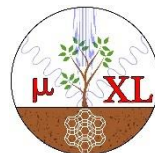




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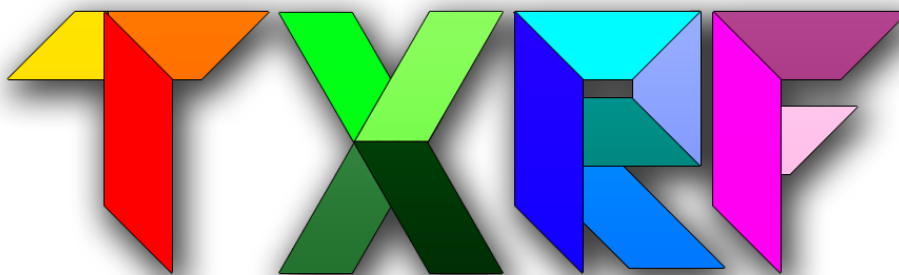


COST ACTION CA18130



Micro X-ray Lab
DiSSPA., University of Bari

1st International Summer School on



20-24 September 2021
University of Bari
Bari (Italy)

BOOK OF ABSTRACTS

Sponsored by



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PROGRAMME

	20/09	21/09	22/09	23/09	24/09
8:30-9:00	Module 0				
9:00-9:45	Module 1	Module 5	Module 8	Module 11	Module 15
9:45-10:30	Module 2	Module 6	Module 9	Module 12	Module 16
10:30-10:45	Coffee Break	Coffee Break	Coffee Break	Coffee Break	Coffee Break
10:45-11:30	Module 3	Module 13	Module 13	Module 14	Module 14
11:30-12:15	Module 4	Module 7	Module 10		
12:15-12:30					

 Welcome and closing ceremony

 Tutorial sessions

 Theoretical lessons

 Participants' presentations

Modules:

1. Introduction to X-ray fluorescence
2. Fundamentals of TXRF
3. Instrumentation for TXRF
4. Qualitative and quantitative analysis
5. Sample preparation
6. TXRF applications (Part 1)
7. LAB: Sample preparation
8. Synchrotron
9. TXRF vs GI-XRF and thin film analysis
10. LAB: Quantitative analysis and calibration

11. Preconcentration Strategies
12. LAB: Software
13. Poster and video discussion
14. Participants' presentations
15. TXRF applications (Part 2)
16. Standards

Module 0 and 17: Welcome and closing sessions

DETAILED PROGRAMME

Day 1 – 20/09/2021

- 8:30-9:00 – **WELCOME CEREMONY**
- 9:00-9:45 – **Introduction to X-ray Fluorescence**
Kouichi Tsuji – Osaka City University (Japan)
- 9:45-10:30 – **Total reflection X-ray fluorescence analysis (TXRF) – Introduction, basics & fundamentals**
Peter Kregsamer – Technical Universitat of Wien (Austria)
- 10:30-10:45 **Coffee Break**
- 10:45-11:30 – **Total reflection X-ray fluorescence analysis (TXRF) – Instrumentation**
Peter Kregsamer – Technical Universitat of Wien (Austria)
- 11:30-12:15 – **TXRF point of view of qualitative and quantitative elemental analysis**
Ramón Fernández-Ruiz – Universidad Autónoma de Madrid (Spain)

Day 2 – 21/09/2021

- 9:00-9:45 – **Basic principles, practical considerations and constraints of sample preparation strategies used in TXRF analysis**
Eva Marguí – University of Girona (Spain)
- 9:45-10:30 – **Applications of TXRF: an overview of last decade experiences**
Fabjola Bilo – University of Brescia (Italy)
- 10:30-10:45 **Coffee Break**
- 10:45-11:30 – **POSTER SESSION**
- 11:30-13:00 – **TUTORIAL SESSION: TXRF Sample preparation**
Hagen Stosnach – Bruker Nano GmbH (Germany)

Day 3 – 22/09/2021

- 9:00-9:45 – **Synchrotron Radiation Induced Total Reflection X-ray Fluorescence**
Diane Eichert – Elettra Synchrotron (Italy)
- 9:45-10:30 – **TXRF vs GI-XRF (and XRR) for non-destructive thin film analysis**
Dieter Ingerle – Technical Universitat of Wien (Austria)
- 10:30-10:45 **Coffee Break**
- 10:45-11:30 – **POSTER SESSION**
- 11:30-13:00 – **TUTORIAL SESSION: Quantitative analysis and calibration**
Hagen Stosnach – Bruker Nano GmbH (Germany)

Day 4 – 23/09/2021

- 9:00-9:45 – Recent trends in preconcentration strategies used in combination with TXRF analysis
Eva Marguí – University of Girona (Spain)
- 9:45-10:30 – **TUTORIAL SESSION:** Peak deconvolution for TXRF measurements - free software options
Dieter Ingerle – Technical Universität of Wien (Austria)
- 10:30-10:50 Coffee Break
- 10:50-11:10 – **001:** Biomonitoring of human health using TXRF method
Regina Stachura – University of Kielce (Poland)
- 11:10-11:30 – **002:** Elemental variability of fine atmospheric aerosols in Old Jeddah, Saudi Arabia
Abdallah Shaltout – National Research Centre (Egypt)
- 11:30-11:50 – **003:** Development of reference material for direct TXRF analysis of air filters
Paola Cirelli – University of Brescia (Italy)
- 11:50-12:10 – **004:** Quantifying cytotoxicity and cellular uptake of naked gold nanoparticles in breast cancer cells using total reflection X-ray fluorescence
Natasha Hedden – Ryerson University (Canada)

Day 5 – 24/09/2021

- 9:00-9:45 Applications of TXRF: innovations for screening and quantitative analysis of unconventional samples
Laura Borgese – University of Brescia (Italy)
- 9:45-10:30 – Development of TXRF standards for environment and health
Laura Depero – University of Brescia (Italy)
- 10:30-10:50 Coffee Break
- 10:50-11:10 – **005:** The investigation of potentially toxic elements in soil-plant-air system in vineyards in Serbia
Tijana Milićević – University of Belgrade (Serbia)
- 11:10-11:30 – **006:** The role of Americium-241 for the metal detection of solids, liquids and environment contaminants using a portable spectrometer device
Claudio Larosa – University of Genova (Italy)
- 11:30-11:50 – **007:** Multi-technique instrumental approach for the characterization of metallic archaeological artifacts
Nicoletta Sgarro – University of Basilicata (Italy)
- 11:50-12:10 – **008:** Total X-ray Fluorescence as a technique for measure the progress of the separation of Lu and Yb in a chromatographic column
Cynthia Caceres Rivero – Peruvian Institute of Nuclear Energy (Perù)
- 12:10-12:30 **AWARDS AND CLOSING CEREMONY**

SPEAKERS' TALKS

Introduction to X-ray Fluorescence

Kouichi Tsuji

Graduate School of Engineering, Osaka City University, Osaka, Japan

X-ray fluorescence (XRF) analysis is useful analytical technique, which enables us nondestructive elemental analysis at ambient air pressure. We can understand this unique analytical advantage, when compared with other analytical techniques such as ICP-AES/MS, AAS, SEM-EDS, SIMS, XPS, etc. Total reflection XRF (TXRF) is one of the special configurations of XRF. In this lecture, I will introduce fundamental X-ray physics, production of X-ray fluorescence, XRF analysis by wavelength dispersive XRF (WD-XRF) and energy dispersive XRF (ED-XRF), showing some figures from the reference books [1-5]. These books are recommended to study further details of XRF and TXRF.

Topics in this lecture:

Emission of radiation from atoms,
Energy levels and X-ray lines,
Production of X-ray fluorescence,
Moseley's law, Lambert-Beer law,
Bragg's diffraction law, WDS and
EDS, continuous X-rays, EDS
spectrum, matrix effects, etc.

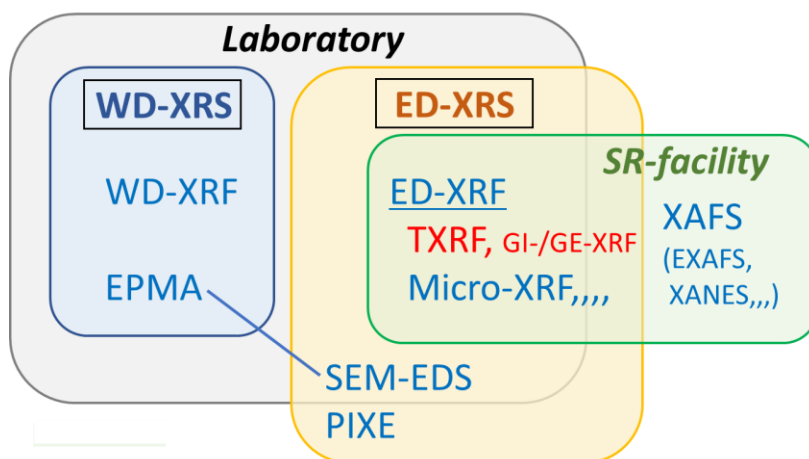


Figure 1. Various X-ray spectroscopic methods.

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- [1] Janssens, K.H.A., Adams, F.C.V., Rindby, A. (Eds.), 2000. Microscopic X-ray Fluorescence Analysis, John Wiley & Sons, Inc., Chichester.
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- [4] Beckhoff, B., Kanngießer, B., Langhoff, N., Wedell, R., Wolff, H. (Eds.), 2006. Handbook of Practical X-ray Fluorescence Analysis, Springer, Berlin.
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Total reflection X-ray fluorescence analysis (TXRF) – Introduction, basics & fundamentals

Peter Kregsamer

Atominstitut, TU Wien, 1020 Wien, Stadionallee 2

peter.kregsamer@tuwien.ac.at

Total reflection X-ray fluorescence analysis (TXRF) is a variation of standard energy-dispersive X-ray fluorescence analysis (EDXRF). In contrast to standard XRF, where the primary beam strikes the sample at an angle of about 45°, TXRF uses a glancing angle of less than 0.1°. Owing to this grazing incidence, the primary beam shaped like a strip of paper is totally reflected at the sample support. TXRF is primarily used for chemical micro- and trace analyses. For this purpose, small quantities, mostly of solutions or suspensions, are placed on optical flats (e.g., quartz glass) serving as sample support. After evaporation, the residue is excited to fluorescence under the fixed small glancing angle and the characteristic radiation is recorded by a Si(Li), or by a Si-drift detector, as an energy-dispersive spectrum. It is the high reflectivity of the sample support that nearly eliminates the spectral background of the support and lowers the detection limits as compared with standard XRF. Besides its high detection power, simplified quantification is made possible by suited internal standardization and matrix effects usually can be ignored, because of the minute residues or thin layers of a specimen.

