EXSA

European X-ray
Spectrometry Association

1st virtual conference on X-ray Spectrometry

#EXSA2021

Book of Abstracts

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1st Virtual Conference on X-ray Spectrometry

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EXSA
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EXSA (www.exsa.hu) is a non-profit organization founded in 2004 for promoting cooperation and scientific exchanges between X-ray spectroscopists and analysts within Europe. It brings together users of X-ray spectrometry in various fields of research as well as manufacturers of X-ray devices and developers of X-ray methodologies. EXSA aims to stimulate interaction and communication between young and experienced scientists, between academia and industry, thus fostering scientific progress and innovation.

EXSA's scopes and objectives can be resumed as follow. EXSA uses its financial budget allocated by the members (especially the institutional and sponsoring members) to support its main objective: ***to promote innovation and cooperation of X-ray spectroscopists and analysts within Europe*** by

- supporting financially talented young scientists via travel grants, or reduction of conference fees, to enhance their participation in X-ray spectrometry related events;
- improving and fostering the interface between the academic and industrial sector (via activities such as the Fundamental Parameter Initiative);
- promoting X-ray spectrometry courses in European university curricula;
- providing high-quality training;
- co-organizing summer schools and dedicated workshops on novel and emerging X-ray spectrometry topics.
- supporting the European X-Ray Spectrometry (EXRS) conference series;

JOIN US!

More information at www.exsa.hu

Contact: excom@exsa.hu

Monday June 21, 2021

12:30 - 13:30	Get Together!
13:30 - 13:45	Welcome & Introduction #EXSA 2021 Chairs: Michael Kolbe & Diane Eichert
13:45	**INSTRUMENTAL DEVELOPMENTS** Session 1 Chair: Michael Kolbe
13:45 - 14:15	**Invited - René Bes**
14:15 - 14:35	Christopher Schlesiger
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15:45	**INSTRUMENTAL DEVELOPMENTS** Session 2 Chair: Jens Kessler
15:45 - 16:05	Philipp Hönicke
16:05 - 16:25	Sven Hampel
16:25 - 16:45	Pawel Jagodziński
16:45 - 16:55	BREAK
16:55	**NOVEL MATERIALS** Session 1 Chair: Terrence Jach
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18:00 -19:00	**ROUND TABLE** Moderator: Bernhard Nensel

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13:30 - 14:00	**Invited - Hikari Takahara**
14:00 -14:20	Yves Kayser
14:20 - 14:40	Ottó Czömpöly
14:40 - 15:00	Eva Marguí
15:00 - 15:15	BREAK
15:15	**ENVIRONMENTAL APPLICATIONS** Session 2 Chair: Janós Osan
15:15 - 15:35	Artem Maltsev
15:35 - 15:55	Victor Chubarov
15:55 - 16:15	Siwen An
16:15 - 16:30	BREAK
16:30	**ENVIRONMENTAL APPLICATIONS** Session 3 Chair: Yves Kayser
16:30 - 17:00	**Invited - Graham N. George**
17:00 - 17:20	Davide Ciniglia
17:20 - 17:40	Diane Eichert
17:40 - 17:45	BREAK
17:45 - 19:00	**POSTER SESSION**

Wednesday June 23, 2021

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15:00	**NOVEL MATERIALS** Session 2 Chair: Peter Brouwer
15:00 - 15:30	**Invited - Claudia S. Schnohr**
15:30 - 15:50	Claudia Zech
15:50 - 16:10	Diego Osmar Galeano Espinosa
16:10 - 16:30	Kloudene A. Salazar
16:30 - 16:45	BREAK
16:45	**INSTRUMENTAL DEVELOPMENTS** Session 3 Chair: Wolfgang Malzer
16:45 - 17:15	**Invited - Christopher Heirwegh**
17:15 - 17:35	Antoine Trosseau
17:35 - 17:45	BREAK
17:45 - 19:00	**OPEN DISCUSSION in XRS** Moderators: **Michael Kolbe, Burkhard Beckhoff & Diane Eichert**

Thursday June 24, 2021

13:30	**FUNDAMENTAL PARAMETER** Chairs: Marie-Christine Lépy & Burkhard Beckhoff
13:30 - 13:35	Opening Remarks
13:35 - 14:00	Victor H. Elvira
14:00 - 14:30	Matias Rodrigues
14:30 - 15:00	Burkhard Beckhoff
15:00 - 15:30	Csilla I. Szabo-Foster
15:30 - 15:40	**#EXSA 2021 Concluding Remarks & Awards**
15:40 - 15:50	BREAK
15:50 - 17:50	**Meeting of the FUNDAMENTAL PARAMETER INITIATIVE** **Chairs:** **Burkhard Beckhoff** **Marie-Christine Lépy** **José Paolo Santos**

GENERAL INFORMATION

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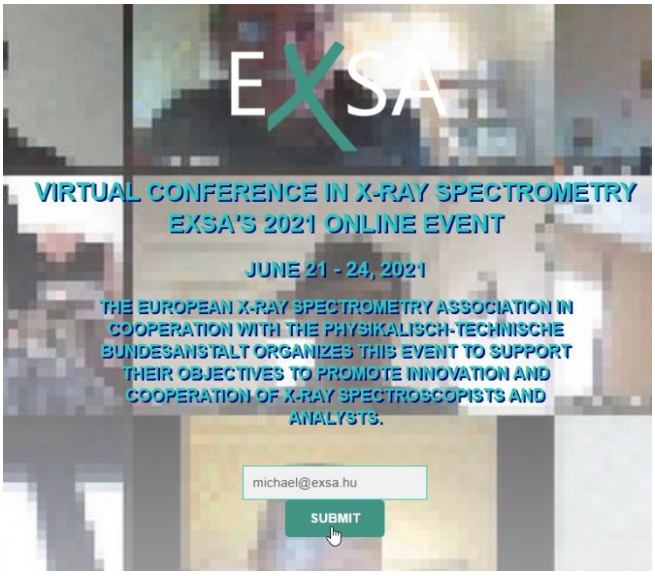
Dear #EXSA2021 participant,

We are happy to count you amongst us for our **1st virtual conference on X-ray spectrometry**. The conference will take place on the Webex system, which was set up in cooperation with PTB. The presentations for the oral contributions will be conducted simply by sharing your screen, as we are all used to do these days!

The heart of #EXSA2021 is, however, our website www.exsa.hu/conf2021, which is the starting point to access the various sessions of the conference. From now on, you should be able to log in by pressing the login button and then entering the email address you are registered with.

VIRTUAL CONFERENCE IN X-RAY SPECTROMETRY
EXSA'S 2021 ONLINE EVENT
JUNE 21 - 24, 2021

THE EUROPEAN X-RAY SPECTROMETRY ASSOCIATION IN COOPERATION WITH THE PHYSIKALISCH-TECHNISCHE BUNDESANSTALT ORGANIZES THIS EVENT TO SUPPORT THEIR OBJECTIVES TO PROMOTE INNOVATION AND COOPERATION OF X-RAY SPECTROSCOPISTS AND ANALYSTS.



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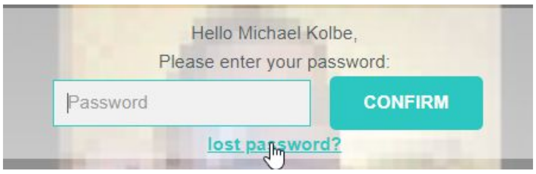
michael@exsa.hu

If the email address is valid for the conference you will be asked to enter your password. If you do not remember it, you can click on lost password? and a new one will be set and send to you.



Hello Michael Kolbe,
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Clicking on “To the sessions” will bring you to the event schedule, where you will find the shortcuts to the different sessions. These links will only work when logged in. Clicking on the sessions will open the session and clicking on the title of the talk will open the corresponding abstract. Moving the mouse over the given times should show them to you in your timezone.

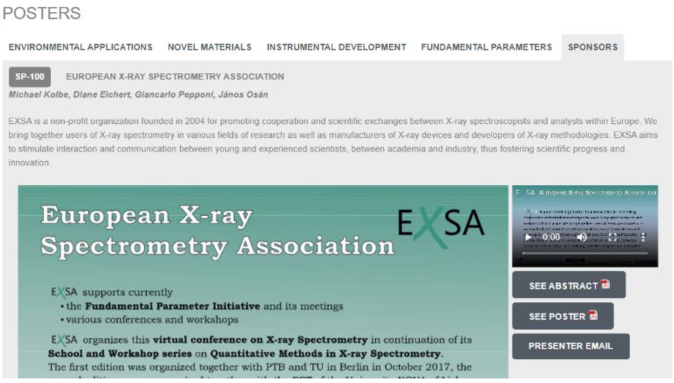
Before we start with the first session, we would like to welcome you in the EXSA2021 lounge, at www.exsa.hu/?VC21=g2g or https://www.exsa.hu/?VC21=lounge This lounge is based on wonder.me and is designed for use on desktop and laptop computers. The EXSA2021 lounge does not currently function on tablets or mobile devices. This application excludes iPads, iPhones, or other similar devices. The lounge is optimized exclusively for Google Chrome and Microsoft Edge.

This lounge is self-explaining, and we hope you will join us and your colleagues for some small talks. The lounge will be open during the entire event and you are welcome to make an appointment with other participants or our sponsors to meet there during the breaks, and before and/or after the sessions.

When the session starts we kindly ask you to change to www.exsa.hu/?VC21=welcome

This link will open a Webex website which will guide you to our scientific sessions.

The posters presented at #EXSA2021 are set on display during the entire event and you can visit our poster exhibition already from now on at:



EUROPEAN X-RAY SPECTROMETRY ASSOCIATION

Michael Kolbe, Diane Eichert, Giancarlo Pepponi, János Osán

EXSA is a non-profit organization founded in 2004 for promoting cooperation and scientific exchanges between X-ray spectroscopists and analysts within Europe. We bring together users of X-ray spectrometry in various fields of research as well as manufacturers of X-ray devices and developers of X-ray methodologies. EXSA aims to stimulate interaction and communication between young and experienced scientists, between academia and industry, thus fostering scientific progress and innovation.

European X-ray Spectrometry Association

EXSA supports currently
- the **Fundamental Parameter Initiative** and its meetings
- various conferences and workshops

EXSA organizes this **virtual conference on X-ray Spectrometry** in continuation of its **School and Workshop series** on **Quantitative Methods in X-ray Spectrometry**. The first edition was organized together with PTB and TU in Berlin in October 2017, the

https://www.exsa.hu/?VC21=poster

Clicking on the poster title will open the abstract and the poster will be loaded. We put only a preview of the pdf files on the website to avoid long loading times. Hence you will need to wait some seconds for the poster to appear.

If the presenter agreed to share his/her email address with the participants, you will find a button with it to contact him/her directly.

During the dedicated poster sessions (Tuesday after the talks and Wednesday before the talks) there will be sub-sessions of the main Webex session for each poster, where the presenter will be available for a scientific exchange.

Please be aware that some of our colleagues from outside Europe will be available at one of those sessions only. You can take an appointment with them via email and meet in the designated poster sub-session or even in our lounge.

If you have problems to reach the conference website, a duplicate can be found at https://exsa2021.r-hal.de

It works with the same credentials.

If we face issues with our Webex system, we have backup system available and we will inform about that via email and on the #EXSA2021 website. Please make sure that you can receive emails from conf2021@exsa.hu

Please be aware that we have no huge technical help desk available otherwise we would have had to increase the registration fee by a factor of ten. We count on your willingness and patience to support us having a successful event.

Furthermore, we ask you to refrain from taking any photos or screenshots, and to adopt respectful online behaviour.

We wish you all a very fruitful event!

Michael Kolbe and Diane Eichert, #EXSA2021 chairs

#EXSA2021 Program Committee

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Diane Eichert	ELETTRA – Sincrotrone Trieste, Italy
Michael Kolbe	PTB Berlin, Germany

#EXSA2021 Contact :

conf2021@exsa.hu

WILEY X-RAY SPECTROMETRY

Conference proceedings of #EXSA2021 1st Virtual Conference on X-ray Spectrometry

DEADLINE: OCTOBER 1st, 2021

EXSA established in 2017 a series of biennial workshops, first focused on quantitative aspects in X-Ray Spectrometry. These events support EXSA's primary objective to foster the innovation and cooperation between X-ray spectroscopists and analysts and to have a platform for scientific exchanges. This workshop series is well received by EXSA members and by the XRS community. With the COVID-19 pandemic persisting, many conferences worldwide are cancelled. To maintain the interactions between scientists working in the field of XRS, EXSA decided to organise a virtual conference, June 21st – 24th, 2021, which will cover applications relevant to the following topics:

- XRS for environmental applications
- XRS for novel materials including batteries, nanostructures, etc.
- Instrumental development for XRS and its applications
- Fundamental parameters

EXSA/XRS is calling for **submissions of original works** that describe the application of XRS in the environmental field as well as for novel materials, (e.g., batteries, solar cells, nanostructures). Other complementary aspects relate to instrumental developments for XRS and their applications and fundamental parameters.

