspensions conditions by mean of the size modulation, the correct election of the suspension fluid or the addition of adequate surfactants and also, the check of the adequate morphology of the final depositions by means of microscopy techniques and/or GI-XRF studies of the evaluated elements around the critical angle, are the main keys of our actual research in this area. Up to now, nanoparticle systems have been the most investigated; mainly magnetite nanoparticles as ferrofluids [16] and carbon and/or carbon nanotubes nanoparticles [17] but also microparticles of glass where it was shown that the modulation of the size distribution has serious implications in the analytical parameters [18]. Our experience indicates that TXRF is a great candidate for the quantitative DSA-TXRF analysis but nevertheless, more research in this field is necessary to understand it in depth completely.

Finally, the "TXRF uncertainty" field has been studied from several approximations. From purely empirical, where the influence of different morphological aspects of the TXRF depositions, such as reflector material, distribution size or homogeneity, were correlated with the accuracy and uncertainty of their analytical results [19] to others more formally with the analysis of the TXRF uncertainty from a theoretical point of view for the more conventional quantification method of internal standard addition [20]. In any case, this field is yet open and many questions are still to solve.

Outlook

Our laboratory has a long trajectory in the TXRF field. During this time, the number and variety of research problems addressed has been very diverse. This fact has allowed us to acquire a broad, real and dimensioned perspective of the potentialities and drawbacks of the TXRF

in the analytical field. With this background in our hands, our lab is always open to collaborate with the international community interested in the advance of each one of the multiple fields where TXRF can be developed or show its power.

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India

Multi-Dimensional Applications of TXRF in Science and Technology

Total Reflection X-ray Fluorescence (TXRF) is being progressively used in different areas of science and technology. In TXRF analysis, X-rays fall at an angle less than the critical angle (< 1 Degree) on a flat polished surface and get totally reflected. If a thin sample specimen is placed on this surface, it leads to double excitation of this specimen by incoming as well as totally reflected X-ray beams. The sample on the support should be so thin that it does not produce absorption – enhancement effects during X-ray excitation of the elements present in the sample. As the X-ray beam falls and gets totally reflected at the support at such a low angel, a detector can be kept very near to the sample support surface to detect the X-rays emitted from the sample as a result of sample excitation. Since the X-rays do not penetrate deep inside the support, the background due to scattering is very low. All these features result in the better sensitivity of X-rays detection and improvement of the
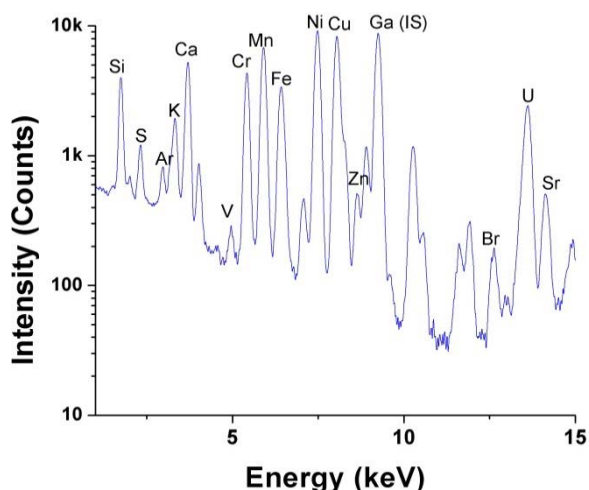
Figure 19: TXRF Spectrum of a processed uranium oxide standard (Ga was added as internal standard) excited by Mo Kα radiation.