Total reflection X-ray fluorescence analysis (TXRF) – Instrumentation

Peter Kregsamer

Atominstitut, TU Wien, 1020 Wien, Stadionallee 2

peter.kregsamer@tuwien.ac.at

In case one doesn't want to work with this technique in a black box manner it will be of interest what main components, as part of a TXRF spectrometer, influence its performance. Due to the fact that TXRF – still an energy dispersive XRF analysis method – has different requirements compared with the standard technique, the features of the commonly employed core instrumentation will be discussed in detail:

- X-ray tube for excitation,
- Monochromator,
- Alignment requirements, sample supports (reflectors) and
- Energy-dispersive detection of the characteristic lines of the chemical elements of interest.

TXRF point of view of qualitative and quantitative elemental analysis

Ramón Fernández-Ruiz

Servicio Interdepartamental de Investigación (SIdI). Laboratorio de TXRF, Universidad Autónoma de Madrid (UAM), Cantoblanco 28049, Madrid, Spain.

This talk aims to present elemental atomic analysis from the point of view of Total Reflection X-ray Fluorescence (TXRF). In this way, the basic notions necessary for the qualitative identification of the elements present in real TXRF spectra are presented. From a quantitative point of view, the most conventional methods used in practice employing TXRF are presented: internal standardization and standard addition. The peculiarities of the TXRF from the analytical point of view will be exposed in a practical way based mainly on real problems. The recommended reference book for all the doubts and questions related to the TXRF in general but particularly for the best understanding of their qualitative and quantitative practical application is the excellent monograph of Klockenkämper and Von Bohlen [1].

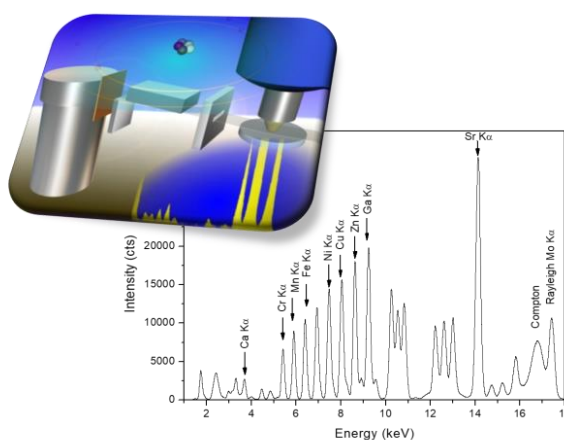


Figure 1. TXRF spectrum from a complex sample.

REFERENCES:

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Basic principles, practical considerations and constraints of sample preparation strategies used in TXRF analysis

Eva Marguí

Department of Chemistry. University of Girona. C/M.Aurèlia Capmany, 69. 17703 Girona (Spain)

A wide variety of sample types may be analyzed by TXRF, including solids, liquids, and even gases; hence, a wide variety of sample preparation techniques is at present available.

In most applications, the main objective of TXRF is to obtain information about elemental composition of the samples with enough quality for the intended purpose, and this cannot be done unless the specimen is adequately prepared. It is well known that improper specimen preparation can cause large errors of the obtained results. Moreover, sample preparation will also influence the quantification approach used and the type of information that can be derived from the TXRF measurements [1].

In this session, the basic principles, practical considerations and constraints of sample preparation strategies used in combination with TXRF analysis will be overviewed [2]. First, the basic requirements to fulfill the conditions of total reflection will be summarized. Then, a brief description of the most commonly used sample preparation procedures used for TXRF analysis of liquid, solid and gaseous samples will be presented [3]. In this sense, simpler and more sophisticated sample treatments (suspension, digestion, extraction, ...) will be considered and advantages and disadvantages of each procedure will be critically evaluated. Finally, future perspectives and the role of TXRF in the frame of green analytical chemistry will be also discussed.

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- [1] Marguí, E., Queralt, I., Van Grieken R., 2016. Sample preparation for X-ray fluorescence analysis in Encyclopedia of Analytical Chemistry edited by Meyers, R.A. John Wiley & Sons. (ISBN-978-0-471-97670-7).
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Applications of TXRF: an overview of last decade experiences

Laura Borgese^{a,b,c}, Fabjola Bilo^{a,b,c}, and Laura E. Depero^{a,b,c}

^aDepartment of Mechanical and Industrial Engineering, University of Brescia, Via Branze 38, Brescia Italy

^bConsorzio INSTM, Via G. Giusti 9, Firenze Italy

^cSmart Solutions srl, via Corfù 106, Brescia Italy

TXRF is a niche technique mainly used today for micro and trace analysis due to its high sensitivity. Literature reports many successful applications of TXRF in environment, and food, while new applications are emerging principally in the fields of medicine, biology, pharmacology, and nanotechnology. An overview of the research experiences gained in these fields during the last decade and the main results obtained will be given. Challenges and opportunities will be presented with reference to the sample matrix, elements of interest, determination accuracy, and sample preparation method. Examples will cover the environment: soil, bio-indicators, and water [1]; food: beans [2], wine [3], teas and herbs; biology and pharma: cell extracts, fish embryos, hair, and drugs [4-6].

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Tutorial Session – TXRF Sample Preparation

Hagen Stosnach & Armin Gross

Bruker Nano Analytics, Berlin Germany

This tutorial session will be divided in three sections. It will start with a general overview on the general principles of sample preparation for TXRF analysis. Here some general pitfalls starting with the sampling itself and limiting factors like sample thickness and homogeneity as well as risks for the operator and the instrumentation in sample preparation will be discussed. After a detailed look on the different available sample carrier types the second part of the tutorial session will start.

This second part will be a live video presentation of different sample preparation techniques for the following sample types:

- Inorganic liquid samples (low to very high matrices)
- Organic liquid samples (volatile and non-volatile)
- Solid samples (partly soluble, organic, inorganic solids and samples, which are not suitable for TXRF analysis)

The tutorial session will end with an open Q&A session for all participants.

Synchrotron Radiation Induced Total Reflection X-ray Fluorescence

Diane M. Eichert^a

^aELETTRA – Sincrotrone Trieste, S.S. 14 - Km 163.5 in Area Science Park, 34149 Basovizza, Trieste, Italy

diane.eichert@elettra.eu

Total Reflection X-ray Fluorescence (TXRF) Spectroscopy is one of the most impressive analytical technique providing spectral signatures of materials that can be used to unravel their elemental composition. Within a few seconds and with limited sample preparation, a first characterization of qualitative character can be obtained, whereas thorough and quantitative information will require a full experimental design approach.

The advent of synchrotron facilities exploiting the unique qualities of synchrotron radiation (SR) has offered TXRF a new source of unprecedented chemical sensibilities for the determination of trace element concentrations, with high spectral and potential high spatial resolution. A brief description of synchrotron radiation properties will be given in order to discuss the improved analytical capabilities, and in particular the improved detection limits compared to laboratory TXRF.

As SR is being produced over a wide range of energies from the soft (100–2000 eV), tender (2000–7500 eV) to the hard X-rays (>7500 eV), its energy tunability is a strength to excite preferentially selected analytes of a material, and to assess simultaneously, or by correlation of techniques, the different chemical and physical properties of the sample (e.g. X-ray Absorption Spectroscopies for chemical speciation determination). For each domain of energy however, the characteristics of the potential X-ray sources and detectors, of the experimental chamber requirements, especially with angular scans possibilities, as well as sample preparation and handling have to be optimised. In particular with SR, a high stability, high photon flux and a high spectral purity of the illuminating beam onto the sample is required, along with a good flexibility of the beam transport system for rapid changes of the photon energy without any need for a sample re-alignment.

Instrumental and experimental parameters knowledge, and thorough qualification of the TXRF set-up, are indeed keys to a successful chemical measurement process, together with sample handling and data analysis procedures.

The strengths, drawbacks and challenges of TXRF analysis with a synchrotron source will be highlighted, and illustrated with applications from the main application fields.

TXRF vs GI-XRF (and XRR) for non-destructive thin film analysis

Dieter Ingerle^a, Giancarlo Pepponi^b, Peter Wobrauschek^a, Christina Strelia^a

^a Atominstitut, TU Wien, Stadionallee 2, 1020 Vienna, Austria

^b MiNaLab, CMM-irst, Fondazione Bruno Kessler, Via Sommarive 18, 38050 Povo, Italy

Grazing Incidence XRF (GIXRF) is a Total Reflection X-Ray Fluorescence Analysis (TXRF) related technique, which varies the angle of incidence in the grazing incident regime and is makes use of the phenomenon of total external reflection of X-rays on smooth polished surfaces. The penetration depth of the incident X-ray beam in the total-reflection regime is very small and depends on the incident angle. Therefore, GIXRF spectra are a result of the elemental depth distribution of this near surface region, but suffer from an ambiguity mainly concerning density and depth.

In order to overcome the ambiguities of GIXRF the method is combined with X-ray reflectometry (XRR), which is an established technique for the characterization of single- and multi-layered thin film structures. Both techniques use similar measurement and data evaluation procedures.

The combined measurement and evaluation of Grazing Incidence XRF (GIXRF) and X-ray reflectivity (XRR) for the characterization of layers, implants and particles in the nanometer range offers distinct advantages as it reduces uncertainties and ambiguities of the individual techniques. But it also imposes requirements and challenges on the instrumentation and calculations, which have to be known and considered for successful measurements and reliable evaluation.

We present an overview of the required instrumentation and its influence, the fundamental theory used for the calculations, and discuss fundamental and instrumental parameters, which have to be included in the calculations, in order to fit the measurements.

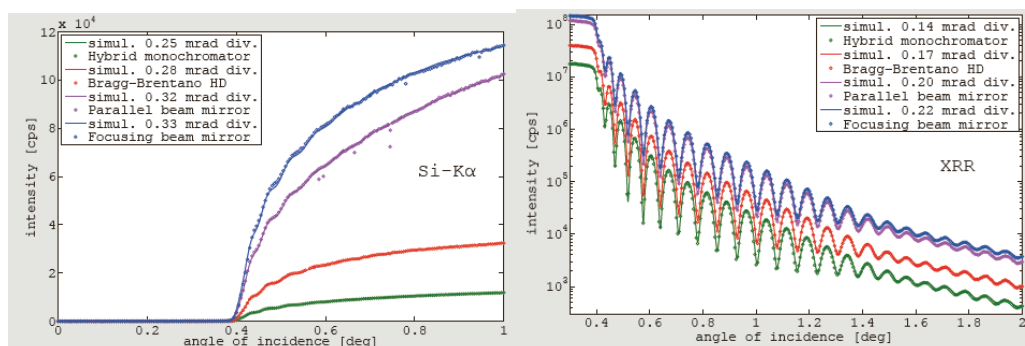


Figure 1. Measurements and simulations of a Ni-layer on Si using different optics

Tutorial Session - Quantitative analysis and calibration

Stosnach, Hagen

Bruker Nano Analytics, Berlin Germany

This tutorial will start with the different approaches for quantitative analysis in TXRF. The historical starting point of TXRF was the direct quantification of surface contaminations in the semiconductor industry. This application is using absolute quantification and calibration methods and the sensitivity calibration of the instrument. The sensitivity calibration can also be applied for the determination of relative element distributions on the basis of the calculated net intensities in the TXRF spectrum.