WILEY X-RAY SPECTROMETRY

Peer-reviewed contributions will be published in a special issue of X-Ray Spectrometry (Wiley Analytical Science).

Registered authors of accepted contributions are invited to submit one manuscript for publication. Please note that no more than one manuscript per participant will be considered.
Manuscripts should be prepared in the strict format of X-Ray Spectrometry. No maximum number of pages has been specified.

Manuscripts should be submitted between June 10th and **October 1st, 2021** following the instructions below.

Instructions for manuscript submission to X-Ray Spectrometry

- Connect to the Manuscript Central of X-Ray Spectrometry here: mc.manuscriptcentral.com/xrs.
- Log in using your XRS credentials or create a new account and select the ✎Author tab.
- At the Author's dashboard, start a New Submission and follow the online procedure which will guide you through.
- The procedure requires the introduction of different types of data from authors' names and affiliations, to title and abstract, to the upload of files for the manuscript, tables, and figures. You can interrupt the procedure and complete it in a successive session. Please, remember to save the last input data.
- To specify that the manuscript is a candidate for the EXSA2021 special issue, you need in the lower part of Step 1 to choose our conference proceedings where you select the special issue.
- In Step 5, you can select an editor and should write there "Guest editor".

For more information, do not hesitate to contact the guest editors.

Submission deadline: **October 1st, 2021**
Guest editors:
Michael Kolbe (michael.kolbe@ptb.de), Diane Eichert (diane.eichert@elettra.eu)

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#EXSA2021

1st Virtual Conference on X-ray Spectrometry

PROGRAM

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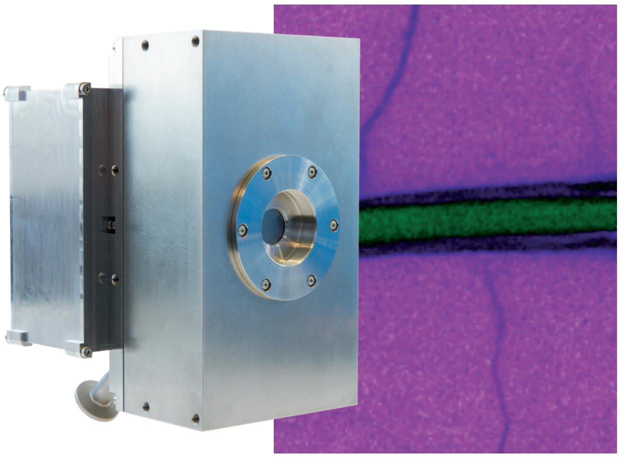

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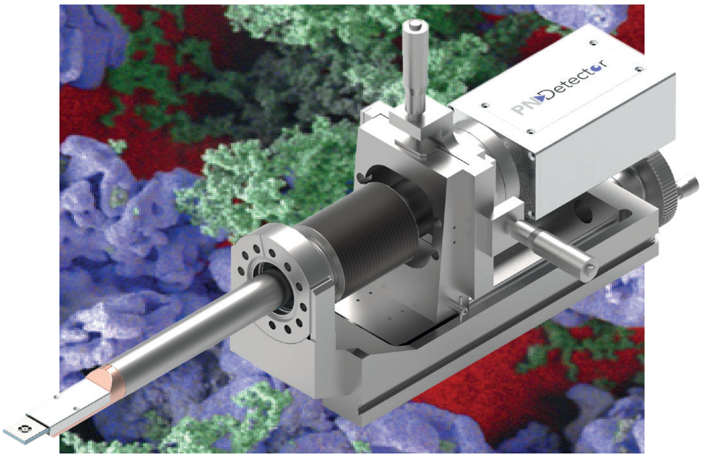

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Monday
June 21, 2021

12:30 - 13:30	Get Together!
13:30 - 13:45	Welcome & Introduction
	#EXSA 2021 Chairs Michael Kolbe & Diane Eichert
13:45	**INSTRUMENTAL DEVELOPMENTS** Session 1 Chair: Michael Kolbe
13:45 - 14:15	**Invited - René Bes**
	Rising of X-Ray Absorption Spectroscopy at the Laboratory Scale: Towards New Research Opportunities
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	Laboratory (E) XAFS with HAPG Von Hámos based Spectrometers
14:35 - 14:55	Sebastian Praetz
	Current Application Fields of laboratory XAFS at the Technische Universtät Berlin
14:55 - 15:15	Adrian Jonas
	Laboratory Optical Pump Soft X-ray probe NEXAFS Spectroscopy for Thin Film Analysis
15:15 - 15:35	Yousuf Hemani
	Comprehensive Signal Collection for Dynamic XAFS in the Home Lab
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15:45	**INSTRUMENTAL DEVELOPMENTS** Session 2 Chair: Jens Kessler
15:45 - 16:05	Philipp Hönicke
	Characterisation of the Geometrical Parameters of Commercial Bruker Instruments for Quantitative in-lab Grazing Incidence X-ray Fluorescence Analysis
16:05 - 16:25	Sven Hampel
	Illustrating Sensitivity Gradients within the Detector Field of View in TXRF using picoliter Droplet Residues
16:25 - 16:45	Pawel Jagodziński
	Properties of Polycapillary Optics dedicated to Low-energy Parallel-beam Wavelength-dispersive Spectrometer for Synchrotron-based X-ray Fluorescence Study
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16:55 - 17:15	Marko Petric
	Electronic Structure of Sulfur Atoms in Li-S Systems studied by Laboratory-based X-ray Emission Spectroscopy
17:15 - 17:35	Anna Andrle
	Machine Learning based Element Sensitive Reconstruction of Periodic Nanostructures from Grazing Incidence X-ray Fluorescence Measurements
17:35 - 17:55	Dieter Ingerle
	Nondestructive Characterization of Light Elements in Nanomaterials with GIXRF in the Laboratory
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18:00 -19:00	**ROUND TABLE** Moderator: Bernhard Nensel
	Towards Market-ready Products: Transferring Techniques from Large Experimental Facilities into Innovation Labs

Rising of X-ray absorption spectroscopy at laboratory scale: towards new research opportunities.

René Bes [1,2]

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(2) Helsinki Institute of Physics, Department of Physics, University of Helsinki, P.O. Box 43, FI-00014 University of Helsinki, Finland

X-ray absorption spectroscopy (XAS) is a non-destructive method allowing the direct characterization of the electronic structure (degrees of oxidation) and the local environment (coordination geometry) of a given element in any kind of materials. Two major strengths of this technique are that no special sample preparation is usually required, and that it is a bulk sensitive method due to the long-range penetration of X-rays in matter. Its sensitivity to local order means that this experimental approach is useful not only for crystalline materials but also for liquids, gases, and amorphous matter, covering the entire spectra of local environments in almost all materials. However, XAS experiments require a monochromatic high flux photon beam that is tunable over a wide range of energy and consequently their development has largely been restricted to synchrotron radiation facilities. Research opportunities are hence strongly limited by the finite access to, and uncertainty in, synchrotron beamtime access, as well as the high costs of invoiced guaranteed beamtime, excluding a large number of potentially important research to be performed because of the lack of alternatives. Therefore, despite its strength for research, making XAS a very efficient and complementary approach in laboratory characterization, such technique has not spread in laboratory routine experiments as much as for example X-ray diffraction.

Thanks to the recent development of more efficient X-ray optics and detectors, alternatives at the laboratory scale are now possible. Based on laboratory-scale sources and crystal optics with typical Von Hamos, Johansson, or Johann geometries, laboratory-scale XAS devices can now produce data with synchrotron radiation quality. Those recent innovation of instrumentation for laboratory based X-ray absorption and emission spectroscopy, has led to rapid revival and growth of a user community beyond synchrotron or free electron laser beamlines. Such laboratory based instrumentation serves a purpose complementary to large scale facility spectroscopy beamlines, enabling application of these techniques to a diversity of research problems which do not require the ultimate brightness, coherence, time structure or imaging capability of a synchrotron or FEL light source. In addition, recent XAS pioneering studies show that one can easily study materials that are not easy to bring to the synchrotron like highly radioactive materials, or perform studies that requires several weeks of continuous measurements, which is unlikely granted at synchrotron facilities.

In my presentation, I will discuss the latest development on laboratory scale XAS setup, covering their commercial availability and the rise of new type of small-scale facilities serving researcher from both academia and industry, and illustrating the benefits they could procure through several research examples.

Laboratory (E)XAFS with HAPG von Hámos based spectrometers

Christopher Schlesiger*, Sebastian Praetz*, Richard Gnewkow*, Wolfgang Malzer*, Jannis Zimbalski*, Birgit Kanngießer*
*Technische Universität Berlin, Institute of Optics and Atomic Physics, Hardenbergstr. 36, 10623 Berlin, Germany
christopher.schlesiger@tu-berlin.de

While the origins of X-ray absorption fine structure spectroscopy (XAFS) go back to the 70s, the nowadays broad range of its application in chemical research developed with the advent and expansion of 2nd and 3rd generation synchrotron radiation facilities. These facilities offer versatile experimental stations, which usually facilitate challenging XAFS studies.

In recent years, one witnessed promising developments of laboratory XAFS. Our own development [1,2], is based on the use of a special, very efficient type of crystal which is used as dispersive element. This graphite mosaic crystal, called Highly Annealed Pyrolytic Graphite (HAPG), is developed by Optigraph GmbH. Its first use in X-ray spectrometers was demonstrated by Legall et al. [3] in 2009. By now, the spectral resolving power can be as high as $E/\Delta E \approx 4000$ in first order of reflection, good enough to resolve major features in the X-ray absorption near Edge Structure (XANES). This has already been shown e.g., in catalysis research [4-10]. Due to its high efficiency, the spectrometer can also take extended X-ray absorption fine structure (EXAFS) spectra within reasonable time, which gives the exciting possibility to determine bonding distances and coordination numbers with laboratory equipment.

While far from being as versatile as synchrotron XAFS, the intriguing perspective that comes with laboratory XANES and EXAFS is the easy access to instrumentation, that one operates in its own laboratory.

Within this contribution we will present an overview of successfully finished, ongoing and future collaboration projects, especially the development of optimized spectrometers for various fields of applications, e.g. (E)XAFS in catalysis research. The emphasis will be on the current possibilities and restrictions. A discussion of future developments to address the latter ones will complete the contribution.

References:

[1] C. Schlesiger et al., J. Anal. At. Spectrom., 2015, 30, 1080-1085.
[2] C. Schlesiger et al., J. Anal. At. Spectrom., 2020, 35, 2298-2304
[3] H. Legall et al., J. Appl. Cryst., 2009, 42, 572-579
[4] M. Dimitrakopoulou et al., Faraday Discuss., 2018. 208, 207-225
[5] H. V. Le et al., ACS Catal., 2017, 7, 2, 1403-1412
[6] X. Zhao et al., J. Am. Chem. Soc., 2019, 141, 16, 6623-6630
[7] P. W. Menezes et al., Angew. Chem. Int. Ed. 2019, 58, 16569
[8] R. L. Oliveira et al., ACS Sustainable Chem. Eng., 2020, 8, 30, 11171-11182
[9] M. F. Bekheet et al., ACS Catal., 2021, 11, 1, 43-59
[10] J. Wang et al., Mater. Adv., 2021, 2, 1715-1730

Current application fields of laboratory-XAFS at the Technische Universität Berlin

Sebastian Praetz*, Christopher Schlesiger*, Wolfgang Malzer*, Birgit Kanngießer*

*Technische Universität Berlin, Institute of Optics and Atomic Physics, Hardenbergstr. 36, 10623 Berlin, Germany

High resolution X-ray absorption fine structure spectroscopy (XAFS) is a frequently used method for chemical speciation, such as the oxidation state or coordination of functionalized materials or biomolecules. This technique is usually performed at synchrotron radiation sources because of the need of a brilliant X-ray source and a high spectral resolving power. A laboratory setup has the advantage of higher accessibility and flexibility, which would open this technique for routine analysis e.g. in catalysis and environmental research or industrial applications.

We have successfully developed an X-ray tube based von Hámos spectrometer using a novel type of HAPG mosaic crystal with which it is possible to perform X-ray absorption spectroscopy in a laboratory setup without the need of a high brilliant synchrotron radiation source and with a wide energy range of 4 keV to 15 keV [1,2]. Even with the limited spectral resolving power up to $E/\Delta E=4000$ in the first order of reflection, the method is more attractive for everyday analysis for material, chemical and biomedical science such as the determination of the composition of amorphous materials, like minerals and catalysts, or liquids like contrast agents for medical use.

In this contribution current and past application examples of laboratory-XAFS will be presented. The applications vary from determination of oxidation states in the field of catalysis research [3,4,5] over the determination of chromium species in filter materials for wastewater treatment to the quantitative chemical speciation in minerals via linear combination of references spectra. Furthermore possible future applications will be discussed. The emphasis will be on the specific scientific question, circumstances and approaches with the laboratory spectrometer and evaluation schemes.