detection limits drastically for the elements being determined by TXRF. The requirement of a thin sample on support is achieved by depositing a few microlitres of the sample with elemental concentration in the range of less than a few mg/L on the support. Since this technique requires sample volumes of few microlitres only, has multi-elemental analytical capability for metals and non-metals alike and is non-consumptive, it has proved to be very useful for analysis of precious, biological and hazardous materials. These features of TXRF are very much suitable for the analysis and thereby quality control of nuclear materials also which are precious and radioactive. The above features of TXRF, when applied to such materials, shall result in requirement of very small amount of sample and the generation of a very small amount of radioactive analytical waste and protection of the analyst and instrument from high radiation dose while analyzing radioactive samples. In addition, the wastage of such precious nuclear materials, during their quality control, can be minimized. In order to beneficially exploit these features of TXRF for nuclear materials, an ITAL Structures (Italy), TXRF spectrometer model TX-2000, was procured and installed in our laboratory in November 2003. Since then, research and development activities have been taken up to develop different TXRF methodologies for the quality assurance of nuclear materials [1] along with analytical support to the R&D activities of different Universities and Institutes. The spectrometer has a W–Mo dual target tube for X-ray production and W–C multilayer for mono-chromatiation of X-rays. However, the X-ray tube can be replaced with suitable target X-ray tube if required. The instrument is equipped with a twelve-position sample chamber. A Si–Li detector with a resolution of 139 eV at Mn Kα (5.89 keV) is used for the detection and measurement of X-rays. For detection and measurement of low atomic number elements TXRF spectrometers with a vacuum chamber for samples and ultrathin window detector, at Atominstitut, Vienna, Austria and Institute of Chemistry, L. Eötvös University, Budapest, Hungary, were used. In order to expand the elemental analytical range of the TXRF

analysis, a low Z – high Z TXRF spectrometer with two low power X-ray tubes, single power supply, detector and sample chamber with air and vacuum atmosphere measurement facility was installed in our laboratory in March, 2015. This spectrometer can be used for measurement of elements C to U with variable detection limits. A brief description of these activities is presented hereafter.

Technological Applications

Determination of trace elements in nuclear materials is very important for the safe and efficient performance of these materials in nuclear reactors. Uranium and plutonium in their different forms are used as nuclear fuel.

Thorium-232 is used as fissile material along with uranium and plutonium as nuclear fuel. The amount of trace elements present in these materials change their properties. Hence, these materials should satisfy the specifications for their safe and efficient usage for generation of electricity from reactors. TXRF methodologies for the determination of trace elements in these materials were developed in our laboratory. These methods involve dissolution of the these materials in nitric acid, selective extraction of the major matrix using tri-n-butyl phosphate (TBP), addition of internal standard in the aqueous phase and determination of trace elements in the aqueous phase by TXRF using predetermined sensitivity values. The results of the TXRF determinations were counterchecked by analyzing standard materials and participating in inter-laboratory comparison experiments [2]. The TXRF spectrum of the aqueous phase obtained after processing one such Certified Reference Material (CRM) is shown in figure 19. The TXRF analytical results for trace elements of the CRMs were compared with the certified values with good agreement. Since low atomic number (Z) elements X-ray lines have lower energies, low fluorescence yield and may get absorbed in air and parts of the spectrometer, a TXRF spectrometer with vacuum chamber is needed for such elemental determinations. Under scientific collaborative programs, vacuum chamber based TXRF analytical methods were developed for the determination of low atomic number elements in uranium matrix [3].

Consequent to these collaborative activities, a low Z - high-Z TXRF spectrometer developed by Atominstitut, Vienna, was installed in our laboratory. The spectrometer has two low power X-ray tubes having Cr and Rh targets and fitted with Ni/C and Pd/B_4C multilayers, respectively. The power supply and sample chamber for both the tubes are common. The tubes along with respective multi-layers can be fitted easily in the sample chamber as per the requirement. With the help of the vacuum sample chamber, efficient excitation geometry and a KETEK silicon drift detector with 20 mm^2 active area having an ultra-thin polymer window (300 nm thickness) and a resolution of 140 eV (FWHM for Mn Kα) the elemental analytical range of the TXRF analysis could be extended to C-U. This spectrometer is being used for similar activities
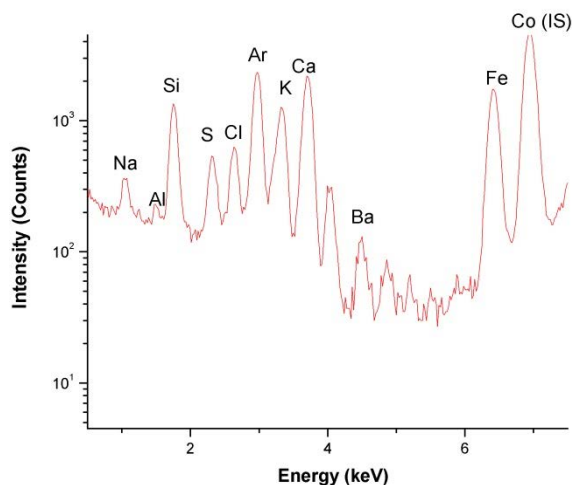
Figure 20: A part of the TXRF spectrum of pyrohydrolysis condensate of a (U, Pu) C sample excited using Cu Kα radiation (Co was added as internal standard).