Most commonly the element concentrations in liquid or solid samples are determined on the basis of internal standardization. Here the connection between sample preparation and quantification model will be discussed. Not widely used but also discussed is the quantification of TXRF measurements based on an external calibration with matrix-corrected net intensities.

Basis of all quantification approaches is the sensitivity calibration of the applied instrument. Even though the manufacturers deliver these with the instruments it will be discussed how to set up a complete calibration.

These setup calibrations are valid for concentrations in the $\mu\text{g/l}$ to mg/l (respectively $\mu\text{g/kg}$ to mg/kg) concentrations range and ideal thin film samples. If the prepared samples have a higher thickness or elements are present in very high concentrations, the calculated concentrations will at least in parts not be correct. The same is valid for systematic errors in sample preparation, e. g. when parts of an element are lost due to evaporation. This tutorial will show how to compensate these effects by adjusting the calibration of the instrument.

Recent trends in preconcentration strategies used in combination with TXRF analysis

Eva MarguÍ

Department of Chemistry. University of Girona. C/M.Aurèlia Capmany, 69. 17703 Girona (Spain)

Element determination and quantification in liquid samples is a topic of great interest in many fields. In TXRF analysis, the specimen is prepared as a residue of drying a drop (5–50 µL) on a pre-cleaned proper sample carrier. In principle, low salinity water samples are ideal for TXRF because the dried residues can be easily prepared from droplets, in agreement with the TXRF prerequisites, simply by using micropipettes. However, for more complex liquid samples or when element concentrations are at the ultratrace level, the use of preconcentration strategies becomes necessary [1, 2]. The application of suitable sample preparation procedures before the analysis of the liquid sample can also expand the applications of TXRF analysis for the determination of low-Z elements, specific elemental species, volatile elements such as Hg or even environmentally relevant emerging pollutants such as metallic nanoparticles [3].

This session gives an overview of the state-of-the-art of recent preconcentration strategies used in combination with TXRF. Taking into account the microanalytical capability of TXRF spectrometry, microextraction procedures are powerful methodologies to be combined with TXRF spectrometry for the determination of low levels of inorganic analytes in aqueous samples in a simple, non-time consuming and low-cost way. When using such approach in combination with TXRF, after the extraction procedure, the few µL of organic solvent or loaded solid adsorbent (containing the extracted analytes) can be directly analyzed. Other preconcentration procedures such as functionalization or immobilization of membranes on the quartz reflector will be also discussed.

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Peak deconvolution for TXRF measurements - free software options

Dieter Ingerle^a

^a. *Atominstitut, TU Wien, Stadionallee 2, 1020 Vienna, Austria*

The quality of the quantification in TXRF (like for other XRF techniques) relies heavily on the evaluation of the measured spectra and the accuracy of the extracted peak areas. Although many commercial TXRF instruments come with their own software package, the freely available options presented here are nevertheless helpful to understand the underlying principles, verify reported results, and of course for custom-built instrumentation or at the synchrotron.

These software packages rely on the underlying model as described by Van Espen et al. [1], which is basically a mixture of physical and mathematical modelling. The background in the measured spectrum is approximated by a mathematical function or obtained by peak filters. The peaks are of Gaussian shape with energy dependent FWHM (due to the detector response) and optional corrections. In order to reduce the free parameters, the peaks are not fitted individually, but in groups corresponding to the emitted fluorescence line groups, with the corresponding relative intensities obtained from a database. This approach also enhances the capability to resolve peak overlaps.

We will demonstrate the deconvolution of spectra with three different software packages: PyMCA [2] can be downloaded at [3], QXAS/AXIL [4] (includes a quantification module), and WinQXAS. QXAS and WinQXAS, which can be downloaded from the IAEA [5], do not run natively on modern 64-bit operating systems but require emulation or virtualization.

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Applications of TXRF: innovations for screening and quantitative analysis of unconventional samples

Laura Borgese^{a,b,c}, Fabjola Bilo^{a,b,c}, and Laura E. Depero^{a,b,c}

^aDepartment of Mechanical and Industrial Engineering, University of Brescia, Via Branze 38, Brescia Italy

^bConsorzio INSTM, Via G. Giusti 9, Firenze Italy

^cSmart Solutions srl, via Corfù 106, Brescia Italy

The ease of use of commercially available TXRF instrumentation has considerably extended its fields of application. However, the prerequisites for the applicability of the method are not always respected. In fact, matrix effects are often not negligible, and this affects the accuracy of the experimental results. Trying to turn this disadvantage into an opportunity responding our analytical needs, we have gone beyond the confines of the traditional TXRF technique, overflowing into a regime not yet well defined, where we can still exploit the linear relationship between fluorescence intensity and concentration for calibration and quantitative analysis. We consider this as a great opportunity for the expansion of this technique.

The TXRF instrumentation can be conveniently used for the screening of materials such as food and cosmetics, coupled if needed with the more traditional analytical techniques for elemental analysis. Our main interest is the analysis of particulate matter in air filters, that were extensively studied to develop a suitable calibration method for quantitative analysis, recently proposed for a standard to the International Standard Organization [1]. But also, non-conventional solid samples, such as leaves can be measured [2]. This innovative approach is based on the use of a new preparation method invented by us called Smart Store®.

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Development of TXRF Standards for environment and health

Laura E. Depero^{a,b,c}, Laura Borgese^{a,b,c}

*^aDepartment of Mechanical and Industrial Engineering, University of Brescia, Via Branze 38,
Brescia Italy*

^bConsorzio INSTM, Via G. Giusti 9, Firenze Italy

^cSmart Solutions srl, via Corfù 106, Brescia Italy

The development of standards is fundamental for spreading any chemical analysis or technique in the society. In particular, the TXRF is a technique of quantitative and qualitative analysis, which shows several advantages. Indeed, the normation of TXRF as an alternative technique is of great interest to the scientific community, environmental agencies, public health authorities, and private stakeholders. Quantification is straightforward since the method of internal standardization can be applied. Fields of application are environment (air, water, soil, biomonitors), biology (blood, urine, nails, cell extracts, hair, drugs), food (honey).

An overview of the stages required leading to the publication of an international standard within the ISO is presented, with examples related to the development of “Technical Specification for the use of TXRF spectroscopy in biological and environmental analysis” [1] and the “International Standard for TXRF analysis of water” [2].

Since the mandatory preliminary step for method validation and the definition of standards is pre-normative research and, in particular, the inter-laboratory tests, the related activities developed in the COST Action ENFORCE TXRF (<https://enforcetxrf.eu/>) will be discussed.

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ORAL PRESENTATIONS

Biomonitoring of human health using TXRF method

R. Stachura^a, D. Banaś^{a,b}, A. Kubala-Kukuś^{a,b}, S. Gózdź^{b,c}, P. Kowalski^a,

U. Majewska^b, I. Stabrawa^{a,b}, K. Szary^{a,b}, J. Wudarczyk-Moćko^b

^aInstitute of Physics, Jan Kochanowski University, Uniwersytecka 7, 25-406 Kielce, Poland

^bHolycross Cancer Center, Artwińskiego 3, 25-734 Kielce, Poland

^cInstitute of Public Health, Jan Kochanowski University, IX Wieków Kielc 19, 25-317 Kielce, Poland

The use of chemicals in a wide range of products, including food and pharmaceutical products, as well as in the protection and fertilization of plants, provides numerous benefits for society. However, the widespread use of chemicals can significantly reduce the quality of the natural environment and have a negative impact on human health. Humans are exposed to chemicals artificially introduced in the environment as a result of their inhalation, ingestion and absorption through the skin. Human biomonitoring (HBM) takes into account all these exposure pathways by measuring the concentrations of a chemicals, their metabolites or reaction products in human specimens [1]. HBM involves measurements of biomarkers in a human bodily fluids, such as blood, serum, plasma, urine, saliva, breast milk, sweat but also other specimens such as tissue, hair, teeth, or nails, and thus directly reflects interindividual variability in exposure levels, metabolism and excretion rates [2].

One of the methods that may be useful for HBM is elemental analysis using total reflection X-ray fluorescence (TXRF). This method allows to estimate exposure of human to macro (e.g. P, S, K, Ca, Fe) and trace (e.g. Cr, Mn, Cu, Zn, Rb, Pb) elements, and to evaluate reference values within a population [3]. In this work the TXRF technique has been used for elemental analysis of human serum, hair, urine and tissue samples. The measurements were performed using benchtop TXRF system (Bruker, GmbH, Berlin, Germany). The TXRF experimental setup, sample preparation methodology, and procedure of measurements and quantitative analysis are described in details. The information regarding the detection limit value and the accuracy of the method are also presented.

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Elemental Variability of fine atmospheric aerosols in Old Jeddah, Saudi Arabia

Safaa S. M. Ali^a, Mohamed H.H.Mahmoud^b, Abdallah A. Shaltout^a

^aSpectroscopy Department, Physics Division, National Research Centre, El Behooth Str., 12622 Dokki, Cairo, Egypt

^bDepartment of Chemistry, College of Science, Taif University, P.O.Box 11099 Taif, 21944 Saudi Arabia

Air particulate matters with an aerodynamic diameter equal or less than 2.5 micrometers (PM_{2.5}) have been collected from the historical old Jeddah district (downtown) throughout the whole year. Additional PM_{2.5} aerosols have been collected during the autumn and winter seasons from another newly constructed district inside Jeddah city (Alnaeem). The annual mass concentrations of the PM_{2.5} aerosols from old Jeddah and Alnaeem sites were found to be $43 \pm 6 \mu\text{g}/\text{m}^3$ and $61 \pm 14 \mu\text{g}/\text{m}^3$, respectively. These values are greater than the recommended annual mass concentration of the air quality standards of the European Commission (EC, $25 \mu\text{g}/\text{m}^3$) and the world health organization (WHO, $10 \mu\text{g}/\text{m}^3$). The elemental analysis of the collected fine atmospheric aerosols has been carried out using an energy dispersive X-ray fluorescence with multi-secondary targets [1-4]. Twenty-two (22) elements have been determined, namely Na, Al, Si, S, Cl, K, Ca, Sc, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Br, Rb, Sr, Y, Ta, and Pb. Although the old Jeddah site is not well organized, the elemental concentrations and total mass concentrations are lower than other sites. The statistical analysis including enrichment factors, Pearson's correlation analysis, and principal component analysis reveals more information about the source identification of the PM_{2.5} samples collected from both locations. It was found that the quantified elements originate from a natural source, anthropogenic source, and sea spray source.