References:

[1] C. Schlesiger et al., J. Anal. At. Spectrom. (30), 2015, 1080-1085.
[2] C. Schlesiger et al., J. Anal. At. Spectrom. (35), 2020, 2298-2304.
[3] M. Dimitrakopoulou et al., Faraday Discuss., 2017
[4] X. Zhao et al., J. Am. Chem. Soc. 141, 2019, 6623–6630
[5] P. W. Menezes et al., Angew. Chem. Int. Ed. 2019, 58, 1656

Laboratory optical pump soft X-ray probe NEXAFS spectroscopy for thin film analysis

Adrian Jonas(1), Richard Gnewkow(2), Birgit Kanngießer(1), Holger Stiel(3), and Ioanna Mantouvalou(1,2)

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(3) Max-Born-Institute, Max-Born-Straße 2 A, 12489 Berlin, Germany

Near edge X-ray absorption fine structure (NEXAFS) in the soft X-ray region as a means for the elucidation of the dynamics of electronic properties is still widely performed at large scale facilities. The ongoing development of brilliant laboratory soft X-ray sources enables an increasing number of transient NEXAFS experiments using laser-based sources. These studies are widely focused on the investigation of ultrafast processes in the gas or liquid phase. But many scientific questions deal with dynamics in the solid phase. Especially the field of organic electronics or photovoltaics can profit from new experimental possibilities for the investigation of thin organic films.

We present a laboratory soft X-ray NEXAFS spectrometer which is optimized for transient investigation of thin organic films with a time resolution of 0.5 ns. It is based on a laser-produced plasma source [1] and a twin arm spectrometer using reflection zone plates [2]. It operates in the soft X-ray regime up to about 1300 eV with a resolving power of $E/\Delta E > 900$, where not only the main constituents of organic molecules can be probed, but also the L edges of 3d transition metals, which often play a central role in the properties of such molecules. We demonstrate the possibility for optical pump soft X-ray probe spectroscopy of thin organic films [3] and discuss optimized sample preparation.

[1] I. Mantouvalou et al., Rev. Sci. Instrum., 2015, 86, 35116.

[2] A. Jonas et al., Optics Express, 2019, 27:25, 36525.

[3] A. Jonas et al., Anal. Chem. 2020, 92:23, 15611–15615.

Compressive signal collection for dynamic XAFS in the home lab

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X-ray Absorption Spectroscopy (XAFS) is a widely used powerful technique for obtaining elemental and chemical information in many fields such as biosciences, material sciences, catalysis and physical chemistry. XAFS utilizes a large bandwidth radiation that is tuned sequentially to capture the entire spectrum where the resolution is dependent on the monochromator bandwidth. The entire scanning of certain samples can take relatively long times and high brightness is essential for enough sensitivity. Additionally, time resolved XAFS need complex optical setups and fast signal processing techniques to resulting in a data deluge. Few of such synchrotron sources exist worldwide, with limited access due to large amount of proposals.

Ideally, one would like to have a single shot acquisition of the entire spectrum, where the entire scanning should be faster than the chemical reaction being studied. Furthermore, the source show operate at low damage intensity, without sacrificing information and the required resolution should be close to few meV. Advantageously, this method should be available in each laboratory.

Aim of this study was to develop a method, which can match as much as possible such requirements. The method mentioned relies on efficient data processing, where it is possible to compensate for the reduced complexity of the instrumentation used, with more advanced data treatment. Compressed Sensing (CS) is a well-known procedure in signal processing used to acquire and reconstruct under-sampled data sets without losing any important information about the signal. Taking advantage of the sparsity of spectral signal, the data acquisition can be dynamic, where in one case the sampling rate is varied or in the second case the acquisition time. Aided by signal processing techniques, faster and reliable data acquisition is possible with competent results.

This research shows as a proof of concept, the advantages and limitations of the compressed sensing technique and puts forward an experimental setup to acquire, in real time, XAFS signals using a laboratory X-ray source and the compressed sensing algorithm. The results from different samples show that the percentage of the acquired data directly corresponds to the accuracy of reconstruction of XAFS signal, more sampling results in more accurate reconstruction. Additionally, even with as less as 25 % of sampling , the error for reconstruction of the XAFS spectrum for different samples is less than or equal to 1% which shows with acquiring only a few amount of components, XAFS data can be accurately reconstructed for analysis.

Characterization of the geometrical parameters of commercial Bruker instruments for quantitative in-lab grazing incidence X-ray fluorescence analysis

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Grazing incidence X-ray fluorescence analysis is a very powerful technique for the in-depth analysis of many types of technologically relevant samples, e.g. nanoparticle depositions, shallow dopant profiles or thin layered samples. However, the extraction of the desired depth dependent information is usually based on a modelling of the experimental data. This requires a profound knowledge on the geometrical parameters of the employed setup, especially the incident beam as well as the detector aperture parameters. Together, they determine the incident angle dependent so-called effective solid angle of detection which must be known in order to reliably model any experimental dataset.

In this work, we demonstrate how theses instrumental parameters determining the effective solid angle of detection can be characterized using well-known calibration samples. The calibration samples are characterized beforehand using PTB's reference-free GIXRF technique [1] so their angular fluorescence emission can be absolutely predicted for the experimental conditions the respective in-lab tool is offering. By comparing this with the in-lab experimental data, key parameters of the instrument can be determined and the tool thus be used to perform quantitative GIXRF depth profiling without the need for any further calibration.

We will show how this approach is performing by applying it on two different in-lab tools, namely a benchtop TXRF instrument [2] as well as a full wafer in-fab TXRF tool.

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Illustrating sensitivity gradients within the detector field of view in TXRF using picoliter droplet residues

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A thin film-thin deposit sample preparation is crucial to ensure an elemental analysis free of matrix effect in TXRF. The drying of large microliter volumes often produces “coffee rings” [1]. A disadvantage of the ring like deposit is the large part of material positioned in an offset to the optimal position under the detector. This can result in higher limits of detection and if the elemental distribution is inhomogeneous may also result in a determination bias. An alternative preparation with smaller volumes *e.g.* picoliter droplets, which usually yield homogenous specimens, is achieved by “drop on demand” printing. The good reproducibility of elemental composition and spatial dimensions of the droplets derived deposits allows to use those for calibration [2]. It allows the study of physical interactions of X rays with the sample [3,4]. Picoliter residues can serve as reference to study various aspects of instrumental performance in TXRF and other techniques *e.g.* determination of detector signal in dependence of specimens position. This has been studied so far using microliter volumes on a glass surface. The residues were probed with a TXRF table top device equipped with a 7 mm² active area SDD [5].

We previously introduced a picoliter printing device, which is capable of pattern printing with defined elemental concentrations as a function of quiet times (time between two printed droplets) [6,7]. Within a defined composition matrix the reliably delivered volumes corresponds to 130 – 140 pL. The delivered masses then only depend on the elemental concentration inside the nozzle, which is determined by initial formulation and quiet time [8].

In this work these well-defined residues are used to illustrate the sensitivity gradient within the detector field of view of a table top TXRF instrument (S4 T-Star, 60 mm² SDD area, Bruker Nano, Berlin, Germany). A deposit with defined offsets to the middle was printed on a carrier. With each offset, an individually carrier was prepared. First, a large field of view was studied using 37 samples with an offset of up to 5 mm in x- and y-direction. Second, a finer resolution for offsets up to 1.6 mm was used (81 samples). Using a four element formulation, local differences of the relative sensitivities were made visible.

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Properties of polycapillary optics dedicated to low-energy parallel-beam wavelength-dispersive spectrometer for synchrotron-based X-ray fluorescence study

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The polycapillary X-ray optics is widely used technology in the X-ray fluorescence applications, for guiding X-ray beams. The development of the polycapillary optics is an active direction for X-ray research due to its wide potential applications in many fields, such as high-quality X-ray diffraction [1], chemical mapping [2], a variety of clinical applications [3], or fluorescence techniques and X-ray focusing optics for synchrotron radiation. The X-ray polycapillaries can work in different geometries. They can be used to collect the radiation emitted from a small source into a large solid angle, to collimate the divergent photons to the quasi-parallel X-ray beam, or to focus the nearly parallel X-rays beam into small spot. In the context of elemental analysis, for example surface mapping or depth profiling, a significant improvement of the X-ray fluorescence study sensitivity can be achieved by applying polycapillary optics in the grazing emission X-ray fluorescence (GEXRF) [4], or total reflection X-rays fluorescence (TXRF) methods [5]. Moreover, the combination of the polycapillary and diffraction spectrometer features allow to obtain both high spatial and energy resolution of the measurement.

A straightforward procedure to determine the characteristics of a polycapillary optics as well as the optical properties of crystal spectrometer is a X-ray-tracing simulation approach. In presented studies, the Monte – Carlo simulations of X-ray tracing in parallel-beam wavelength-dispersive spectrometer (PBWDS), equipped with polycapillary optics are discussed. The study concentrate on the polycapillary model description, simulations of X-ray polycapillary optics properties and on the simulations of X-ray track in the PBWDS spectrometer. By using geometrical parameters of the polycapillary, its characteristics such as transmission, exit divergence, spatial distribution of X-rays behind the polycapillary, were determined and used for optimization of the PBWDS spectrometer energy resolution. The results of simulations were compared with experimental data obtained for different spectrometer crystals and energies of fluorescence X-ray. The developed simulation code can be successfully used for the construction of X-ray spectrometers with different geometries.

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Electronic Structure of Sulfur Atoms in Li-S Systems Studied by Laboratory-Based X-ray Emission Spectroscopy

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The 2019 Nobel Prize in Chemistry was awarded to John Goodenough, M. Stanley Whittingham and Akira Yoshino for the development of lithium-ion batteries. They initiated rechargeable world, but the need for high gravimetric energy density required for the goals of transportation still makes the batteries very interesting research area. Lithium-sulfur (Li-S) batteries are one of the most promising candidates for next generation of batteries in applications where high energy density is required. In general, the electrochemical reaction in the Li-S batteries is known, the elemental sulfur (α-S8) is reduced to lithium sulfide (Li2S). In reality, the process goes through a series of stepwise redox reaction forming various long-chain lithium polysulfides, which are soluble in the electrolyte and affect the overall battery performance. In order to understand complex electrochemical reactions during battery charge/discharge process, numerous analytical techniques have been used [1].

In the present work, the laboratory-based x-ray emission spectroscopy (XES) is used to perform chemical speciation of the sulfur atom in Li-S standards, pre-cycled battery cathodes, and also in the Li-S battery during cycling (operando conditions). The high-resolution Kα (Core-to-Core) and Kβ (Valence-to-Core) x-ray emission spectra of sulfur were recorded by in-vacuum crystal spectrometer [2] combined with the particle induced x-ray emission (PIXE). Energy shifts of the Kα line were correlated with the calculated effective charge of sulfur atoms and used to track the reduction of the elemental sulfur to lithium sulfide [3]. The measured Kβ spectra of lithium polysulfides Li2Sx (x = 2,…,8), which appear in the Li-S systems, were interpreted using ab-initio quantum chemical calculations based on density functional theory (DFT), employing the StoBe-deMon and cp2k software packages [4]. The results presented here have the potential to bring the characterization of the sulfur based systems from synchrotrons down to smaller laboratories.

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Keywords: Li-S battery, laboratory-based XES, DFT calculations

Machine Learning based element sensitive reconstruction of periodic nanostructures from Grazing incidence X-ray fluorescence measurements

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Reliable and non-destructive characterization of the material composition and dimensional parameters of nanostructures is required for the fabrication of current and next generation semiconductor devices. A measurement technique based on grazing incidence X-ray fluorescence measurements is applied here to lamellar nanoscale gratings of various materials. The X-ray standing wave field, which is created by the interference between the incident and reflected radiation, is used as a nanoscale sensor in this technique. Depending on the elemental composition and dimensional parameters of the nanostructures, different angle-dependent fluorescence signals are observed when the sample is rotated with respect to the incident radiation. The X-ray standing wave field can be calculated using a finite element Maxwell solver to model the experimental data using a parameterized model of the nanostructure. This modeling allows the derivation of the spatial distribution of the elements and the cross-section shape with sub-nanometer resolution. The computational cost of such a reconstruction can be very large depending on the dimensional parameters of the nanostructure. Using a Bayesian optimization approach, this effort can be kept at a reasonable level.

Nondestructive characterization of light elements in nanomaterials with GIXRF in the laboratory

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Grazing Incidence XRF (GIXRF) is a technique related to Total Reflection X-Ray Fluorescence Analysis (TXRF), which takes advantage of the phenomenon of total external reflection of X-rays on smooth polished surfaces. As the penetration depth of the incident X-ray beam in the total-reflection regime is in the order of a few nanometers, the technique provides nondestructive information on the composition of materials in the nanometer range with excellent sensitivities and detection limits for many elements.