Figure 21: Difference in TXRF spectra of tagged and untagged ink samples obtained using Cu Kα excitation.

with extended elemental analysis range [4, 5] and also to support research activities in Indian universities.

Some elements require special sample treatment for TXRF determinations. Chlorine and fluorine are corrosive elements. These elements get lost as HCl/HF gas while preparing the TXRF sample specimen on support by heating for TXRF determinations, especially in acidic medium. In order to overcome this problem for TXRF determination of chlorine in nuclear materials, these materials were subjected to pyrohydrolysis and the condensates obtained were collected in alkaline solutions. The TXRF spectra of the condensates were measured in helium atmosphere in order to remove any possible interference of Ar Kα (2.957 keV) with Cl Kα (2.622 keV). A TXRF spectrum of such specimen of (U, Pu) C is shown in figure 20 [6]. Similar studies on F determinations in different matrices are being pursued using low Z - high Z TXRF spectrometer.

The flexible instrumentation of TXRF determinations makes the analysis of elements feasible even in non-supportive situations. Indium determination is very important in nuclear materials because even ultra-traces of indium, if present in these materials, can give high radiation dose to the reactor operator because of the activation of [115]In to [116]In^m after neutron absorption in a reactor. The [116]In^m emits high energy γ -radiation of energy >1 MeV and has short half life of 54 minutes. In absence of suitable excitation sources for In Kα (24.21 keV), In Lα (3.29 keV) is used as analytical line for TXRF determinations. However, such approach is problematic as In Lα lies in low energy and high background region, has low fluorescence yield (thereby giving higher TXRF detection limits) and interferes with elements like K (K Kα = 3.31 keV).

These problems were solved by using In Kα as an analytical line. Excitation of In Kα (In K$_{ab}$ = 27.94 keV) was achieved by choosing a narrow strip of continuum in the energy range of 28-35 keV from Mo X-ray tube with the help of a
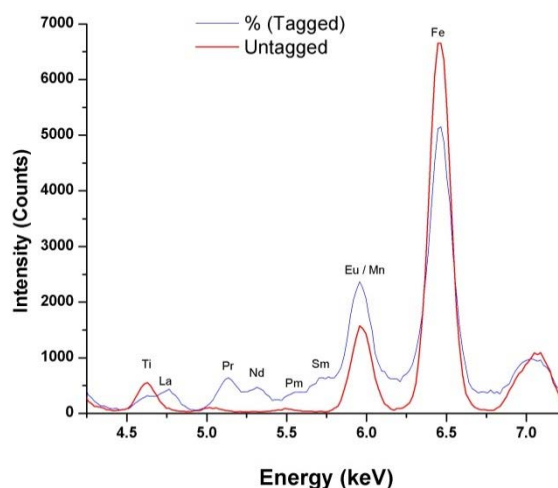
multilayer. Using this approach the purity of heavy water for indium contamination at level of 1 ng/mL could be ascertained [7].

Dissolution of mixed oxide fuels of U, Th and Pu is a difficult task as these materials are often sintered and refractory. We have developed an almost nondestructive method for major element determinations in mixed $(U, Th)O_2$ pellets by TXRF. The method involves gently rubbing the TXRF supports with these pellets and measuring the TXRF spectra of such specimen [8].

Forensic Applications

TXRF is well suited for forensic applications as it requires very small amount of sample and is a multi-elemental analytical technique. We developed a simple non-destructive TXRF method for the differentiation of ink samples used for the manuscript printing. Ink samples tagged with rare earth elements could be differentiated from the untagged ink samples [9]. A very small amount of ink from the printed documents was gently rubbed with a clean blade without destroying the manuscript. An aliquot of Milli-Q water (about 50 µL) was pippeted out on this loose ink on the manuscript and was agitated by sucking and releasing the suspension with the help of a micropipette. These solutions / suspensions were subjected to TXRF measurements. The TXRF spectra of these specimens could clearly differentiate the two types of inks in an almost non-destructive manner as shown in figure 21.