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Development of reference material for direct TXRF analysis of air filters

Paola Cirelli^a, Fabjola Bilo^{b,c}, Laura Borgese^{b,c}

^a Department of Information Engineering, University of Brescia, Via Branze 38, 25123 Brescia, Italy

^b Department of Mechanical and Industrial Engineering, University of Brescia, via Branze 38, 25123 Brescia, Italy

^c SMART SOLUTIONS s.r.l, via Corfù 106, 25124 Brescia, Italy

There is the demand for sensitive and reliable analytical techniques for environmental monitoring purposes. Total reflection X-ray fluorescence (TXRF) may be used as a complementary technique with respect to reference methods as ICP-MS and AAS. My research is focused on developing and optimizing a novel method for the direct analysis of particulate matter (PM) on membrane filters, prepared by the SMART STORE[®] procedure, by means of TXRF spectrometers. This handling procedure, that consists in enclosing the filter between two adhesive polypropylene foils, avoids material loss and sample damages. A recent work has shown the suitability of this method for the direct analysis of Pb-loaded reference filters [1]. A calibration curve, used to quantify real air filters, was built analyzing mono-element reference samples, relating the net fluorescent intensity detected by the spectrometer to the known concentration of the sample. A deeper study was performed by measuring the same set of reference samples, using 3 commercial Mo-TXRF spectrometers [2]. Empirical and theoretical approaches have been explored to define a method for quantitative analysis of Pb, determining detection limit and linearity range (Figure 1). Based on the satisfactory research we are moving toward the preparation of reference materials for other elements of environmental interest (i.e. Cu). Reference samples with different mass loading can be built using an aerosol generator, nebulizing a solution of a metal containing compound onto a filter.

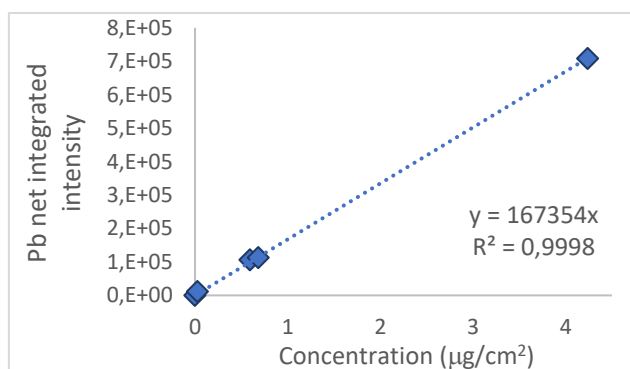


Figure 1. Pb calibration curve

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Quantifying cytotoxicity and cellular uptake of naked gold nanoparticles in breast cancer cells using total reflection X-ray fluorescence

Natasha Hedden^a, Gabriella Mankovskii^a, Ana Pejović-Milić^a

^aDepartment of Physics, Faculty of Science, Ryerson University, 350 Victoria Street, Toronto, Ontario, M5B 2K3, Canada

Gold nanoparticles (AuNPs) have unique characteristics compared to their bulk counterpart that makes them ideal for various medical uses such as biomedical imaging, photothermal therapy, and drug delivery. With higher concentrations used in cancer therapy, it is imperative to have a thorough understanding of both the benefits and the potential side effects of AuNPs. Several studies have been done to quantify the toxicity of naked AuNPs, but it is unclear whether the trends in toxicity can be attributed to variations in cell line, size, and shape of the AuNPs or to the absolute gold nanoparticle mass taken up by the cell. Utilizing the total reflection X-ray fluorescence (TXRF), rapid and precise quantification of uptake for trace-levels of gold complemented with a cell assay to measure short-term toxicity is proposed. By incubating breast cancer cells MDA-MB-231 with different sizes, concentrations, and shapes of naked AuNPs while measuring total gold uptake, the correlation between these parameters and cytotoxicity is investigated. Completing these experiments also with human mammary epithelial cells, a comparison of AuNP toxicity in both cancerous and non-cancerous cell-lines is investigated. We trust that this work will provide insight on the safety of AuNPs prior to their implementation in a clinical setting.

The investigation of potentially toxic elements in soil-plant-air system in vineyards in Serbia

Tijana Milićević^a, Relić D.^b, Anićić Urošević M.^a, Jovanović G.^a, Popović A.^b

^a*Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia,*

^b*University of Belgrade, Faculty of Chemistry, Studentskitrg 12-16, 11000 Belgrade, Serbia*

The agricultural land covers 40% of the Earth's surface and the monitoring of potentially toxic elements in these areas represents the first step regarding safe food production. Three experiments were performed in the in a conventional vineyard in Serbia for investigating element bioavailability accompanied by an assessment of the environmental implications and human health risk. In parallel, mosses were tested as potential air biomonitors in vineyard areas. The element (Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Ca, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, Sb, Sr, V, Zn) concentrations were determined in soil and plant samples by ICP-OES and ICP-MS. In addition, the single extraction procedures (CH₃COOH, Na₂EDTA, CaCl₂, NH₄NO₃, deionised H₂O), and pseudo-total digestion were applied to determine elements mobility and bioavailability from soil [1,2].

The element bioavailability in the soil–grapevine system accompanied by an assessment of the ecological implications and human health risk was investigated. The most suitable extractants for assessing the element bioavailability were CaCl₂, NH₄NO₃, Na₂EDTA, but deionised H₂O could be suitable, as well. Contamination factor implied moderate soil contamination ($1 < CF < 3$). Notable environmental implications of the soil samples were estimated for As, B, Cd, Co, Cr, Cu, Mn, Ni, Sr. According to biological accumulation concentration (BAC), the grape seeds and leaves mostly accumulated Cu and Zn from the soil, respectively. The influence of atmospheric deposition on the air-exposed grapevine parts (leaves and grape skin) was observed ($RF > 1$). Low health risk ($HI < 1$; $R \leq 1 \times 10^{-6}$) was estimated for farmers and grape/wine consumers. In parallel, the moss (*Sphagnum girgensohnii* and *Hypnum cupressiforme*) bags were exposed in vineyard parcels to investigate an appropriate period of the element enrichment during the season [3]. The elements were significantly enriched in moss bags during 2-month exposure, and the enrichment gradually increased up to 6-months. The 6-month exposure could be recommended for comparative studies among different vineyards because it reflects the pollution during the entire grapevine season.

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The role of Americium-241 for the metal detection of solids, liquids and environment contaminants using a portable spectrometer device

Claudio Larosa^a, Attilio Converti^a

^a Department of Civil, Chemical and Environmental Engineering, Pole of Chemical Engineering, via Opera Pia 15, I-16145 Genoa, Italy.

The current demand for new portable devices from the citizen community has opened new prospective of analysis in the fields of antiquity [1], relics [2], sedimentary of ferrous rocks, pollution and radioactive contaminants [3–5]. Based on these topics of interest the physical principle of XRF fluorescence [6] was applied to develop a portable device, starting from an americium source with radial dislocation of eight units, able to remove the last electrons from the orbitals shall of elements at lower energies. The problem solving was applied to realize a portable spectrometer device with high sensibility vs. elements commonly analyzed in spectroscopy using a brass O-ring structured in order to generate photons from the natural decay and then by scintillation, suitable for generate weak signals. Furthermore, another aspect concerns the threshold limit value of detection, was investigated in order to offer a significant highlight signal intensity output. Device was assembly based on two modules: first of al. a sensor with a radial dislocate detector, second, there are two electronic cards with an analogic multi-pins and a master USB connector.

In the experimental section two different hardware were compared in order to define the best solution that have shown a major stability at lower current intensity using a minor number of electronic compounds. Data acquired from samples of mineral nature were acquired and elaborate with a freeware software of analysis in order to show how the element`s signal are generated. Parts of device are innovative in the logical concept able to change and drive the sampling rate, the gain and signal/noise ratio, the device is also able to detect elements near the Americium probe at ~1-2 cm, tailored for small object, potter fragments, oil painting, coins on the surface and from elements mixed in an alloy. The graph output shows elements from which is possible measured the intensity and ratio between the elements. In conclusion an innovative detection part and an analogic card configured with a master USB card is proposed as a versatile system able to acquire signals without employing a pre-amplify circuit working at low pass-band filter.

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Multi-technique instrumental approach for the characterization of metallic archaeological artifacts

Nicoletta Sgarro^a, Savino Gallo^b, Giovanna Rizzo^a, Laura Scrano^c

^aDipartimento di Scienze, Università della Basilicata, Via dell'Ateneo Lucano 10, Potenza, Italy

^bDirettore del Museo Archeologico Nazionale della Siritide, Policoro, Italy

^cDipartimento delle Culture Europee e del Mediterraneo, Università della Basilicata, Matera, Italy

The study of the grave goods has long been the subject of study by many researchers who, through the finds, try to reconstruct the habits and customs of disappeared civilizations. In particular, the characterization of metal artifacts (weapons, jewelry, everyday objects) allows to identify the source of the raw materials used for their manufacture, forging technologies, trade routes, and cultural interactions [1,2].

The aim of this preliminary study was, by using a multi-technique instrumental approach (XRD, Raman, XPS, XRF), the chemical-mineralogical characterization of archaeological metal finds (figure 1) from the necropolis of Siris - Heraclea (Basilicata region). The analyzes highlighted, in some of these objects, the presence of a superficial state of alteration confirming what was reported by [3]. We are carrying out biological analyzes in order to verify the presence of biological agents, which, if present, could have triggered the corrosion processes.



Figure 1. Archeological objects: (a) Stick, (b) Arrowhead, (c) Spicillo

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Total X-Ray Fluorescence as a technique for measure the progress of the separation of Lu and Yb in a chromatographic column

Cynthia Cáceres Rivero^a, Patricia Bedregal Salas^a

^aPeruvian Institute of Nuclear Energy

¹⁷⁷Lu is produced by irradiation of enriched ¹⁷⁶Yb in a nuclear reactor. The final product contains ¹⁷⁷Lu and ¹⁷⁷Yb, so they need to be separated [1]. Lanthanide separation is one of the most complicated separations in chemistry due to the similar characteristics of these elements. At an industrial scale, solvent extraction is used, while when high purities are desired, the ion-exchange chromatography is preferred. Among the methods used for detection, XRF is one of the best options since it is reliable, rapid, straightforward, and selective for all lanthanides. The analytes of interest eluate from the chromatographic column in the aqueous form and conventional XRF requires a sample preparation step consisting of taking an aliquot with a micropipette and pour it on a filter paper, which after dried is put onto the detector [2]. With TXRF this step is eliminated, and the drop can be put directly on the sample carrier. Peaks integration of each volume sample can depict a separation-like trend.