Furthermore, by changing the incident angle of the monochromatic low-divergence exciting beam from zero up to several times the critical angle, the penetration depth and the beam interferences can be varied. The angle-dependent measurement data obtained in this way contain information on composition, density and thickness of layers, as well as depth distributions of implanted atoms or the size and composition of nanoparticles.

For a wide range of materials, the acquisition of data is straightforward, but light elements (below Magnesium), typically pose significant challenges for a GIXRF setup in the laboratory. Some reasons for this are the small X-ray fluorescence cross section and the high absorption of the produced X-ray photons even in air or Beryllium, which is commonly used for detector entrance windows. Thus, by using a specialized setup, which places the sample in vacuum, has an X-ray tube with Chromium anode, and a Silicon drift detector (SDD) with ultra-thin window (UTW), data for light elements down to Carbon can be obtained.

An overview of results for different types of samples, which were obtained by the use of laboratory-based equipment at the Atominstitut of the TU Wien, as well as a discussion of the specific requirements and challenges will be presented.

ROUND TABLE

Towards Market-ready Products: Transferring Techniques from Large Experimental Facilities into Innovation Labs

Moderator: Bernhard Nensel

CrossRoads Scientific, Germany

Panelists:

- Ioanna Mantouvalou *BLIX Technical University Berlin and HZB, Germany*
- Andreas Pahlke *KETEK GmbH, Germany*
- Gerald Seidler *University of Washington, USA*
- Bruno Vrebos *Malvern Panalytical, The Netherlands*
- Dirk Wissmann *SPECTRO Analytical Instruments GmbH & Co. KG, Germany*

Tuesday
June 22, 2021

13:30	**ENVIRONMENTAL APPLICATIONS** Session 1 Chair: Diane Eichert
13:30 - 14:00	**Invited - Hikari Takahara**
	Quantitative Analysis of Environmental Samples with a Laboratory GIXRF Spectrometer
14:00 -14:20	Yves Kayser
	Traceable and Reliable Chemical Analysis of Aerosols by Reference-free X-ray Spectrometry
14:20 - 14:40	Ottó Czömpöly
	Characterisation of Unique Aerosol Pollution Episodes in Urban Areas using X-ray Fluorescence and Absorption Methods
14:40 - 15:00	Eva Marguí
	Simplifying the Control of Inorganic Pollutants in Water: the Combined Use of Smart Materials and XRF Detection
15:00 - 15:15	BREAK
15:15	**ENVIRONMENTAL APPLICATIONS** Session 2 Chair: Janós Osan
15:15 - 15:35	Artem S. Maltsev
	Study of Matrix Effects in the Analysis of Alcoholic and Non-alcoholic Beverages by Total Reflection X-ray Fluorescence
15:35 - 15:55	Victor Chubarov
	WDXRF and TXRF Analysis of Continental and Lacustrine Ferromanganese Nodules
15:55 - 16:15	Siwen An
	Geometry Optimization for a portable XRF Analyzer of Hg Contamination in Wet Sediments using an Isotope Source
16:15 - 16:30	BREAK
16:30	**ENVIRONMENTAL APPLICATIONS** Session 3 Chair: Yves Kayser
16:30 - 17:00	**Invited - Graham N. George**
	Environmental Toxicity of Mercury: Insights from X-rays
17:00 - 17:20	Davide Ciniglia
	Characterization of Aerosols Dispersion and Depositions generated for Calibrating a Laser-induced Breakdown Spectroscopy Prototype by means of Total Reflection X-ray Fluorescence
17:20 - 17:40	Diane Eichert
	Do Anthropogenic Activities Threaten the Naica's Giant Crystals?
17:40 - 17:45	BREAK
17:45 - 19:00	**POSTER SESSION**

Quantitative analysis of environmental samples with a laboratory GIXRF spectrometer

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GIXRF (TXRF) method has been expected for environmental analysis because of its high sensitivity and simple sample preparation. For environmental waters such as waste waters and river waters, the dried residues of samples deposited on the reflectors are measured. Aerosol particles, collected on filters with impactors, are measured together with filters. Quantitative analyses of such solid samples involve possibilities of errors owing to matrix absorption, sample shape, particle size, inhomogeneity, and so on. Especially, X-ray intensities significantly vary with sample thickness in grazing incidence. To suppress error in quantification results, optimizing glancing angle in measurement condition and correcting the effect in data processes will be required.

The effects of sample thickness and particle size can be investigated by angular-resolved XRF. A few laboratory TXRF spectrometers are commercially available for it, and NANOHUNTER II (Rigaku) is one of them. The spectrometer has a unique optics composed of a curved multilayer mirror and a variable slit to functionalize angular-resolving simply. Monochromatized X-ray beam is focused on a fixed position on a sample surface, and the slit between the mirror and the sample has a linear opening to restrict a width of passing X-ray beam. Moving upper and lower blades of the slit individually, the glancing angle and convergence angle can be set in each measurement.

In this talk, the effect of sample properties to quantitativity will be discussed using angular scan by the laboratory GIXRF spectrometer. For high matrix waste waters, the fluorescence X-ray intensities showed almost constant values for glancing angle due to the thick dried residues, resulting good reproducibility in quantitative results with internal standard calibration. The underestimation in the values was considered due to matrix absorption effect. On the contrary, for low matrix samples showed thinner dried residues, the X-ray intensities increased with increasing up to around the critical angle of the glass substrate, and the angular dependence caused the variation in quantitative results.

Since any characteristic X-ray was not observed from PTFE composition of aerosol filters, the scattered radiation of primary beam was used as an index. The scattered X-ray intensities were very high due to the rough surfaces of films and independent of glancing angle. Even though the background intensities were enhanced by the rough surface, the grazing incidence measurements showed better sensitivity for metallic elements on filters compared to a commercial XRF spectrometer. GIXRF intensities were quantified using an external calibration curve of Zn and the relative sensitivities to the other elements. The quantification results agreed with XRF analysis values with FP calculation. The experimental results for collecting aerosol continuously will be shown.

Traceable and reliable chemical analysis of aerosols by reference-free X-ray spectrometry

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The physical and chemical analysis of aerosols using reliable and physically traceable methods is of importance for a thorough investigation of airborne particles in order to support a better understanding of their origin and impact on health and climate effects. Within the AEROMET II [1] project the aim of PTB's X-ray spectrometry group is to further develop and establish traceable and reliable X-ray methods to measure the elemental mass deposition per unit area, the elemental composition and the chemical binding state of particulate matter supported by a flat substrate. This approach can substantially contribute to support quantitative analytical methods during on-site measurement campaigns where portable instrumentation is employed by qualifying suitable calibration samples and by investigating a posteriori samples collected during the field campaign.

Airborne particles were sampled in a time and size-dependent partitioning using cascade impactors in which they were deposited on substrates suitable for TXRF analysis. A selection of the samples collected and monitored during the field campaigns has been reinvestigated using reference-free X-ray spectrometry. In comparison to the mobile TXRF instrumentation used on-site, a mapping of the collected samples was required due to the smaller spot size, hence smaller investigated area when using synchrotron radiation. A reference-free quantification of the total mass of the deposited material could be carried out and the results allow for a validation of the quantitative results reported from the field campaign. This is important in view of the qualification of mobile instrumentation. Indeed, an accurate quantification relies heavily on the sample loading on the top of the substrates, hence on the collection time and the pollution level. It was found that the X-ray standing wave field is drastically changed for high particulate load which makes a correct quantification tedious and requires correction factors for the absorbance within the collected deposit.

The project is supported by the EMPIR initiative of the European Union's Horizon 2020 program, through grant agreement 19ENV08 AEROMET II.

Characterization of unique aerosol pollution episodes in urban areas using X-ray fluorescence and absorption methods

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The task of identifying sources of aerosol pollution is becoming a more and more important topic, since the PM_{10} (particulate matter with an aerodynamic diameter less than 10 µm) concentration exceeds the recommended level in many urban locations. To draw conclusion on reducing the concentration of aerosol particles in the atmosphere the availability of an appropriate source profile is essential. The types of aerosol sources show a wide variety like natural/anthropogenic, point/diffuse or repetitive/occasional in time. Apportionment of sources showing a characteristic pattern in time are usually carried out using statistical methods like positive matrix factorization (PMF). PMF requires large input data sets and presumptions on the number of sources (or factors) being present. Identifying unique pollution episodes is a difficult task hence the presence of emitted particles could be only a couple of hours.

Size fractionated aerosol sample sets (51) were collected with May-type cascade impactor (70 nm – 9 µm, 7 stages) at urban locations. Sampling onto silicon wafers enables multiple non-destructive analytical methods like total-reflection X-ray fluorescence (TXRF), X-ray absorption near edge structure (XANES) or even scanning electron microscopy (SEM). Using a low-power, laboratory TXRF spectrometer 0.1 ng/m^3 detection limit could be reached for transition metals with 4 m^3 of air sampled [1]. By combination of cascade impactor sampling and TXRF analysis, the particle size dependence of concentrations was obtained for both major (S, K, Ca, Fe) and trace elements (Cu, Zn, Br, Pb). Based on elemental size distribution determined by TXRF pollution episodes were identified. Samples with elevated Cu, Br concentration were subjected to XANES measurements at the XRF beamline of Elettra (Trieste, Italy). The XANES spectra were analyzed through linear combination fitting of spectra from reference compounds. With the combination of elemental size distribution and ratio of chemical species source apportionment was carried out.

In accordance with the presumptions drawn by TXRF measurements Cu present in the samples could be successfully linked to traffic related source. The ratio of the markers of exhaust and non-exhaust type emission sources show a tendency related to the size of aerosol particles. Regarding Br the ratio of organic/inorganic species could be determined which are characteristic to two different sources.

This work was supported by the European Structural and Investment Funds jointly financed by the European Commission and the Hungarian Government under grant no. VEKOP-2.3.2-16-2016-00011 and the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme, through grant agreement 19ENV08 AEROMET II.

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Simplifying the control of inorganic pollutants in water: the combined use of smart materials and XRF detection

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In the last years, great concern has been raised about chemical pollution of water bodies. In fact, at European level, in addition to the well-known Water Framework Directive, the health of water resources has been identified as a mission area in the next research and innovation framework programme Horizon Europe. Conventional water monitoring relies upon manual or automated sampling followed by laboratory analysis using costly instrumental analytical techniques (and sometimes sophisticated sample treatments) demanding specially trained operators. Despite this approach is essential in some environmental studies, in others, where a rapid and cost-effective screening and monitoring of specific pollutants in waters is pursued, is not adequate. In such cases, the development of simpler and low-cost analytical tools but which can provide an adequate quality of the results is worth of investigation.

The analytical approach proposed in this contribution consists of combining innovative sampling tools using smart materials in combination with X-ray fluorescence spectrometry (XRF) detection. Considering that XRF gives optimal sensitivity and accuracy for thin and homogeneous solid targets, it can be used as a powerful technique to detect inorganic chemical pollutants collected from water samples using an adequate extraction material [1]. In this sense, commercial filter paper retainers and functionalized solid-phase extraction disks have been successfully used for element preconcentration in combination with XRF analysis [2-3]. However, these commercial supports are usually expensive and they allow only the determination of a specific group of elements which limits their application in some environmental studies. For this reason, it is of paramount importance the design of novel focussed-tuneable adsorbent materials (i.e. nanostructured carbonaceous materials and polymer inclusion membranes) [4-5] to expand the applications of XRF in the field of water analysis, even for inorganic speciation studies.

The potential of different commercial and laboratory smart materials in combination with laboratory and portable XRF systems have been explored in this contribution to cope with some of the current analytical challenges in the field of water analysis, including the fast and simultaneous determination of metals, environmentally relevant inorganic species and also for the in-situ control of inorganic pollutants.

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Study of matrix effects in the analysis of alcoholic and non-alcoholic beverages by total-reflection X-ray fluorescence

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Total-reflection X-ray fluorescence (TXRF) is one of the promising methods for the fast and cost-efficient analysis of liquid samples. However, the method has some issues in the quantitative analysis due to the possible matrix effects. Since alcoholic and non-alcoholic beverages contain a high percentage of carbohydrates (especially sucrose), ethanol, and other organic compounds the issues of matrix effects are significant and should be studied. Basically, absorption effects appear in the determination of elements with an atomic number Z <20 [1]. This study is devoted to the demonstration of absorption effects influenced on the accuracy of TXRF analysis of drinks. The study is based on the comparison of two sample preparation techniques: direct analysis and acid decomposition. The application of chemometric approaches helps to understand the influence of absorption effects and how to avoid them.