Environmental Applications

The TXRF determinations are very much suitable for environmental samples e.g. different type of waters (rain water, river water, drinking water, waste water etc), air, ice, flowers, leaves, etc. as these materials do not have high atomic-number major-matrix and the elements present can be pre-concentrated simply by evaporation or drying. Ground water in some parts of India is reported to be contaminated
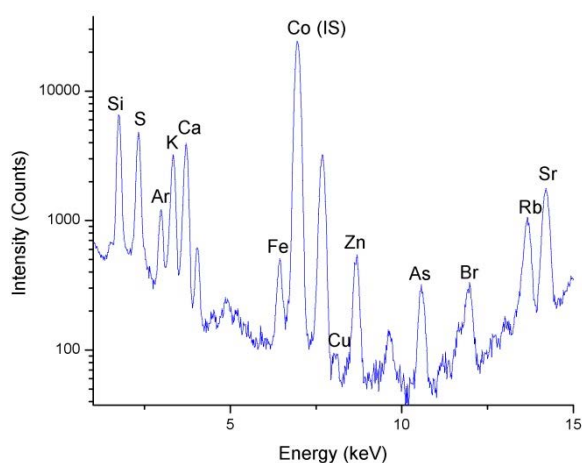
Figure 22: TXRF spectrum of a water sample from Eastern part of India (Co was added as internal standard). The As Kα peak with appreciable intensity can be seen.

Figure 23: A TXRF spectrum of an underground water sample from central part of India. F Kα peak of appreciable intensity can be seen (Ti was used as internal standard).

with elements like F, As, U, and Se. TXRF could be successfully used for determination of these elements in such water samples. One of the water samples received from the eastern part of India was found to have arsenic concentration in μg/mL level and could be analyzed by TXRF (figure 22).

For the determination of fluorine, vacuum-chamber based TXRF was used under a collaborative program with Vienna University of Technology, Vienna, Austria using Cr Kα excitation. The TXRF spectrum of one such water sample from central part of India is shown in figure 23. It can be seen that this water contains a lot of F, Cl, Ca, etc. We also participated in the development of trace element standards of rain water [10] conducted by National University of Singapore and our results were in good agreement with the analytical results of other laboratories and were helpful in development of these standards.

Seawater contains trace amounts of uranium (about 3 ng/mL). Considering the huge amount of seawater all over the world, the total amount of uranium in seawater works out to be very large. This uranium can be recovered from the seawater and used for producing electricity in nuclear reactors. Such research activity requires determination of uranium in seawater. In addition, analysis of other trace elements in seawater is required for environmental quality control. For such determinations, the large amount of salt matrix present in seawater should be first separated so that a thin film of the analyte can be formed on TXRF support. In one of our studies for uranium determination in seawater, uranium was selectively extracted using diethyl ether and determined by TXRF after pre-concentration by evaporation and subsequent dissolution in a small volume of 1.5% supra-pure HNO_3. Using such an approach the detection limit of TXRF methodology for uranium could be improved to 67 pg/mL [11]. The uranium concentration in sea water samples collected from the Arabian Sea near Mumbai were found to be similar to those reported in literature.
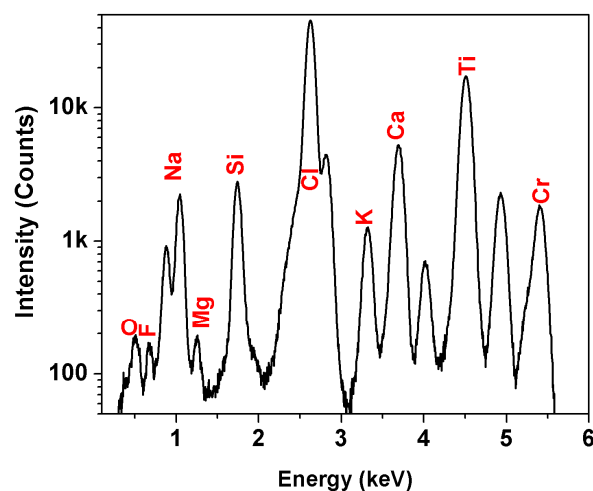
Coal fly ash disposal from coal based power plants is an important environmental problem. Fly ash contains a lot of elements including U and Th. Determination of these elements in coal fly ash is required for its safe disposal. We could determine elements present in a fly ash sample of a thermal power plant by TXRF and EDXRF. The TXRF spectrum of a fly ash particle is shown in figure 24.
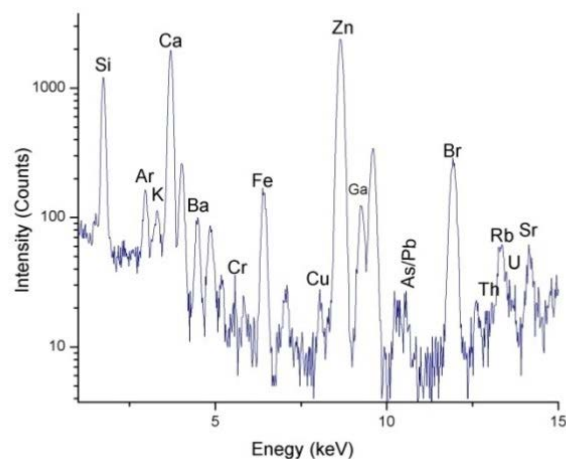