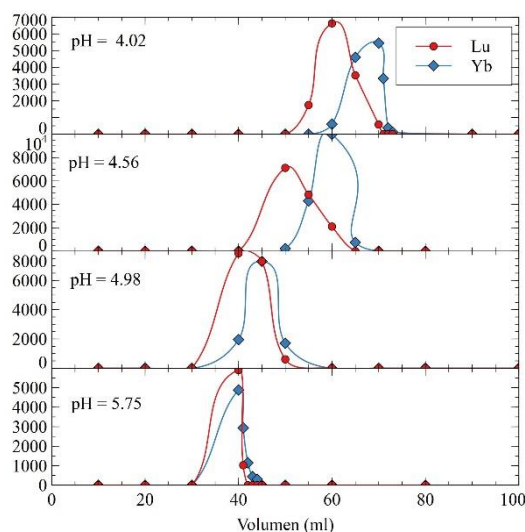


Figure 1. Separation of Lu and Yb in a ion-exchange chromatographic column using citrate at different pH values

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POSTERS

FTIR-HSI analysis of Triple-Negative Breast Cancer (TNBC)

Alessia Belloni^a, Valentina Notarstefano^a, Chiara Pro^a, Giorgia Gioacchini^a, Alfredo Santinelli^{b,c}, Elisabetta Prete^c, Paola Lorenzini^c, Simona Cerioni^c, Vincenzo Catalano^d, Donatella Sarti^d, Anna Maria Baldelli^e, Francesco Graziano^e, Elisabetta Giorgini^a

^aDipartimento di Scienze della Vita e dell'Ambiente, Università Politecnica delle Marche, Ancona (Italy); ^bSezione di Anatomia Patologica, Dipartimento di Scienze Biomediche e Sanità Pubblica, Università Politecnica delle Marche, Ancona (Italy); ^cU.O.C. Anatomia Patologica, A.O. Ospedale Riuniti Marche Nord, Pesaro (Italy); ^dU.O.C. Oncologia, A.S.U.R AVI - Ospedale di Urbino, Urbino (Italy); ^eU.O.C. Oncologia, A.O Ospedali Riuniti Marche Nord, Pesaro (Italy).

Triple Negative Breast Cancer (TNBC) is a complex disease characterized by the lack of expression of estrogen receptor (ER), progesterone receptor (PR) and Human Epidermal Receptor 2 (HER2) [1]. This invasive breast cancer malignant subtype is also characterized by recurrence and resistance after routinely chemotherapy drugs and an approved target therapy still remains absent [2]. Some 'omics' technologies, have highlighted the high heterogeneity of TNBC and then the occurrence of several typologies and sub-variants of the tumour itself, well explaining the variability of response to treatments [3]. For all these reasons, we propose Fourier Transform Infrared Spectroscopy - HyperSpectral Imaging (FTIR-HSI) analysis as an innovative diagnostic tool able to investigate cancer biopsies, and to distinguish biochemical differences among heterogeneous tissues without using any labels or staining [4]. In this light, we have analysed TNBC paraffin-embedded biopsy samples by FTIR-HSI with the aim (1) to evaluate the mechanisms of interaction of the tumour mass with the surrounding stromal tissue, focusing on the healthy gland epithelium, the tumoral mass, and the surrounding stroma, and (2) to define new spectral biomarkers able to improve the classification of TNBCs in relation with similar histological features.

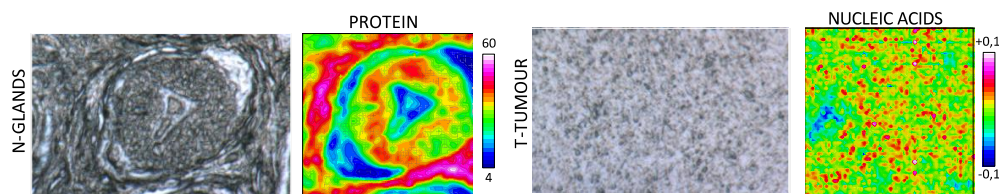


Figure 1. FTIR Hyperspectral imaging analysis of a healthy gland and tumour mass.

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Determination of uranium in aqueous samples treated with *Perlite* by TXRF

Malena Cabranes^{a,b,c}, Gabriela Leyva^{a,b}, Roxana Leguizamon^a, Florencia Gonzalez^a, Paola Babay^{a,b}

^aNational Commission of Atomic Energy, Av. General Paz 1499 (1650) San Martín, Buenos Aires, Argentina

^bNational University of General San Martín, Irigoyen (1650) San Martín, Buenos Aires.

^cNational Council of Scientific and Technical Research, Godoy Cruz (2290) CABA, Buenos Aires, Argentina.

In the nuclear industry, management of effluents is an important challenge. Diverse processes have been developed for their treatment, being the adsorption onto solid materials one of the most popular to eliminate radioactive and toxic ions from aqueous solutions. Adsorption usually offers ease of operation, simplicity of design and applicability to eliminate (or minimize) various types of contaminants, allowing the concentration of radionuclides in small volumes of solid waste.

UO₂ is the raw material for nuclear fuel of electric power generating reactors. Therefore, UO₂²⁺ ions (uranyl ions) are often present in residual effluents from the nuclear industry. On the other hand, *Perlite* is an abundant natural mineral that requires minimum processing before use, either as raw or expanded *Perlite*, resulting in a low cost, natural porous material.

In the context of a research aimed at investigating the potential of this natural material for the removal of UO₂²⁺ from aqueous effluents, TXRF was applied for quantification of remaining UO₂²⁺ in laboratory experiments with synthetic effluents. The samples were analyzed with the S2 PICOFOX (Bruker) with Mo target. Measurement time was 300 sec and Ga was used as internal standard.

The properties of the substrate to retain UO₂²⁺ were evaluated by batch tests, through a thorough study of the variables affecting the process, like material dosage, contact time, adsorption isotherm, and effect of pH, among others. Through these experiments, *Perlite* showed a good potential for removal of uranyl ions. The variables investigated affected removal efficiency to different extents.

TXRF proved to be suitable for the quantification of uranium in the samples treated with *Perlite*. The effect of the matrix provided by the natural substrate did not cause interference for the analysis of remaining uranium.

Analysis of macro and micronutrients in legumes via total-reflection x-ray fluorescence spectroscopy

Antonio Cicchetti^a, Ignazio Allegretta^a, Concetta Eliana Gattullo^a, Giacomo Squeo^a, Carlo Nicoletto^b, Stefano Cesco^c, Roberto Terzano^a

^a*Department of Soil, Plant and Food Sciences, University of Bari “Aldo Moro”, Via G. Amendola 165/A, 70126, Bari, Italy*

^b*Department of Agronomy, Food, Natural Resources, Animals and Environment, University of Padua, Viale dell’Università, 16, 35020 Legnaro, PD, Italy*

^c*Faculty of Science and Technology, Free University of Bozen-Bolzano, Piazza Università 5, 39100 Bolzano, Italy*

Legumes are one of the most important food of the Mediterranean diet. They are rich in carbohydrates and proteins (more than double of cereals and more than meat) and they are poor in fats. Legumes can contain several important macro and micronutrients (K, Ca, Fe, Ni, Cu, Zn, etc), whose content depends on the species, genotype and on the soil where they grow. Toxic elements can also accumulate into legumes. In order to determine the legumes nutritional content, track their provenance and detect toxic elements, a fast, sensitive and reliable analytical method is needed. Among the most recognized instrumental techniques of elemental analysis, total-reflection x-ray fluorescence spectroscopy (TXRF) has demonstrated to be a very useful tool for food analysis since it is fast, requires a small amount of sample as well as a simple sample preparation. In the present work, a new method for the elemental analysis of legumes using TXRF has been developed. For this purpose, 24 different genotypes of beans, grown on two different sites, one at the sea level (Legnaro, Italy) and the second at 1000 m a.s.l. (Asiago, Italy), were investigated.

After harvesting, beans were dried in an oven at 105 °C for 48 h. Then, 10 beans per sample were finely ground with a vibro-milling system. For the analysis, samples were prepared as slurries and Ga was added as internal standard. The slurries were sonicated for 15 minutes and, after vortexing, 10 µL of the suspension were pipetted on a siliconized quartz disk reflector, that was left drying on a heating plate at 50 °C. TXRF analyses were carried out for 1000 s, using a benchtop commercial spectrometer.

In order to validate the method, TXRF results were compared with those obtained after sample acidic digestion and ICP-OES analyses.

Results show that the genotype and the growing site influence the concentrations of macro and micronutrients in beans. These pieces of information may pose the basis for the development of a legume tracking-method using TXRF.

Application of TXRF and ICP-OES in metal uptake studies of argillaceous rocks

Ottó Czömpöly, István Tolnai, Margit Fábián and János Osán

czompoy.otto@ek-cer.hu

*Environmental Physics Department, Centre for Energy Research, Konkoly-Thege M. út 29-33., H-1121
Budapest, Hungary*

In Hungary, Boda Claystone Formation (BCF) have been selected for the study of potential host rock for high level and long lived nuclear waste (HLW) repositories. Several of the safety approaches for the geological disposal of HLW rely on the strong uptake of radio-contaminants by clay minerals. Micro- and macrospectrometric analyses are necessary to determine the uptake capacity of mineral phases present in the host rock for key cations. Se(IV) and Ni(II) chemically representing radionuclides dissolved from HLW were involved in the present study.

The concentration dependence of sorption (sorption isotherm) was studied through macroscopic experiments involving crushed rock samples and synthetic porewater. Since a wide concentration range (10^{-2} - 10^{-10} M) was studied different analytical methods were performed. The high-concentration part (10^{-2} - 10^{-5} M) of the isotherms for Se(IV) and Ni(II) could be recorded by TXRF. ICP-OES measurements could be performed in the range of 10^{-2} - 10^{-8} M via hydride generation for Se. Radiotracer (Se-75) was involved for comparison with the other methods.

The comparison of results and the advantages and drawbacks of each were performed and evaluated. According to the presumptions cationic specieses (Ni^{2+}) showed a higher sorption than anionic compounds (SeO_3^{2-}). Ni and Se have different sorption sites on Boda Claystone which was studied by the competition of these metallic ions.