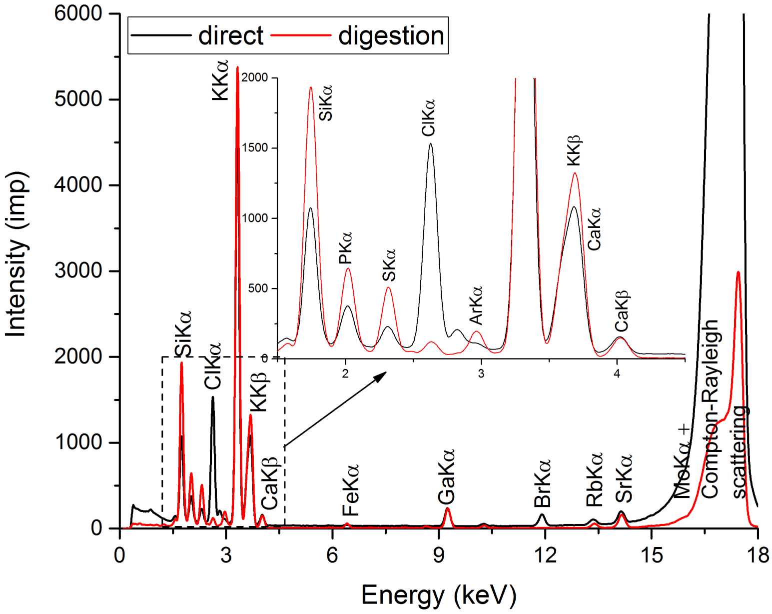

Figure 1. TXRF spectra of drink sample obtained after direct analysis and acid digestion procedure.

The reported study was funded by RFBR, project number 19-33-90192. The research was performed using the equipment of SB RAS center for Geodynamics and Geochronology.

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WDXRF and TXRF analysis of continental and lacustrine ferromanganese nodules

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In contrast to oceanic nodules and crusts, lacustrine and continental ferromanganese nodules are poorer in industrially important metals (Fe, Mn, Ni, Cu, Co), however, they are relatively widespread in various regions of the continental freshwater basins and more accessible for mining. Lacustrine and continental nodules have a specific elemental and mineral composition which is substantially different from silicate sedimentary rock and oceanic nodules and crusts. The problem of lack of the matrix-matched certified reference materials (CRMs) can be solved using methods that allow minimizing the influence of mineral composition to the accuracy of results. A fusion of powder with borate fluxes allows us to homogenize the sample, decrease matrix effects, and use CRM of rocks with various compositions for calibration for wavelength-dispersive X-ray fluorescence (WDXRF) analysis. On the other hand, the determination of minor elements using the fusion technique is significantly limited by the high dilution of glass beads by flux. The total reflection X-ray fluorescence (TXRF) method provides quantitative analysis by an internal standard method and there is no need to use the matrix-matched CRMs. However, the issues of particle size, heterogeneity, and matrix effects can lead to poor accuracy of results.

The major rock-forming (Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe), minor and some trace elements (V, Cr, Co, Ni, Cu, Zn, As, Rb, Sr, Y, Zr, Ba, and Pb) were determined in four samples of continental and lacustrine ferromanganese nodules. The applying of fusion for WDXRF allowed us to use CRM with a different composition including igneous and sedimentary rocks and oceanic ferromanganese nodules for major rock-forming elements determination. The results of the WDXRF analysis of fused beads are comparable with the results obtained by certified methods and more accurate than WDXRF of pressed pellets. WDXRF and TXRF methods can be applied for minor and several trace elements determination (Ni, Cu, Zn, Sr) with comparable accuracy. A poor TXRF results for V, Cr, Ba, As and Pb are caused by the strong peaks overlapping but can be considered as indicative. Additionally, Pb, Co, and Zr can be evaluated by WDXRF analysis of pelletized powder samples. TXRF method allows quantifying some major elements (Ti, Mn, and Fe) using an internal standard method with accuracy similar to WDXRF analysis of pressed pellets requiring a large set of CRMs. Based on the presented figures of merit the proposed combination of methods may be used as a rapid and simple analytical tool for geological and geochemical applications.

The research was performed using equipment of the SB RAS joint use centers (Geodynamics and Geochronology Center, Isotope-geochemical Research Center, Ultramicroanalysis Center) with the financial support of the Russian Foundation for the Basic Researches (project № 18-33-20104). We thank Nikolay Akulov, Svetlana Shkolnik, Liba Granina for providing samples.

Geometry optimization for a portable XRF analyzer of Hg contamination in wet sediments using an isotope source

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Large amounts of contaminated cellulose and untreated process wastewater from the pulp and paper industry was emitted directly along the Swedish coastline of the Baltic sea before environmental regulation was established (1969 in Sweden) [1]. Remnants of discharges of contaminated suspended solids (fiberbanks) are continuously being discovered on the seabed. To quickly identify polluted sites, X-ray fluorescence (XRF) offers a rapid total elemental analysis of sediments that is sufficient to be used in environmental research. Reductions in the size of detectors have made it possible to bring an XRF spectrometer into direct contact with varying samples to measure heavy metal contaminants. However, when in-situ analyses are considered, water content in the sample will interfere with the measurement [2]. The choice of source-sample-detector geometry plays an important role in minimizing the Compton backscatter in the measurement conditions [3], which will strongly affect the sensitivity in XRF analysis for wet sediments [4].

This paper presents a geometry optimized prototype for in-situ XRF mercury (Hg) measurements of wet-contaminated sediment. The measurement system consists of a ^{57}Co excitation source and a CdTe X-ray spectrometer (9 mm^2). The point isotope source emits gamma rays at 122 keV and 136 keV, efficient energies for K-shell ionization of Hg. Mercury K-shell fluorescence photons can travel a relatively long distance under water, compared to L-shell photons, and are only weakly absorbed in the plastic housing of the waterproofing shell. The influence of the geometric factors (angle and distance) and the scattered background were investigated using Monte Carlo simulations. The source-sample-detector geometry was arranged so that maximal characteristic X-ray peak counts from Hg were obtained. Moreover, this arrangement shifted the backscatter peak and the Compton continuum of the scattered photons, resulting in lower background at the Hg Kα_1 peak. A calibration method was developed for in-situ underwater sediment analysis based on geometry optimization derived from simulation results and measurements with standardized Hg concentrations. For element detection in wet-bulky samples, the detector should be set 90° to the shaped beam and as close to the specimen as possible. We submerged this prototype in a laboratory aquarium-setup to detect Hg contaminated sediment using a 3.7 MBq ^{57}Co excitation source and an energy-dispersive XRF spectrometer. The presented results show that it is possible to detect Hg by K-shell emission thus enabling XRF analysis for under water sediment.

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Environmental Toxicity of Mercury: Insights from X-rays

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The compounds of mercury can be more toxic than those of any other non-radioactive heavy element. Mercury is a natural part of the environment and human exposure, at some level, is therefore inevitable. Nonetheless, there is increasing concern about recent and substantial environmental increases due to anthropogenic mercury emissions. Because of this, mercury is listed by the World Health Organization as among the top-ten chemicals of public health concern. Despite its importance many questions remain about how mercury exerts its toxic effects and about the risks posed to human populations. X-ray spectroscopy and X-ray fluorescence imaging provide valuable in-situ tools that allow researchers to probe both chemical speciation and localization of mercury in tissues and other complex samples. The presentation will review some recent insights using these methods into the toxicology of mercury.

Characterization of aerosols dispersion and depositions generated for calibrating a laser-induced breakdown spectroscopy prototype by means of total reflection X-ray fluorescence

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Laser-induced breakdown spectroscopy (LIBS) analysis of particulate matter is possible both in the aerosol phase and collected on PTFE filters [1]. Quantitative analysis is achieved by external calibration based on measurements of standards with known concentration. In this context, the characterization of aerosols and/or solid samples is fundamental to increase the determination accuracy.

The aim of this study is to analyse the distribution of aerosol produced by a nebulizer (1178, GRIMM), using a solution of $Cu(NO_3)_2$·hydrate. The spatial distribution is determined by measuring the Cu content of plexiglass reflectors by total reflection X-ray fluorescence (TXRF) spectroscopy, after exposure to the nebulizer flow in the centre and 4 radial positions inside a chamber. The disks were exposed to the particles flux, at a fixed distance from the aerosol generator nozzle, for different times. After every time step a TXRF analysis was carried on each sample to analyse the mass concentration in the different positions and the correlation between mass deposition and time. Deposition is also evaluated analysing one sample lying at the bottom of the box for different aerosol generator fluxes. Size distribution of the aerosol was also measured with an optical particle counter (0,25- 32 μm; EDM107, GRIMM).

Results highlight a linear correlation between the exposure time and the deposited mass, with different slopes depending on the radial position (Fig 1a). The mass deposition at the bottom of the chamber decreases exponentially with the aerosol generator flow (Fig 1b).

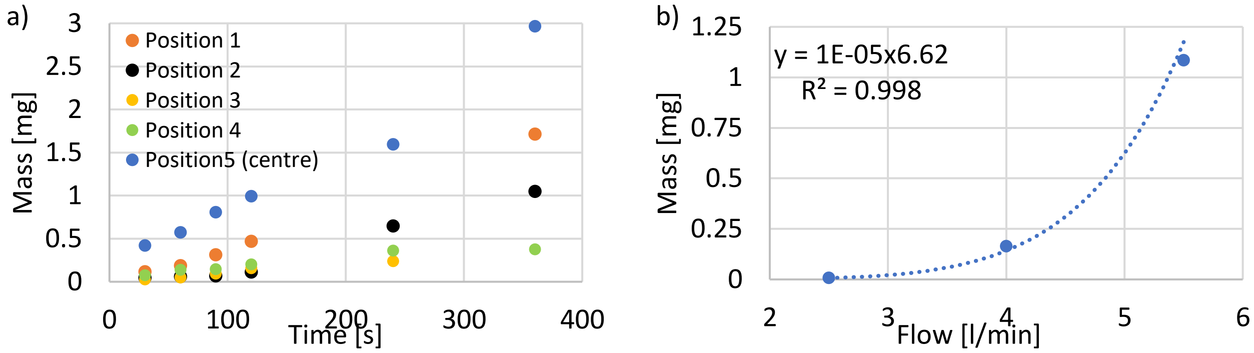

Figure 1: a) correlation between time and mass in the 5 sampling positions; b) deposited mass in function of aerosol generator's flow

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Do anthropogenic activities threaten the Naica's giant crystals?

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The giant crystals of the Naica mine have fascinated scientists from all around the world since the year 2000, when the "Cave of the Crystals" was discovered. It houses crystals of selenite ($CaCO_4$ $2H_2O$) longer than 11 m. The human activity has changed the microclimate conditions inside this cave, raising the question of whether anthropogenic action resulted in the deterioration of its gypsum single crystals and in the deposition of impurities on their surfaces. The present work provides a detailed characterization of representative samples of this cave and elaborates on the origin of the impurities on the surface of these nature-made large crystals.

The investigation was focused on two main aspects: the detailed chemical-structural characterization of these impurities and the experimental simulation of possible deterioration. The surface impurities of various samples from the "Cave of the Crystals" and especially of the "Cave of Swords" were investigated [1,2]. To conventional laboratory-based techniques such as petrography, optical and electronic microscopy, and X-ray diffraction were added synchrotron radiation –based techniques, i.e. 2D grazing incidence X-ray diffraction (2D GI-XRD), micro-X-ray fluorescence (µ-XRF) and micro-X-ray absorption near edge structure (µ-XANES). The phases and elements detected are consistent with the minerals present in the mine. However, calcium carbonate, product of incongruent dissolution was not detected. The surface impurities were deposited in the latest stage of the gypsum crystal growth, as a result of the fluctuations of the water table or due to the descent of the extraction cone of water from the mine. Subsequently, the impurities chemistries have evolved with this environment of high relative humidity and possible condensations produced when the cave is opened.

The effects of various microclimatic conditions were simulated as well. In experiments performed in a microclimatic chamber the formation of carbonates on the surface of the crystals was not detected, but the dissolution of the crystals was observed, due to high concentration of CO_2 and permanent fog. The modification of the appearance of the crystals predominates with short exposure times. With longer exposure times, the surface defects tend to disappear as the chemical equilibria are reached and dissolve and recrystallize calcium sulfate.