Figure 24: TXRF spectrum of a Fly ash sample received from a thermal power plant.

Conclusion and Future Perspective

The above short presentation of TXRF applications in our laboratory indicates the important role TXRF spectrometry can play in multidimensional scientific research for the benefit of mankind. It has proved very helpful in determinations of elements with atomic number 6 (C) to 92 (U) using different types of TXRF spectrometers in our laboratory. In addition, the Micro focus beamline is operational at Synchrotron Light Source INDUS-2, Indore and at present, TXRF, EDXRF and Micro-XRF facilities are available. Recently TXRF-EXAFS and XANES facilities

have also become operational at this beam line. We have used this beamline for different applications. In one such application of this beamline, the oxidation state of U in U_3O_8 and U_3O_7, mixed valent oxides of uranium, is being studied and we have obtained very encouraging results. This approach is very simple as it uses almost no sample preparation. The specimen is prepared by gently rubbing the sample on TXRF support and measuring its XANES spectrum in TXRF mode. Using the above laboratory and synchrotron based TXRF techniques we shall be able to do trace element analysis as well as speciation studies on different types of samples.

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Publications of Potential Interest

1. *"The application of XRF and PIXE in the analysis of rice shoot and compositional screening of genotypes"*
   S. Bado *et al.,* NIMB 371 (2016) 407–412 DOI: 10.1016/j.nimb.2015.08.081

2. *"Use of reference materials for assessment of measurement result uncertainty in determination of 210Pb"*
   A. R. Iurian *et al.,* Appl.Radiat.Isotopes 109 (2016) 61-69 DOI: 10.1016/j.apradiso.2015.11.067

3. *"The mystery of mercury-layers on ancient coins – a multianalytical study on the Sasanian coins under the reign of Khusro II"*
   K. Uhlir *et al.,* Microchemical Journal 125 (2016) 159-169 DOI: 10.1016/j.microc.2015.10.024

4. *"Prediction of salt tolerance in rice (Oryza sativa) based on shoot ion content under non-stressed conditions"*
   S. Bado *et al.,* Journal of Materials Science and Engineering A 6 (1-2) (2016) 1-16 DOI: 10.17265/2161-6213/2016.1-2.001

5. *"Uso de nuevas tecnologias para el diseno, modernizacion y automatizacion de sistemas y procesos relacionados ocn aplicaciones nucleares",*
   IAEA-TECDOC-1765, 2016 http://www-pub.iaea.org/MTCD/Publications/PDF/TE-1765_web.pdf

6. *"LabVIEW interface with tango control system for a multi-technique X-ray spectrometry IAEA beamline end-station at Elettra Sincrotrone Trieste"*
   P. Wrobel *et al.,* NIMA 833 (2016) 105 – 109 DOI: 10.1016/j.nima.2016.07.030

Upcoming Events

LASNPA & WONP-NURT	ICXOM 24	TXRF 2017
October 23 – 27 Havana, Cuba http://www.wonp-nurt.cu/	*September 25 – 29* Trieste, Italy http://www.icxom24.it/	*September 19-22* Univ Bresica, Italy http://txrf2017.unibs.it
	IAEA HQ, Vienna, Austria: http://www-pub.iaea.org/iaeameetings/ Training Workshop on **Quality Assurance for Nuclear Spectrometry** *19-23 June* Technical Meeting on **Trends in Analytical Applications and Instrumental Developments of Synchrotron Based X-Ray Spectrometry Techniques** *October 2-6*	

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Material should be submitted in word or other simple text editor program. Short articles should be no more than 800 words with 2 figures (including captions) and a maximum of 3 short form references (no paper titles, references are optional). Submissions for the "Laboratory Portrait", published 1 per issue may be up to 1500 words, 4 figures and 6 short form references.

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