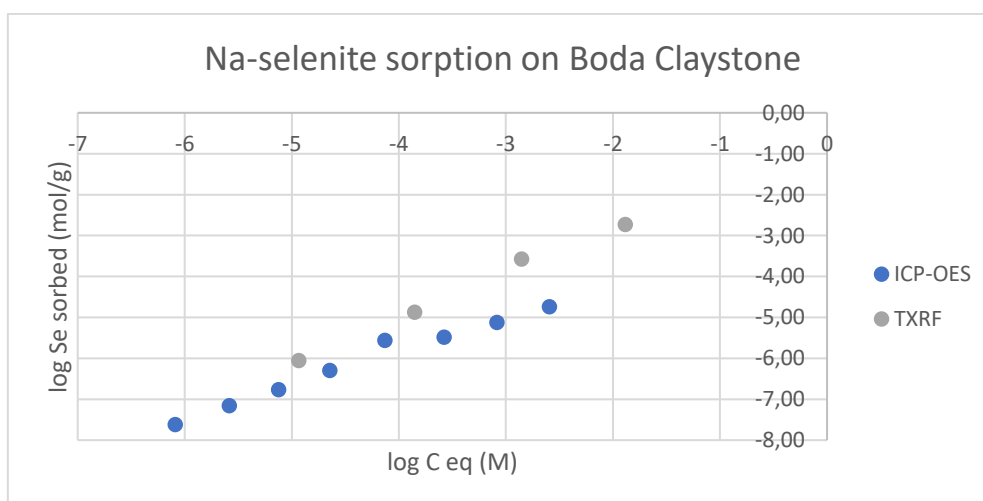


Figure 1. Sorption results of Na-selenite in the high concentration range

TXRF applications at the Department of Analytical Chemistry, National Commission of Atomic Energy (CNEA), Argentina – Part II

Lautaro Valenzuela, Roxana Leguizamon, Florencia Gonzalez, Paola Babay

National Commission of Atomic Energy (CNEA)

TXRF has an important role in CNEA as it serves, together with other analytical techniques, to find solutions to everyday problems of nuclear industry and related research topics. It has applications in different areas, like remediation and monitoring projects, and nuclear materials characterization. I have been working in the XRF laboratory at CNEA for the last 6 month, actively collaborating in several works carried out by the group.

One of the most important projects where we participated was the impurities characterization of uranium concentrates (the raw material for nuclear fuel), in the context of the certification of three reference materials. The work was interdisciplinary; first of all the impurities were separated from the powder by column chromatography and then measured by TXRF with the S2 PICOFOX and the S4 TSTAR (Bruker), and by ICP-MS. TXRF allowed a quite comprehensive characterization of the impurities present in the three materials, and the concentrations measured by ICP-MS were comparable.

In the frame of a remediation work, we collaborate in the monitoring of closed uranium mining sites that have been remediated. Through TXRF analysis of a variety of digested seeds (like cucumber, turnip, lettuce and mustard) that act as bio-monitors, we study the absence of metal contamination to assure that the environmental status of the site is in optimal conditions. The seeds are microwave digested and measured with the S2 PICOFOX.

We also participated in the validation of a TXRF method for measurement of remaining Mo and U after passing through a synthetized resin, in the context of radioisotopes production and separation. Mo-99 is produced by U-235 fission, and is the father radionuclide of Tc-99, widely used in medical imaging. We employed W-Brems excitation of the S4 TSTAR.

Enhancement of hexavalent chromium bioreduction by indigenous microorganisms from polluted groundwaters and sediments

Marina Tumolo^{a,b}, D. de Paola^c, Angelo Tursi^a, V.F. Uricchio^b, V. Ancona^b

^a Department of Biology, University of Bari Via Orabona 4, 70126 Bari, Italy; ^b Water Research Institute-Italian National Research Council (IRSA-CNR), V.le F. De Blasio 5, 70132, Bari, Italy;

^c Institute of Biosciences and Bioresources-Italian National Research Council (IBBR-CNR), Via G. Amendola 165/A, 70126 Bari, Italy

Hexavalent chromium (Cr(VI)) pollution represents a widespread environmental issue, because of its use in several industrial applications and the inadequate management of the related waste and wastewater, with implications on ecosystems and human health [1]. The toxic action of Cr(VI) is due to its ability to easily penetrate cellular membranes. Cell membrane damages caused by oxidative stress induced by Cr(VI) have also been extensively reported, both in eukaryotic and prokaryotic cells [2;3]. Cr(VI) remediation is generally based on the reduction to the less toxic and less mobile trivalent state [4]. Among the strategies commonly used for chromium reduction, bioremediation shows some advantages in terms of economic and environmental sustainability, especially in the case of large volumes of water to be treated. Particularly, several bacteria are able to reduce Cr(VI) to Cr(III) directly or indirectly, either as a survival mechanism aimed at reducing the toxicity around the cell, or as a means of deriving metabolic energy for cell growth [5]. Bioremediation of hexavalent chromium by pure cultures of microorganisms isolated from contaminated matrix has been reported in numerous studies at laboratory scale. However, almost no single strain can compete with the native microbial community during *in situ* applications. Thus, the whole native microbial community have to play a key role for the successful outcome of the intervention [6]. Furthermore, most known species capable of chromate reduction are heterotrophic, and need extra nutrition addition during the reduction process, especially in an oligotrophic groundwater environment [7]. Ancona *et al.*, [8] evidenced the key role of amendment, particularly yeast extract in order to stimulate the proliferation of indigenous microorganisms from oligotrophic contaminated groundwater, reaching the 99,47% of Cr(VI) removal at batch laboratory scale.

In my research project, the enhancement of microbial-mediated reduction processes will be study at laboratory scale, using environmental matrices collected from an industrial site polluted by Cr(VI) located in the Barletta Municipality, Apulia. Microcosms will be set up in different experimental conditions: sediment and water sterilized with and without amendments, sediment and water not

sterilized with and without amendments. Control test lines, set up by using sterilized matrices and amendments, will be employed to assess the occurrence of the pollutant reduction via chemical processes. Research activities will combine molecular analyses for studying the indigenous microorganisms capable of Cr(VI) bioreduction, with innovative techniques that must not induce reduction of native Cr(VI) to Cr(III), neither cause oxidation of native Cr(III) contained in the samples to Cr(VI).

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Compositional and structural investigations of the archaeometry samples from Corvins Castle, Hunedoara, Romania

Anca Irina Gheboianu^a, R. M. Ion^b, C. Radulescu^a

¹*Valahia University of Targoviste, Targoviste, Romania; anca@icstm.ro*

²*National R&D Institute for Chemistry and Petrochemistry – ICECHIM, Research Group „Evaluation and Conservation of Cultural Heritage“, Bucharest, Romania*

The aim of this work is an archaeometry study of some samples from the Corvins' Castle, Hunedoara, Romania. New and modern techniques have been adopted for the study of archaeological samples, including: X-Ray Fluorescence (XRF), as an ideal method for analyzing low concentrations of specific elements and helps in the provenance studies, determining major and minor elements and a selected number of trace elements of the investigated sample, and identifying of the provenance their manufacture materials, X-ray diffraction (XRD), as the most popular technique for determining mineral phases of ancient ceramics.

The diffraction data (XRD) have been recorded with a XRD Rigaku Ultima IV and the WDXRF was performed with a Rigaku Supermini200 in order to provide qualitative and quantitative elementary composition and to complete the chemical analysis (elements ranging from O to U). The presence of apatite in the deeper layers at the base of the tower could be an explanation for the durability of the old floor (pre-historic material). Apatite derivatives are recognized as good stabilizer and antimicrobial agents. Except the above-mentioned minerals, mica, zircon and titanite could be identified by the XRD analysis, but in very low concentration. From compositional point of view, the samples could contain magnesium, calcium, manganese, limestone granules, sulphates, aluminum hydrate especially in the production of bricks, and different organic substances with various effects on the timing of the bricks.

Redox-driven changes in the distribution of Fe minerals between aggregate-size classes in the topsoil and subsoil of temperate paddy soils

Beatrice Giannetta^a, DOdS^b, GA^b, DS-P^c

^a*Department of Biotechnology, University of Verona, Verona,* ^b*Elettra Sincrotrone Trieste, Basovizza,*

^c*Department of Agriculture, Forest and Food Sciences, University of Torino, Grugliasco*

Paddy soils represent excellent ecosystems to study the effects of alternating soil redox conditions on the interactions between the biogeochemical cycling of iron (Fe) and carbon (C), and implications on the C source/sink functions of these ecosystems [1]. However, little is yet known on how redox cycling affects organo-mineral associations and their dependence on changes in Fe (hydr)oxide mineral composition. We hypothesized that under paddy management (i) frequent redox cycles may lead to a relative higher proportion of short-range ordered (SRO) Fe oxides associated with the free fine particles with respect to similar size fractions within microaggregates in the topsoils; (ii) the enhanced input of dissolved Fe into the subsoil leads to the preferential formation of SRO Fe oxides mainly associated with the finer particle size fraction. Soil samples were collected from different horizons (up to c. 60 cm) from soil profiles opened in two adjacent fields under long-term paddy, and non-paddy management [2]. Aggregate and particle-size fractionation was carried out to separate 8 fractions including coarse and fine sand, and coarse silt, fine silt clay, free or within microaggregates. Organic C and Fe (hydr)oxide contents in bulk soils and their distribution between size fractions were evaluated by elemental analysis and selective extractions. Characterization of Fe mineral composition was also evaluated by X-ray diffraction (XRD) and Fe K-edge extended X-ray fine structure (Fe EXAFS) spectroscopy at the XAFS beamline at Elettra. Statistical methods have been used to determine goodness-of-fit parameters for linear combination fitting (LCF) of XAS data. Wavelet transformation (WT) has been particularly useful to qualitatively discriminate between elemental signal contributions of backscattering neighboring atoms [3].

Our results evidenced that paddy management resulted in lower amounts of Fe (hydr)oxides in the topsoils with respect to non-paddy soils, with a relative higher proportion of ferrihydrite particularly in the finer soil fractions not associated with microaggregates. In the paddy topsoils, the clay fraction within microaggregates was the only fraction to show the presence of more crystalline Fe forms. Redox cycling even favored the increase in ferrihydrite in the subsoil where the formation of more crystalline phases was not observed. More crystalline Fe forms were only detected in the clay fraction relative to the deepest Brd2 horizon. These findings suggest that the dynamic redox cycling in

temperate paddy topsoils is affected by microaggregation, and leads to a distribution of pedogenetic Fe along the soil profile contributing an increase in subsoil C stocks.

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Analysis of a ferrochrome slag by means of suspension assisted Total Reflection X-ray Fluorescence Spectrometry (TXRF)

Jessica Hiller^a, Ursula E. A. Fittschen^a

^a *Clausthal University of Technology, Institute of Inorganic and Analytical Chemistry,
38678 Clausthal-Zellerfeld, Germany*

Slags are generated in large quantities as by-products especially in the iron, copper and steel producing industries. The slags form during the metallurgical melting processes as floating melt and essentially consist of ecologically harmless silicates and oxides (SiO_2 , CaO , FeO_n , Al_2O_3)^[1]. Depending on the raw material and on which process the slags originate from, they contain certain quantities of heavy metals or other additives (*e.g.* Cr as alloy element in steel). Regarding the large quantities of slag produced during the processes, it is sensible to utilize these by-products in the best possible way. Depending on the type, slags are already used *e.g.* for road construction and fertilizer production if harmlessly possible^[1]. In addition to the direct usage of slags, there are new efforts to use the slags as secondary raw material sources^[2]. For many applications, the slags must first be examined for substances that are hazardous to human health and the environment. Total Reflection X-ray Fluorescence Spectrometry (TXRF) is suitable for the determination of the elemental composition. Especially the possibility to investigate the solid matters directly in form of suspensions without previous wet chemical digestions using toxic hydrofluoric acid makes TXRF attractive and promising. However, the preparation of homogeneous suspensions which are sufficiently stable against sedimentation is challenging for materials having densities above $3 \text{ g}\cdot\text{cm}^{-3}$. From an instable suspension, non-representative aliquots and specimens can result leading to unreliable elemental determinations. Here, we present first results validating methods for suspension assisted TXRF of the certified ferrochrome slag reference material SARM 77 (MINTEK, Randburg, Republic of South Africa). The focus lies on the recovery of the certified contents for Ca, Fe, and Cr under consideration of parameters that reduce the particle settling.