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Wednesday
June 23, 2021

13:30 - 15:00	**POSTER SESSION**
15:00	**NOVEL MATERIALS** Session 2 Chair: Peter Brouwer
15:00 - 15:30	**Invited - Claudia S. Schnohr**
	Structural and Compositional Inhomogeneity in Thin-Film Solar Cell
15:30 - 15:50	Claudia Zech
	Development of Spatially and Time Resolved X-ray Fluorescence based-quantification for Energy Materials
15:50 - 16:10	Diego Osmar Galeano Espinosa
	Spectroscopy and In-situ X-ray Diffraction Analysis on the Corrosion Process of the Negative Electrode by using a Low-cost Lead-acid Electrochemistry Cell
16:10 - 16:30	Kloudene A. Salazar
	Structural Investigation of Fe^{3+} -doped ZnO via XANES Spectroscopy
16:30 - 16:45	BREAK
16:45	**INSTRUMENTAL DEVELOPMENTS** Session 3 Chair: Wolfgang Malzer
16:45 - 17:15	**Invited - Christopher Heirwegh**
	The elemental Calibration of PIXL and X-ray Instrument Development beyond Mars 2020
17:15 - 17:35	Antoine Trosseau
	Exploring a New Semi-quantification Procedure of the Coloring Matters used in the Complex Systems of Prehistoric Paintings
17:35 - 17:45	BREAK
17:45 - 19:00	**OPEN DISCUSSION on XRS** Moderators: Michael Kolbe, Burkhard Beckhoff & Diane Eichert

Structural and compositional inhomogeneity in thin-film solar cells

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Thin film solar cells based on $Cu(In,Ga)(Se,S)_2$ absorbers have reached a record efficiency of more than 23% [1], thus closing the gap to silicon based technologies. Other promising absorber materials include the so-called kesterites, such as $Cu_2ZnSn(Se,S)_4$ or $Cu_2Zn(Sn,Ge)Se_4$, which mostly contain non-toxic and earth-abundant elements. A record efficiency of 12.6% has been achieved so far [2]. One of the key strengths of these complex semiconductors is the fact that their optical and electronic properties can be tuned by adjusting the material composition. However, this complexity also leads to an intrinsic structural inhomogeneity on the subnanometer scale, which arises from populating a specific site of the crystal structure with two different types of atoms. As a consequence, the local atomic arrangements in these semiconductor alloys often differ from the average long-range crystal structure. This deviation may affect important material properties such as the bandgap energy.

Furthermore, these thin film solar cells consist not only of the polycrystalline absorber but also contain a number of other thin layers in order to create a p-n-junction and to provide front and back contacts. Therefore, they feature numerous interfaces and grain boundaries. Additionally, the absorber layer often exhibits chemical gradients or compositional fluctuations, that may either be grown deliberately or that may emerge unintentionally. In general, all these characteristics may affect the functionality of the solar cell, either improving or diminishing its conversion efficiency.

A comprehensive understanding of structural and compositional inhomogeneity from the micrometer down to the subnanometer scale is thus essential in order to further improve the solar cell performance. The talk presents two powerful synchrotron-based techniques, namely X-ray absorption spectroscopy and high resolution X-ray fluorescence analysis, that allow the investigation of (i) the element-specific local structure of complex semiconductor alloys [3,4] and (ii) compositional fluctuations in actual thin film solar cells [5,6]. Results are presented from different studies centered on $Cu(In,Ga)Se_2$ and $Cu_2Zn(Sn,Ge)Se_4$.

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Development of spatially and time resolved X-ray fluorescence-based quantification for energy materials

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The increasing demand for secondary electrochemical storage devices requires well characterized battery systems. Each battery suffers from degradation effects which lead to capacity fading and life cycle reduction. With electrochemical methods, the fading can easily be monitored, but to understand the underlying chemical and physical mechanisms, further spatial and time resolving analytic techniques are needed.

In the present work, the use of synchrotron radiation based calibrated instrumentation, an operando coin cell and the combination of operando NEXAFS (near edge X-ray fine structure) and traceable XRF (X-ray fluorescence analysis) measurements enables the investigation of the degradation mechanisms for lithium sulfur[1] and magnesium sulfur batteries. It is known that especially the formation of soluble polysulfides causes capacity fading and limits the cycle life, so that their evolution, behavior and transport between the electrodes is of interest. Our method enables the absolute quantification of the mass deposition for sulfur in dissolved polysulfides for the first time. With our reference-free quantification method, no calibration samples have to be used. Moreover, with a new cell design we got access to polysulfides at both electrode sides for several full charge-discharge cycles which lead to the simultaneous investigation of conversion reactions and transport mechanisms and therefore the possibility to evaluate the polysulfide shuttle phenomena. Additionally, we got access to the change of the average polysulfide chain length which enables a deeper understanding of the capacity fading processes.

The presented measurement cells as well as the quantification method can be adopted for other cell chemistries, like lithium ion batteries or even all solid state batteries. Last but not least, the cell design is also applicable for different, complementary analytical methods, such as optical Raman spectroscopy.

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Spectroscopy and in-situ X-ray diffraction analysis on the corrosion process of the negative electrode by using a low-cost lead-acid electrochemistry cell

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Spectroscopy techniques such as X-ray fluorescence, inelastic X-ray scattering and energy dispersive spectroscopy (EDS) joined with X-ray powder diffraction (XPD) have been widely used for ex-situ and in-situ electrochemistry cell characterization [1-4]. Herein, we mounted two types of low cost lead-acid electrochemistry cells for following, by in-situ XPD (CuKα, 8keV) and by ex-situ EDS measurements, the corrosion process on the active lead (Pb) surfaces, which are commonly used as negative electrodes of lead-acid batteries.

The first electrochemistry cell was mounted based on a piece of the inner tube of an ballpoint pen [20 mm long polypropylene (PP) tube with internal diameter of 1.7 mm and wall thickness of 1 mm] with a Pb disk (diameter of 1.7 mm and thickness of 0.1 mm) as active electrode at the base. The second one was mounted based on a3D-printed rectangular cell with a Pb active electrode surface of 0.3 X 1 mm^2 (0.1 mm thick). PP windows (0.05mm thick) were employed.

The in-situ XPD measurements, carried out, continuously on the cells, for forty-five days, showed a reduction in intensity of the Pb XPD diffraction peaks in contrast of the emergence of PbSO4 XPD diffraction peaks, whose could be detected only in the grazing-incidence in-situ XPD diffraction measurement carried out on the 3D-printed cells. EDS measurements taken on the Pb electrodes, in the beginning of the process and after 45 days of oxidation (in the cells) confirm the result found in the XPD measurements for both cells

To study the structural evolution of the active surface of lead acid battery electrodes, i.e., the electrolyte contact surface, in-situ, we are developing, compatible with a conventional X-ray diffractometer. The operating energy is limited to the radiation from the CuKα emission line.

In-situ oxidation potential measurements joined with in-situ X-ray diffraction measurements are also envisaged. For that, counter electrodes (such as Cd) are being evaluated. Also, a low-cost free hardware potentiostat is being developed for in-operando studies.

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Structural investigation of Fe^{3+}-doped ZnO via XANES spectroscopy

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Zinc oxide (ZnO) is a promising material for short-wavelength optoelectronic applications because of its efficient UV emission, room-temperature luminescence, and high thermal stability. The optical properties of ZnO are highly dependent on the electronic and atomic arrangement. Crystal imperfections such as vacancies, interstitials, and antisites manifest as visible luminescence. Doping with Fe is a viable technique to tune the optical properties. Fe can substitute to a zinc lattice site or form a defect complex. To investigate the local atomic ordering and the chemical environment XANES measurements along the Fe K-edge were performed. XANES analysis confirmed the incorporation of Fe^{3+} in the crystal lattice [1]. In addition, pre-absorption studies revealed a 6-coordinated geometry, indicating the presence of Fe as a part of a defect complex rather than a substitutional atom [1]. The incorporation of Fe^{3+} in the lattice was confirmed by the enhancement of the visible emission. With these results we aim to develop a comprehensive optical and structural model for Fe^{3+}-doped ZnO microrods.

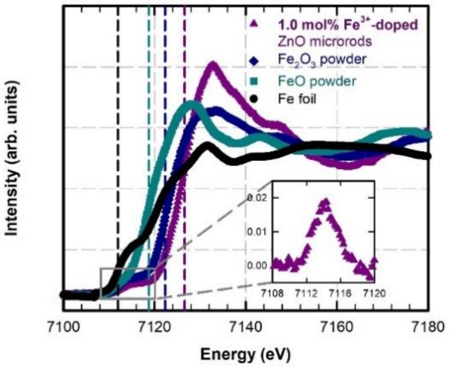

Figure 1. XANES spectra along the Fe K-edge. The inset shows the pre-absorption of the 1.0 mol% Fe^{3+}-doped microrods

Keywords: XANES

Fe^{3+}-doped ZnO

Defect complex

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The Elemental Calibration of PIXL and X-ray Instrument Development Beyond Mars 2020

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For decades the National Aeronautics and Space Administration (NASA) has relied upon X-ray fluorescence (XRF) spectroscopic instrumentation as means to explore solid planetary bodies in situ. Many of these instruments, including the class of highly capable alpha particle x-ray spectrometers, have relied upon radioactive materials as the X-ray source.

NASA's most recent XRF spectrometer, the Planetary Instrument for X-ray Lithochemistry (PIXL) is a compact sub-mm focused-beam X-ray fluorescence spectrometer installed on the arm of the Mars 2020 Perseverance Rover [1]. Unlike its predecessors, PIXL's X-ray sub-system assembly source consists of a thick anode X-ray tube (Moxtek™) design providing the benefit of increased flux delivered within a highly focused interrogation area. Beam focusing is realized via tube coupling to an XOS® polycapillary focusing optic and spectral data is recorded using two Ketek GmbH Vitus H50 detectors linked to an XIA LCC digital signal processor. Precise positioning of the sensor assembly is made possible using an optical fiducial system (OFS) consisting of state-of-the-art camera and LED lighting. A mechanical six-strut hexapod motion system provides PIXL with raster scanning capability to generate 2D elemental map images of Martian rock textures.

Planetary Scientists on the Mars 2020 project will use PIXL's interrogative capabilities to better understand Mars' early origins and search for signs of past habitability and possible biosignatures. A key step toward achieving this goal is reliance upon our ability to calibrate PIXL to convert raw X-ray measurements into quantified bulk elemental abundances. In preparation for Perseverance rover's landing, a first round of elemental calibration has been performed.

As the planetary science community embarks upon exploration of Mars using PIXL, instrument development scientists consider possible future mission applications that might necessitate XRF or X-ray diffraction technology. The likelihood for success to developing the next generation instrument depends strongly on the merger of instrument fidelity, ingenuity with meeting directly the needs of scientific exploration and aligning with funding opportunities.

In this talk I will briefly review some of the goals of the Mars 2020 mission, share results from PIXL's recent elemental calibration, discuss potential future mission prospects that might necessitate XRF or XRD instrumentation and outline challenges faced in developing the next space-bound X-ray instrument.

[1] A. C. Allwood, L. A. Wade, M. C. Foote, et al. (2020) Space Sci. Rev. **216(8),** 134.

Exploring a new semi-quantification procedure of the coloring matters used in the complex systems of prehistoric paintings

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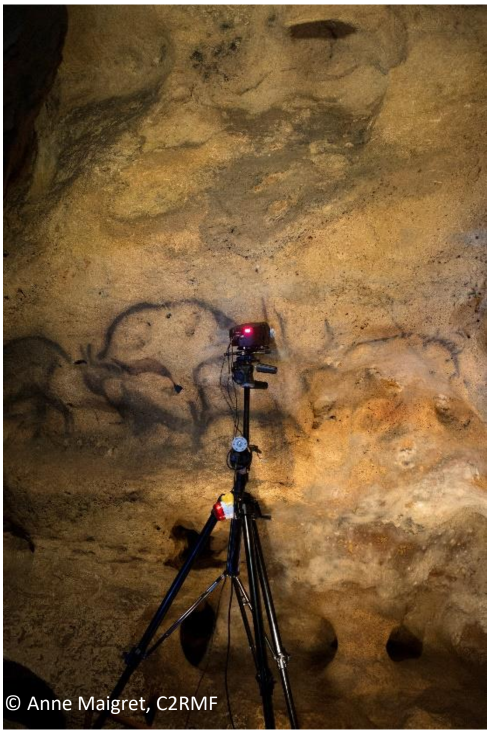
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In-situ X-Ray Fluorescence spectrometry (XRF) has been used for several years to study the parietal art in prehistoric caves and rock shelters [1–4]. This is due to the fact that it is both non-invasive, which is a now a key condition to analyze this kind of heritage, and provides information about the elemental composition of the coloring matter. In the end, characterizing these materials allow discussing the paint palette used [5] and to understand the cave decor organization [6].

However, the application of XRF in these contexts is difficult due to the complexity of the analyzed object [7]. The main difficulty is the penetration of X-rays that produce spectra of the coloring matter along with the substrate. In addition, the substrate is geometrically and chemically variable within the analyzed volume. Last but not least, the coloring matter itself is a powder scattered on the cave wall, so it cannot be considered as a layered system. Thus, to our knowledge only semi-quantification protocols have been developed [2,3,8], but no quantification procedure exists.

A new protocol is proposed to characterize the coloring matter using XRF spectra. It lies on the extraction of the signal compound only due to the coloring matter from a set of spectra. Preliminary results show good accordance between the intensity of the x-ray lines obtained with this protocol and those obtained directly on the same pure material. It will be applied to the prehistoric rock art of the Font-de-Gaume cave in Dordogne, France, which concentrate more than 200 graphical entities.

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[3] M. Gay, K. Müller, F. Plassard, J.-J. Cleyet-Merle, P. Arias, R. Ontañón and I. Reiche, 2016, Journal of Archaeological Science: Reports **10**, 878–886.