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Identification of black inks on Algerian manuscripts using XRF and other spectroscopic techniques.

Lynda Idjouadiene^{a, b}, Toufik A. Mostefaoui^a, Marco Gargano^b, Letizia Bonizzoni^b

*^aEquipe LuMaNo, Laboratoire de Physico-Chimie des Matériaux et Catalyse, Faculté des Sciences Exactes,
Université de Bejaia, 06000 Bejaia, Algeria*

*^bDipartimento di Fisica «Aldo Pontremoli», Università degli Studi di Milano, via Celoria 16, 20133 Milano,
Italia*

ABSTRACT:

Written heritage is one of the most important means to know the cultural history and the intellectual and scientific production of a nation [1]. The analysis of pigments/inks on artworks is of major significance in art conservation as it leads to detailed characterization of materials; it is thus important for dating and authentication, as well as for possible conservation or restoration of artwork [2]. The knowledge of the chemical composition of all the materials employed is indeed particularly useful to study an illuminated manuscript. In our recent studies, we established a methodology for the analysis and characterization of the paper and inks on old Algerian manuscripts used X ray fluorescence. Points discussed in the present work are focused on the discrimination of different kind of black ink (dark black, bright black and brownish black) on north African manuscripts from various historical periods. In all cases, we had measured both areas with and without writings (clear paper). We have selected representative points that allow a comparison between different manuscripts, historical periods and inks. In addition to XRF analysis, we applied other techniques, namely FORS and Raman spectroscopies, to get more complete results and characterize the nature of inks used.

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Implementation of ISO/IEC 17025 standard for TXRF technique accreditation in LANAFONU

Nancy Lara-Almazán^a, Graciela Zarazúa-Ortega^a, Alberto Cedillo-Cruz^a

*^aNuclear Forensic Research Laboratory (LANAFONU), National Institute for Nuclear Research,
Ocoyoacac, Mexico.*

The Nuclear Forensic Research Laboratory (LANAFONU, acronym in Spanish) of Mexico, is a Laboratory with the objective of optimize scientific processes and techniques used to analyze nuclear materials, environmental and biological sources. Another objective of the LANAFONU is consolidate the laboratory through of accreditation of all the analytical techniques that it has, it to guarantee the technical competence of the operators, as well as, the quality of the results. Within these is the total reflection X-Ray fluorescence (TXRF). For this, staff members of LANAFONU implemented NMX-EC-IMNC-17025:2006 / ISO/IEC 17025:2005 Standard through a 3-year process. In the first year, to increase the technical and quality system knowledge's based on the general requirements of ISO/IEC 17025, staff members of the laboratory were training, In the second year, the staff members developed quality system related to the management, besides, the technical requirements. In the third year, the quality system was applied, the TXRF technique was validate and uncertainty of the measures was estimated, it applicable to the determination of the chemical elements K, Cr, Mn, Fe, Ni, Cu, Zn, As and Rb in liquid samples using as a model the quantitative determination in natural waters in the order of $\mu\text{g/kg}$ to mg/kg , an S2 PICOFOX equipment was used. LANAFONU was accredited in 2019 as Research Laboratory by the accreditation organism of Mexico "entidad mexicana de acreditación, a.c. (ema)" and TXRF technique, is part of the scope of accreditation, besides, two staff members were evaluated and received the appointment of authorized signatories to perform analysis by TXRF. The implementation of the quality system and the accreditation, allowed a marked improvement in the skills of the personnel, clearer and more detailed documentation, better maintenance of the equipment and the experienced professional staff, as well as, accuracy and reliability of the analytical data.

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Evaluation of uncertainty in the elemental analysis of Neolithic heterogeneous ceramic using total reflection X-ray fluorescence spectrometry

Maria Mukhamedova^{a,b}, Galina Pashkova^{a,b}, Victor Chubarov^{b,c}

^a*Irkutsk State University, Irkutsk, Russian Federation*

^b*Institute of the Earth's Crust, SB RAS, Irkutsk, Russian Federation*

^c*Vinogradov Institute of Geochemistry, SB RAS, Irkutsk, Russian Federation*

Elemental composition of ancient ceramics are often used in archaeological studies for identification of source areas, characterization of raw materials and manufacturing processes. Information about the parameters, which could aid in the evaluation of analytical uncertainties and/or instrumental error is usually not reported in archaeometric publications [1]. However, evaluating uncertainty in experimental results is an indispensable task because uncertainty can affect the statistical treatment and interpretation of data of the composition [2].

This report focuses on evaluating uncertainties in the elemental analysis of Neolithic heterogeneous ceramic fragments using total reflection X-ray fluorescence spectrometry (TXRF). 10 small subsamples were obtained from the ceramic fragment, powdered and prepared as suspensions and solutions after acid leaching [3]. We considered the instrumental (counting statistical error, spectra deconvolution), sample preparation (errors due to weighing, suspending, acid digestion etc.) and sampling uncertainty introduced by the ceramic inhomogeneity. The calculated uncertainties were compared for these obtained for WDXRF and ICP MS methods.

The research was supported by Irkutsk State University (project № 091-21-311) and Russian Science Foundation (project № 19-78-10084) and performed using the equipment of the Siberian Branch of the Russian Academy of Sciences «Isotope-geochemical Research» and «Geodynamics and Geochronology» Joint use centers.

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Elemental characterization of Quartzite of POUMA-CAMEROON: Radiation attenuation properties based on NIST and GEANT4 simulation.

Patricia-Laurelle DEGBE^{a,b}, Cébastien Joel GUEMBOU SHOUOP^{b,c}, Daniel BONGUE^{a,b},
Maurice MOYO NDONTCHUENG^{a,b,c}.

^a*Centre for Atomic Molecular Physics and Quantum Optics (CEPAMOQ).*

^b*Department of Physics, Faculty of Sciences, University of Douala. P O Box 24157 Douala,
Cameroon*

^c*National Radiation Protection Agency, P O Box 33732, Yaounde, Cameroon*

Pouma quartzites are widely exploited and used as decorative stones for the embellishment of houses, building materials for schools, hospitals, administrative buildings, roads and also as stones for grinding food. To ensure that such commonly used material is safe for the population and the end-users, it is vital to investigate its physical and chemical properties (especially its elemental content and radiation exposure properties). In this study, the chemical composition of these quartzites was assessed to characterize their elemental contents, its minerals constituents, and also to determine the mass attenuation coefficients. Nineteen (19) rock samples were taken from different mining sites in the Pouma sub-division, precisely in the village of Nkondjok. The collected samples were analyzed using an energy dispersive X-ray fluorescence spectrometer (EDXRF) from the laboratory of the National Radiation Protection Agency (NRPA) of Cameroon. The mass attenuation coefficients were computed using the online XCOM program and the Geant4 toolkit. It appears from this analysis that the Pouma quartzites are mainly composed of SiO₂, Al₂O₃, K₂O, Fe₂O₃, CaO and P₂O₅. In addition, radioactive elements such as Thorium and Uranium and heavy metals such as Pb, Zn, Cu, ... were found only in trace amounts in the investigated Pouma quartzites samples. The simulation results showed a good agreement with the theoretical data obtained with XCOM, thus validating the GEANT4 Monte Carlo model developed in the present research.

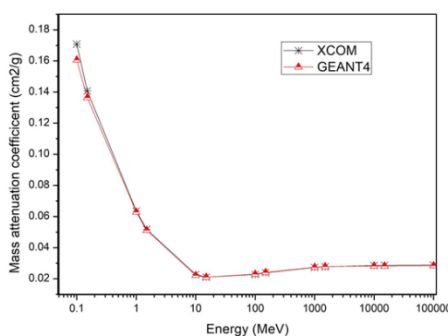


Figure 2. Mass attenuation coefficients of sample rock of Pouma. Comparaision between XCOM and GEANT4 Monte Carlo results.

The sorption of oxybenzone onto soil

Salvatore Rapisarda, C. Ciavatta, L. Cavani

Department of Agricultural and Food Sciences, University of Bologna, Bologna, Italy

A lab-scale experiment was carried out with the aim of investigating the sorption and desorption behaviours of oxybenzone onto four soils with contrasting properties. Oxybenzone is an organic compound belonging to the class of aromatic ketones known as benzophenones. It is one of the most used organic UV filters, molecules capable to absorb the UV radiation that are mainly employed in cosmetic products (i.e., sunscreen lotions, skin care products, lip care products) and objects of common use (i.e., plastics, rubbers, paints).

However, displaying endocrine-disrupting properties [1,2,3] and toxicity towards the marine environment [4,5,6], organic UV filters are considered emerging contaminants.

Oxybenzone (like other organic UV filters) mainly enter the soil through sewage sludge from wastewater plants, which is widely used as organic fertilizer in agriculture.

Adsorption kinetics and adsorption/desorption isotherms were obtained using the batch equilibrium method and determining the concentrations of oxybenzone by the high performance liquid chromatography. Experimental data were described by Freundlich equation. Results show that both the adsorption and desorption constants have a high positive correlation with soil organic carbon and clay percentage. Organic carbon normalized distribution coefficients were also calculated, but it was not found a positive correlation with the Freundlich adsorption constants. More-in depths studies are required to unravel the soil organic matter effects on the adsorption process.

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Assessment of Trace Elements in PM_{2.5} and PM_{2.5-10} Collected in Kenitra City (Morocco) by TXRF Analysis

Mounia Tahri^a, A. Benchrif^a, M. Bounakhla^a, F. Benyaich^b, Y. Noack^c

^a *National Centre of Energy, Sciences and Nuclear Techniques, Rabat, Morocco.*

^b *University of Moulay Ismail, Faculty of Sciences, Department of Physics, Meknes, Morocco*

^c *European Center for Research and Education in Environmental Geosciences, Aix en Provence, France.*

The TXRF is a powerful analysis technique, which is very suitable for small amounts like the ones with aerosol samples. Because of the high detection power and the low sample masses required for TXRF analysis, it was used in many studies to characterize and quantify air particulate matter pollution. Particulate matter (PM) is a complex mixture of extremely small particles and liquid droplets. Particle pollution is made up of a number of components, including acids (such as nitrates and sulfates), organic chemicals, metals and soil or dust particles. The size of particles is directly linked to their potential for causing health problems; In fact, small particles less than 10 µm in diameter can get into your lungs, and some may even get into your bloodstream.