[4] G. Mauran, M. Lebon, F. Détroit, B. Caron, A. Nankela, D. Pleurdeau and J.-J. Bahain, 2019, Archaeol Anthropol Sci **11**, 4123–4145.

[5] C. Roldán, S. Murcia-Mascarós, J. Ferrero, V. Villaverde, E. López, I. Domingo, R. Martínez and P. M. Guillem, 2010, X-Ray Spectrometry **39**, 243–250.

[6] M. Gay, F. Plassard, K. Müller and I. Reiche, 2020, Journal of Archaeological Science: Reports **29**, 102006.

[7] T. Calligaro, M. Castelle, M. Lebon and G. Mauran, 2019, Quels enjeux pour l'archéométrie ?, pp. 21–42.

[8] C. Chanteraud, É. Chalmin, M. Lebon, H. Salomon, K. Jacq, C. Noûs, J.-J. Delannoy and J. Monney, 2021, Journal of Archaeological Science: Reports **37**, 102898.

OPEN DISCUSSION on XRS

Moderators: Michael Kolbe(1), Burkhard Beckhoff(1), Diane Eichert(2)
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Potential Topic

Hybrid Techniques in X-Ray Spectrometry

A few ideas to start:

- Current Needs in Characterisation of Materials
- Holistic Approaches (multidisciplinary, interdisciplinary)
- Combination & Correlation of Techniques
- In-situ Experiments & Experimental Parameters

We are looking forward to receiving your suggestions for further topics to discuss altogether, and to your active participation!

EXSA
European X-ray Spectrometry Association
www.exsa.hu

Thursday
June 24, 2021

13:30	**FUNDAMENTAL PARAMETER** Chairs: Marie-Christine Lépy & Burkhard Beckhoff
13:30 - 13:35	Opening Remarks
13:35 - 13:55	Victor H. Elvira
	Set-up and Upgrade of an Electrical-substitution Radiometer for Absolute Calibration of Photon Fluxes
13:55 - 14:00	Discussion
14:00 - 14:25	Matias Rodrigues
	A High-energy Resolution Metallic Magnetic Calorimeter dedicated to the Metrology of the X-rays emitted by Nuclides below 10 eV
14:25 -14:30	Discussion
14:30 - 14:55	Burkhard Beckhoff
	Methodologies for the Determination of FP Values at PTB and Recent Results
14:55 - 15:00	Discussion
15:00 - 15:25	Csilla I. Szabo-Foster
	Spectral Shapes of Selected L Transitions in Rare Earth Metals
15:25 - 15:30	Discussion
15:30 - 15:40	**#EXSA2021 Concluding Remarks & Awards**
15:40 - 15:50	BREAK
15:50 - 17:50	**FUNDAMENTAL PARAMETER INITIATIVE** Meeting Chairs: Burkhard Beckhoff, Marie-Christine Lépy & José Paolo Santos
	Summary of the FP initiative - history, achievements and challenges
	Summary and retrospective assessment of the virtual 2020 FP workshop
	Special issue on FP determinations
	Proposals for joint collaborative works aiming at FP validations
	Future activities and workshops
17:50	Conclusions and End of the Fundamental Parameter Meeting
18:00	**Closure of #EXSA2021**

Set-up and upgrade of an electrical-substitution radiometer for absolute calibration of photon fluxes

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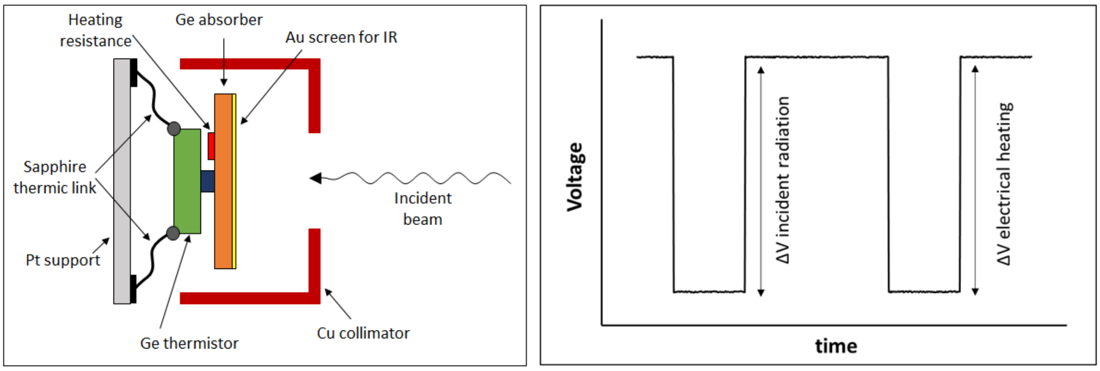
There is a constant need to accurately characterize photon fluxes at the metrological level. Indeed, any experiment aiming at deriving absolute values, such as fundamental parameters or quantitative results based on the X-ray fluorescence technique, relies on well-calibrated photodiodes and/or energy-dispersive spectrometers. The experimental calibration procedure usually requires a precisely characterized photon flux, both in energy and intensity the latter being the critical point. A very suitable option, that is widely exploited in optical photometry and also applied to the X-ray range by PTB [1], is the use of cryogenic detectors, which are based on the measurement of the temperature rise experienced by an absorber when it interacts with radiation [Fig. left]. Under the assumption that the energy transfer is complete, the temperature rise is proportional to the energy of the incident radiation (the proportionality constant being the reciprocal of the heat capacity). In order to improve the sensibility of the technique, the system has to be cooled down to a regime where the heat capacity is low enough (typically helium boiling temperature).



In electrical-substitution radiometers, the amount of energy deposited is known by finding out the electrical power that needs to be transferred to the material in order to obtain the same temperature rise as obtained by means of the absorption of radiation [Fig. right]. Using incident monochromatic X-rays, it is thus possible to get an accurate value of the photon flux, which can be used to calibrate secondary detectors (photodiode or energy-dispersive spectrometers). A first design of such an instrument (BOLUX, BOLometer for Use in the field of X-rays) was successfully employed in the X-UV energy range [2]. It is now intended to be used in a higher energy range (up to 20 keV) and some upgrades are being carried out, such as : i) Improvement of the cooling procedure, ii) Study of different absorbers in order to extend the operating energy range; iii) Automatisation of the measurement sequences; iv) Assesment of uncertainties. Principle and first steps will be presented.

[1] M. Gerlach, M. Krumrey, L. Cibik, P. Müller, G. Ulm, Nuclear Instruments and Methods in Physics Research A 580 (2007) 218–221.
[2] P. Troussel, N. Coron, 2010, Nuclear Instruments and Methods in Physics Research A **614**, 260-270.

A high-energy resolution metallic magnetic calorimeter dedicated to the metrology of the X-rays emitted by nuclides below 10 keV

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X-rays emitted during the decay of radionuclides provide useful information to quantify the amount of radioactive material in a sample, to calibrate energy dispersive spectrometers or to derive nuclear and atomic fundamental parameters. Among these nuclides, those with atomic number (*Z*) below 30 and decaying by electron capture (EC) have high X-ray intensities emitted below 10 keV. However, in this energy range, quantitative measurements with conventional semiconductor spectrometers are difficult due to their insufficient energy resolution, their high threshold and the efficiency losses at the entrance window. Therefore, the experimental X-ray emission intensities often have uncertainties of several percent.In addition, in the field of ionizing radiation metrology, the activity determination of these EC nuclides by means of liquid scintillation counting strongly depends on the atomic and nuclear fundamental parameters; their knowledge has an important contribution to the activity uncertainty budget.

To meet these needs, one of the objectives of the European metrology research project MetroMMC is to measure relevant EC decay data with outstanding accuracy, by means of high energy resolution Metallic Magnetic Calorimeters (MMCs) working at very low temperature [1]. For EC nuclides with $Z < 30$, a dedicated MMC was optimized and developed to provide both a high energy resolution (< 10 eV) and a high intrinsic detection efficiency (> 98%) below 10 keV. The MMC will allow us to measure precisely the X-ray emission intensities for ^{54}Mn, ^{59}Ni and ^{65}Zn. In order to avoid the presence of an entrance window and to benefit from high efficiency at low energy, the detector and the sources will operate at temperatures below 20 mK. Furthermore, a cryogenic sample exchanger has been conceived to change the sources at cryogenic temperatures without warming up the cryostat. The details and the performances of the MMC along with its set-up will be presented and discussed.

[1] Ranitzsch, P.CO., Arnold, D., Beyer, J. et al. MetroMMC: Electron-Capture Spectrometry with Cryogenic Calorimeters for Science and Technology. J Low Temp Phys 199, 441–450 (2020). https://doi.org/10.1007/s10909-019-02278-4

Methodologies for the Determination of FP Values at PTB and Recent Results

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The quantitative analysis of X-ray fluorescence and electron induced x-ray spectroscopic methods requires good knowledge of the atomic fundamental parameters (FP) involved. In addition, the lack of adequate reference-materials and calibration samples, in particular at the nanoscale, reliable quantification schemes in X-ray fluorescence analysis and related methods call for a high accuracy of the X-ray fundamental parameters. However, the respective uncertainties of available tabulated data are usually rather large, especially for low-Z elements or L- and M-shell fluorescence lines. In order to address this issue, different methods for experimental FP determinations have been developed, validated and applied at the PTB. Those activities on the experimental determination of X-ray fundamental parameters cover the determination of low-Z fluorescence yields, subshell photo-ionisation cross-sections and Coster-Kronig factors. Initial examples of FP values determined by these techniques will be complemented by very recent results.

Spectral shapes of selected L transitions in rare earth metals

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In this report previously unpublished spectral shapes of L transitions in rare earth metals will be presented. These spectra were recorded with the Vacuum Double Crystal Spectrometer (VDCS) of the National Institute of Technology (NIST) in the 1990s, and the numerical values of peak positions were included in comprehensive publications [1] and the NIST Standard Reference Database (SRD) # 128. The double crystal method provides a uniquely reliable method for the description of spectral shapes since the instrumental function modifying the intrinsic spectrum is not only very narrow compared to the measured spectral features, but due to the use of nearly perfect crystals, it can be well described by dynamical diffraction theory.

With the improvement of the resolution of energy dispersive detectors, *e.g.*, Transition Edge Sensor (TES) arrays, the spectral shape of x-ray transitions used as standards becomes more and more important during calibration and analysis. While high resolution x-ray spectra were only available with low bandwidth wavelength dispersive instruments through crystal diffractions in the past, today the high-throughput TES arrays can provide high resolution spectra across a wide energy range. Published spectral shapes help with the analysis of newly recorded spectra in high resolution and clarify questions about calibrations; they can also provide chemical information in some industrial applications of interest. A numerical value for peak positions can leave ambiguity about the actual positioning of the spectral shape on a calibrated energy scale. The final goal is to publish the spectral profiles of x-ray transitions on SI traceable energy scales with high precision, a job that the modernized VDCS is now able to perform [2] While this current discussion will provide reliable information about the spectral shape of the transitions, future measurements will place these data on an energy scale with tight relative error bounds ($\sim 10^{-6}$).

The spectra to be published here were retrieved from internal, unpublished lab notebooks and data analysis notes. These notes are very valuable because they were the source for the published numerical transition energy results in the aforementioned tables of Deslattes *et. al*. These line shapes, recorded with the double crystal technique and with crystals whose lattice parameters are traceable to the SI, can be used for comparisons with other wavelengths and energy dispersive methods and can also start the discussion towards general methods for the universal description of spectral shapes of x-ray transitions, an important issue within the International Initiative on X-ray Fundamental Parameters (IIFP).

Acknowledgement: Special thanks to Tim Mooney for keeping and providing these measurement results.

[1] Deslattes RD, Kessler Jr. EG, Indelicato P, *et. al*, 2003, Rev. Mod. Phys. **75**(1), 35.
[2] Szabo CI, Cline JP, Henins A, Hudson LT, Mendenhall MH, 2021*,* J. Res. of NIST (to be published).