In the present study, we have tried to summarize the air quality status in Kenitra city during one-year (2007–2008); the study was focused on the PM_{2.5} and PM_{2.5–10} fractions of particulate matter. The chemical compositions of the collected filters were evaluated by using Total X-Ray Fluorescence. The influence of the atmospheric transport scenarios on the levels of PM was elaborated by means of air mass back-trajectories, using HYSPLIT™ model. This study allowed identifying four main transport patterns: Short local flows over Kenitra region, Northwesterly flows over Atlantic Ocean, Northerly flows, and Southern flows. The highest PM_{2.5-10} concentrations were observed in the summer and the lowest in the winter. However, no significant seasonal were discerned for PM_{2.5} particles. The enrichment factor and risk assessment code were calculated to distinguish between anthropogenic influences and the natural background levels and assess the environmental risks of metals in PM_{2.5-10} and PM_{2.5} particles. The source apportionment in the studied areas was conducted using the positive matrix factorization method. Four sources and their contributions to PM_{2.5-10} and PM_{2.5} mass were identified and quantified. These include metal smelting, road dust, soil dust and motor vehicles for PM_{2.5}; and two stroke engines, road dust, soil dust and motor vehicle for PM_{2.5-10}.

Total reflection X-ray fluorescence analysis of sulfide copper-nickel ores using wet grinding procedure for preparation suspensions

Alena Zhilicheva^a, Galina Pashkova^a, Victor Chubarov^b, Alexander Marfin^a

^a*Institute of the Earth's Crust, SB RAS, Irkutsk, Russian Federation*

^b*Vinogradov Institute of Geochemistry, SB RAS, Irkutsk, Russian Federation*

In this study, total reflection X-ray fluorescence spectrometry (TXRF) was applied to the direct quantification of major compounds (Fe, Cu, Ni, S) in sulfide copper-nickel ores from Noril'sk-Talnakh deposits (Russia) by the internal standard method using S2 Picofox (Bruker Nano GmbH) spectrometer.). The ore samples were prepared as suspensions. The TXRF results were compared with the data obtained by certified «wet chemistry» techniques (gravimetry for S, atomic absorption spectrometry for Fe, Cu and Ni).

It has previously been shown that the reproducibility of the TXRF results strongly depends on the particle size, suspension stability and distribution of the internal standard [1]. To reduce the sample preparation error, the wet grinding was applied [2]. 100 mg of the powdered sample was placed in a grinding jar (10 mL), and 20 g of ZrO₂ balls of 1 mm diameter were added. 250 µL of the 1000 mg/L internal standard (Ga) solution was added to the jar. The final solution was brought to the volume by ultrapure water. The jar was placed to the MM-400 grinding system (Retsch) for 10 min at a frequency of 20 Hz. The sample was transferred to a 50 mL vial after several cleaning cycles. Then 10 µL of the suspension was put onto a quartz carrier and air-dried. Application of the wet grinding allowed to reduce the average size of particles to 2-7 µm that significantly improved the reproducibility of the analysis. Relative standard deviation from measurements of replicates did not exceed 5% on average. Good correlations between TXRF and certified technique data ($R^2 > 0.97$) were observed.

The research was performed using the equipment of the Siberian Branch of the Russian Academy of Sciences «Isotope-geochemical Research» and «Geodynamics and Geochronology» Joint use centers.

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1st International Summer School on Total-reflection X-Ray Fluorescence (ISS-TXRF)

20th-24th of September 2021, University of Bari (Italy)

SHORT VIDEOS

TXRF analysis of the ionome of photosynthetic bacteria

Joanna Fiedor^a, Beata Ostachowicz^b, Marek Lankosz^b, Kvetoslava Burda^a

^aAGH University of Science and Technology, Molecular Biophysics and Bioenergetic Group, *al. Mickiewicza 30, 30-059 Krakow, Poland*

^bAGH University of Science and Technology, Biomedical and Environmental Research Group, *al. Mickiewicza 30, 30-059 Krakow, Poland*

Rhodobacter (Rb.) sphaeroides belongs to the purple non-sulphur photosynthetic bacteria. This species can grow either heterotrophically or photosynthetically, depending on light and oxygen conditions. It is widely utilized as a model organism for investigations of photosynthesis and other metabolic processes. Furthermore, it attracted significant attention due to its increasing potential in various scientific and industrial applications [1].

In the presented short video, a usefulness of TXRF spectrometry as a tool for elemental profiling of photosynthetic bacteria and their photosynthetic structures is shown. The TXRF method showed its potential in studies of biological samples of a highly limited amount and concentration. Here, it provided a complete picture of *Rb. sphaeroides* 2.4.1 ionome and hence allowed for its further analyses and establishing of mutual correlations between elements present within cells and photosynthetic membranes [2].

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Development of a methodology for the elementary determination of suspensions by total reflection X-ray fluorescence (TXRF)

Enmily García, Haydn Barros, Yulimar De Araujo and Eduardo Greaves.

Nuclear Physic Laboratory, Simon Bolivar University, Sartenejas, Caracas, Venezuela

The analysis of solid samples by TXRF requires a pretreatment that usually involves the dissolution of them for later measurement. However, there are materials that due to their chemical composition and crystalline structure are difficult to dissolve; so finding a suitable, economical and fast procedure is usually a challenge. In the Nuclear Physics Laboratory of the Simon Bolivar University (LFN-USB) a methodology has been developed to carry out measurements using TXRF in an easy, fast, economical and versatile way that does not require prior digestion of the material. This has been achieved by direct preparation of the samples in suspension. This methodology has been tested with different materials such as soils, sediments, phosphogypsum, lichens, cereals, among others, and we have obtained reproducible results as these are comparable with the measurements made to their digestions. Although it is still necessary to refine some details, this methodology has proven to be reliable.

Although this method can be improved, it has shown to be suitable for analyzing a great variety of samples.

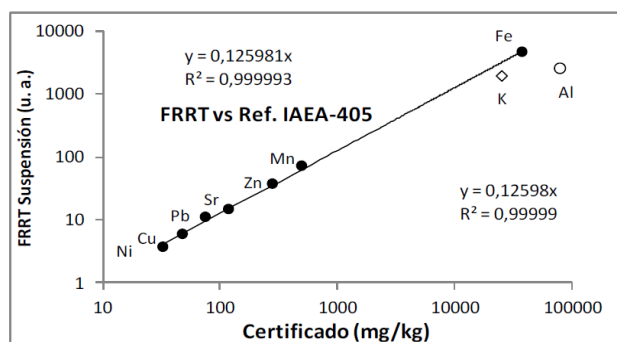


Figure 1: Pseudo quantification by TXRF vs certified values. Sample IAEA-405.

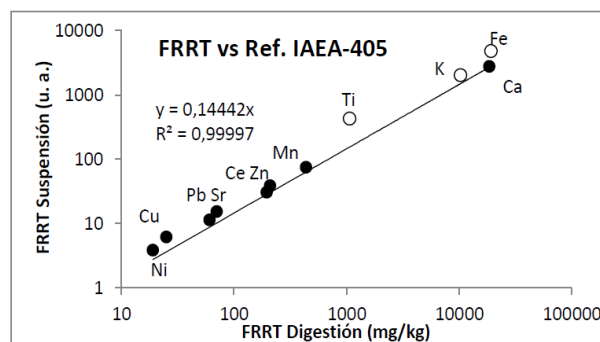


Figure 2: Pseudo quantification by TXRF of suspensions vs quantification of digested. Sample IAEA-405.

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LIST OF PARTICIPANTS

Lorenci	Gjurjaj	Albania	Ludovico	Geminiani	Italy
Bledar	Kola	Albania	Beatrice	Giannetta	Italy
Altin	Mele	Albania	Maria	Lacalamita	Italy
Enida	Nushi	Albania	Claudio	Larosa	Italy
Lynda	Idjouadiene	Algeria			
Paola Alejandra	Babay	Argentina	Arianna	Lodovici	Italy
Marilina	Basso	Argentina	Anna Maria	Maurelli	Italy
Costanza	Bencharski	Argentina	Alessio	Milanesi	Italy
Malena	Cabranes	Argentina	Jacopo	Orsilli	Italy
Lucas Fabián	Dos Santos	Argentina	Davide	Potere	Italy
Florencia	Gonzalez	Argentina	Salvatore	Rapisarda	Italy
Ayelen Maria	Manzini	Argentina	Nicoletta	Sgarro	Italy
Daniela Alejandra	Riego	Argentina	Salvatore	Tripoli	Italy
Lautaro	Valensuela	Argentina	Marina	Tumolo	Italy
Brecht	Dewulf	Belgium	Laura	Zanin	Italy
Ana Gabriella	Miguita	Brazil	Nancy	Lara Almazán	Mexico
Graham	Ferrier	Canada	Jorge Luis	Rodriguez Alejandre	Mexico
Natasha	Hedden	Canada	Graciela	Zarazua-Ortega	Mexico
Gabriella	Mankovskii	Canada	Mounia	Tahri	Morocco
Gabriela	Traplin	Canada	Cynthia	Càceres Rivero	Perù
Degbe	Patricia-Laurelle	Central Africa	Aleksandra	Wandzilak	Poland
Jasna	Jablan	Croatia	Joanna	Fiedor	Poland
Bruno	Komazec	Croatia	Paula	Kasprzyk	Poland
Karla	Kospic	Croatia	Regina	Stachura	Poland
Abdallah	Shaltout	Egypt	Wiktoria	Stanczyk	Poland
Filomena	Bröskamp	German	Anca Irina	Gheboianu	Romania
Jessica	Hiller	German	Marya	Mukhamedova	Russia
Dimitrios	Anagnostopoulos	Greece	Alena	Zhilicheva	Russia
Anastasios	Asvestas	Greece	Ana	Đurović	Serbia
Kalliopi	Tsampa	Greece	Nenad	Grba	Serbia
Otto	Czömpöly	Hungary	Tijana	Milićević	Serbia
Virbahadur	Yadav	India	Mirjan	Petronijević	Serbia
Feni Fernita	Nurhaini	Indonesia	Zorica	Stojanović	Serbia
Leons	Rixson	Indonesia	Paloma	Campos Díaz de Mayorga	Spain
Muhammad Fajar	Sanjaya	Indonesia	Maite	Fernández-Sampedro	Spain
Giulia	Aviano	Italy	Layla	Márquez San Emeterio	Spain
Nicolò	Barago	Italy	Maria Paz	Martin-Recondo	Spain
Alessia	Belloni	Italy	Cisem	Celik	Turkey
Sara	Buoso	Italy	S. Samet	Kaplan	Turkey
Antonio	Cicchetti	Italy	Ercan	Adem	USA
Davide	Ciniglia	Italy	Yulimar	De Araujo	Venezuela
Paola	Cirelli	Italy			
Marco	Colombo	Italy			
Sonia	Conte	Italy			
Marco	Contin	Italy			
Chiara	Di Natale	Italy			