MEETING

Fundamental Parameter Initiative

Chairs:

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Agenda:

- Summary of the FP initiative - history, achievements and challenges
- Summary and retrospective assessment of the virtual 2020 FP workshop
- Special issue on FP determinations
- Proposals for joint collaborative works aiming at FP validations
- Future activities and workshops
- Conclusions and End of FP meeting

LIST OF POSTER CONTRIBUTIONS

LIST OF POSTERS

Instrumental Developments

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Bergmann, Robert	Angular calibration of a compact grazing emission X-ray fluorescence setup by means of shadow casting
Dararutana, Pisutti	X-ray spectroscopic characterization of mosaic Jatim glass bead found in the Philippines
Eichert, Diane	European network for chemical elemental analysis by total reflection X-ray fluorescence
Fatuzzo, Claudia G.	TXRF/GIXRF high precision laboratory setup with high flux monochromatic sources
Müller, Matthias	Combined X-ray fluorescence and photoelectron spectroscopy of silicon surface layers for the realization of the new kilogram
Qu, Di	Laser-Induced XUV Spectroscopy (LIXS) for High-Precision Lithium Analysis of Energy Materials
Sokoltsova, Tetiana	Quantitative element analysis with an energy dispersive X-ray fluorescence instrument equipped with a highly oriented pyrolytic graphite filter
Sottili, Leandro	Development of a compact multi-technique X-ray based instrument for heritage science applications
Till, Heiko S.	Figures of merit and first applications of a prototype benchtop TXRF spectrometer with GIXRF capacities
Wählisch, André	Reference-free high spatial resolution XRF analysis of individual nanoscaled objects

A compact X-ray spectrometer for the investigation of elemental depth profiles with sub-µm resolution

Jonas Baumann(1), Daniel Grötzsch(1), Tim Kodalle(2,3), Fedir Bilchenko(1), Robert Bergmann(1), Steffen Staeck(1), Ioanna Mantouvalou(1,4) and Birgit Kanngießer(1)

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Depth-resolved measurements with X-ray fluorescence (XRF) techniques cannot be achieved in standard geometry. Rather, an information depth in the mm to µm range, depending on the sample matrix and radiation energy, can be defined. To reach the nm-scale, angle-resolved XRF schemes are applied. For samples with flat surfaces and interfaces, interference effects (X-ray standing wave fields) can be exploited for enhanced depths sensitivity in grazing incidence (GI-) and grazing emission (GE-) XRF geometry. Even without the appearance of interference effects, e.g., when analyzing samples with large roughness, sub-µm depth resolution can be achieved.

In the last decade, two-dimensional, energy-dispersive detectors have been successfully applied in GEXRF measurements, drastically increasing the solid angle of detection while also simplifying the setup schemes [1, 2]. We adapted the scanning-free GEXRF scheme to a laboratory spectrometer aiming at simplicity and efficiency, resulting in a particularly easy-to-use and compact design. A low power, micro-focus X-ray tube is used for sample excitation, the sample is mounted in ambient conditions and a conventional CCD camera operated in a single photon mode allows for angle-resolved XRF detection without any moving parts. The angular scale is calibrated with a reference sample, which also allows modeling all distances and solid angles of detection.

In this contribution, the described spectrometer is presented, characterized and first depth profiling applications on copper indium gallium diselenide (CIGS) thin film solar cells are demonstrated.

[1] Y. Kayser, J. Szlachetko, J. Sà, 2013, Rev. Sci. Instrum. 84 (12), p. 123102

[2] J. Baumann et al., 2017, Anal. Chem. 89 (3), pp. 1965–1971

Angular calibration of a compact grazing emission X-ray fluorescence setup by means of shadow casting

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X-ray fluorescence spectroscopy (XRF) is an analytical technique used to determine the elemental composition of a sample. However, conventional XRF is not well suited to gain depth resolved quantitative information of samples with complex layered structures or elemental depth gradients in the sub-µm regime. Varying the incidence angle of the primary X-ray radiation or the angle of detection for the fluorescence radiation are possibilities to gain depth information. Angular profiles of incident or detected X-ray intensities can be used in a fitting approach with a model sample to identify elemental depth compositions and layer thicknesses.

In case of grazing emission (GE-) XRF, the fluorescence radiation is measured at shallow emission angles. By using a 2D energy-dispersive detector the method can be used in a scan-free manner. Here, the spatial resolution of the chip allows to assign emission angles to each pixel, which enables the computation of angular profiles. In the research group “analytical X-ray physics”, a compact, scan-free GEXRF setup with a conventional CCD as 2D energy-dispersive detector is in operation. This setup usually utilizes a reference sample for the angle calibration. This implies that the sample holder must be dismounted and mounted in order to change the samples which leads, for example, to uncertainties in the position of the holder and thus the angular calibration.

In this work, an approach for the angle calibration is presented, which uses the shadow casting of a gold grid. The grid is in the optical path of the emitted X-ray fluorescence radiation and recorded on the “CCD picture”. Position and orientation of this shadow are then used for the calibration. The calibration with this method does not need a sample exchange, granting a better knowledge of the sample holder position. The effect of the new angular calibration on the elemental depth profiles is tested in the analysis of fire gilded silver substrates.

X-ray spectroscopic characterization of mosaic Jatim glass bead found in the Philippines

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It is known that ancient Jatim glass beads are large and small polychrome beads produced in Java (Indonesia) in the first millennium AD. Their styles are influenced by the Roman mosaic and millefiori beads because of the ancient international trade. Unearthed sample found in an archaeological site in the Philippines was characterized morphology and composition using scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy. It included the millefiori mosaic bead that had a thin layer of preformed cane slices over a monochrome core. It was found that the presence of Na and Si was the major component, while Al, K, and Ca were minor ones. Mg and Fe also present as trace ones. The green-colored core consisted of Cr and Cu, while F and Zn were detected in the white opaque millefiori cane slice. However, the Jatim glass bead is found in many areas, especially Asia such as Indonesia, Cambodia, the Philippines, Thailand, and China. It can be concluded that it may trade along the ancient marine time.

European network for elemental analysis by total reflection X-ray fluorescence

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The COST Action CA 18130, "European Network for Chemical Elemental Analysis by Total Reflection X-Ray Fluorescence" [1], acronym ENFORCE-TXRF, aims to coordinate research and building capacity in the field of elemental analysis by total reflection X-ray fluorescence spectroscopy (TXRF) in order to develop and assess new tools, protocols, methodologies, and instrumentation for the screening and accurate determination of elemental and co-elemental presences, occurrences and concentrations. The elements targeted are ranging from potentially toxic elements and heavy metals, to nutrients, beneficial elements and to trace elements, with their delicate threshold between deleterious exposure and beneficial effect. Such analysis may have tremendous repercussions in quality control practices and even in establishing new regulatory policy.

This Action offers an infrastructure for scientific communication, exchange and collaboration to enhance technical standards, and advance measurement science. This aims to foster new research activities and to allow to combine the various partners' related expertise in chemistry, physics, life science and engineering. This network will provide the information and tools to maximize European competitiveness in forming and attracting talented scientists, supporting new sources and capabilities that improve research productivity, quality, dissemination, efficiency, and career development.

The activities strive to enable breakthrough scientific developments leading to new concepts and products, increasing Europe's research and innovation capacities, and supporting European Commission regulation organizations in crucial fields as environmental protection, food safety, life science, and nanotechnologies. ENFORCE TXRF will create well-organized and sustainable partnerships.

ENFORCE-TXRF has formally started on March 13th 2019 with its first Managing Committee meeting and will remain in force until March 12th, 2023. This Action is opened to all researchers interested in contributing in the TXRF field of research, worldwide. Contact us at enforcetxrf@gmail.com.

Acknowledgments: This abstract is based upon work from COST Action CA18130 supported by COST (European Cooperation in Science and Technology), www.cost.eu

[1] https://www.enforcetxrf.eu

TXRF/GIXRF high precision laboratory setup with high flux monochromatic sources

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For incidence angles below the critical angle for total reflection, a standing wave is confined to the sample surface, thus enhancing the XRF signal from the surface while suppressing the background signal coming from the bulk of the sample. Such conditions are particularly suited for the study of thin surface layers of interest in many applications ranging from semiconductors to archaeometry. Furthermore, if the angle of incidence is varied around the critical angle for total reflection (grazing incidence conditions), the depth profile of such surface coatings can also be investigated. It is crucial to observe that both the critical angle for total reflection and the penetration depth at a given angle of incidence are dependent upon the incident energy. High precision TXRF and GIRXF therefore require a highly monochromatic X-ray source with little to no divergence, causing it to be traditionally implemented within Synchrotrons while its implementation into table-top instruments is conditioned by compromises in terms of both directionality and monochromaticity of the incident beams. Thanks to the recent integration of Montel mirror optics, that can select a specific wavelength by means of diffraction patterns, into compact X-ray tubes for laboratory applications, such compromises are no longer necessary. In this work, we present the characterization of a monochromatic laboratory self-assembled set up, optimized for total reflection and grazing incidence geometry (TXRF and GIXRF). A detailed study of the beam spatial distribution and acquisition geometry has been implemented to calibrate our setup for quantitative analysis, following the procedure recently developed for the calibration of a commercial instrument [1].

[1] Philipp Hönicke, Ulrich Waldschläger, Thomas Wiesner, Markus Krämer and Burkhard Beckhoff, 2020, Spectrochimica Acta Part B: Atomic Spectroscopy **174**, 106009.

Combined X-ray fluorescence and photoelectron spectroscopy of silicon surface layers for the realization of the new kilogram

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For the realization and dissemination of the new kilogram, Germany's national metrology institute PTB uses high purity silicon spheres [1]. To determine the mass of such a 1 kg silicon sphere precisely with a relative uncertainty of 14 µg [2], the mass of the surface layer must be measured by a traceable technique with an uncertainty of less than 30 ng/ cm2.

For the quantitative surface characterization of such a monocrystalline silicon sphere PTB has constructed and taken into operation an analytical instrumentation, which combines X-ray fluorescence and X-ray photoelectron spectroscopy techniques [3]. The main objective of this instrumentation is the characterization and quantification of the oxide layer, which is in the order of a few nanometers, and unintentional contaminations, e.g., by hydrocarbons [4]. The quantification is traceable to reference-free XRF by means of calibration samples with thin silicon oxide layers which are regularly qualified by synchrotron radiation based XRF measurements [5].

Applying complementary X-ray methods for quantitative surface characterization allows for minimizing the influence of the surface on the total uncertainty budget for the determination of the silicon sphere's mass. In this poster we will focus on the quantification scheme with a reliable uncertainty budget measuring the surface of a silicon sphere for the realization of the new kilogram.

[1] G. Bartl, et al., A new 28Si single crystal: counting the atoms for the new kilogram definition, Metrologia (2017) 54, 693-715 doi:10.1088/1681-7575/aa7820

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Laser-Induced XUV Spectroscopy (LIXS) for High-Precision Lithium Analysis of Energy Materials

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Laser-induced breakdown spectroscopy (LIBS) is a powerful elemental analysis method thanks to the negligible sample preparation, rapid detection, and a spatially resolved sensitivity down to trace level in any kind of sample matrix [1]. LIBS has also the ability for 2D spatially resolved mapping as well as depth profiling at a given location showing a local 3D mapping [2], such as 3D-mapping of an electrode in a lithium-ion battery. However, conventional LIBS is operated in the UV-visible spectral range (LIBS-OES), where the precision of LIBS is limited by the low stability and repeatability of the plasma emission [3]. This is particularly critical for spatially resolved analysis at nano-scale, where the sample heterogeneity is affected by the measurement precision. Utilization of the plasma emission in the extreme ultraviolet (XUV) wavelength range proved to fully overcome such limitations. Laser-Induced XUV Spectroscopy (LIXS) was applied to quantify lithium in energy materials, where the distribution of this element plays an important role for the functionality, for instance, in battery technology. The LIXS signal (7% RSD) is proved three times more stable than for LIBS-OES (23% RSD) by comparing the spectra of lithium fluoride (LiF) from 20 laser shots in single-shot mode. Moreover, a series of calibration samples Li_2O/Mn_xO_y were processed with LIXS to obtain the Li concentration calibration function for the quantitative analysis. By using the obtained calibration function. The 3s-limit of detection of Li was calculated to be 0.12%. Depending on the level of LOD, LIXS can currently only be used for the analysis of non-trace elements in matrices, where the spatial distribution is the key information. There is an urgent need to optimize the instrumentation of LIXS to further improve its spectral intensity and sensitivity.

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Quantitative element analysis with an energy dispersive X-ray fluorescence instrument equipped with a highly oriented pyrolytic graphite filter

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An energy-dispersive X-ray fluorescence (EDXRF) instrumentation is presented. The setup has been constructed for the quantitative analysis of actinides based on their intense L X-ray lines. The experimental setup is equipped with a cylindrical highly oriented pyrolytic graphite (HOPG) optic placed between a sample and a detection system. In such an arrangement, the HOPG acts as a bandpass filter that helps recording a spectrum in the energy range of interest (from 10 keV to 18 keV), while suppressing parts considered to be useless. In order to perform accurate quantitative analyses of the recorded spectra, the classical quantification algorithm based on the fundamental parameters must be adapted to take into account the spectral modifications provided by the HOPG optics. This requires to determine the transmission function of the HOPG filter and implement it in the algorithm.

Development of a compact multi-technique X-ray based instrument for heritage science applications

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The role of non-invasive non-destructive X-ray based analysis techniques is well established in the field of heritage sciences. INFN-CHNet, the network of the Italian National Institute for Nuclear Physics (INFN) devoted to Cultural Heritage, has been created for developing instruments and methods in this field. Within the network, a MA-XRF (Macro X-Ray Fluorescence) scanner was built-up for both X-ray spectroscopy and elemental imaging. The main features of the instrument are easiness of use, high portability, good performances and ultra-low radiation dispersion. The instrument has been designed as an open system, easy to integrate with further developments [1].

Among others, one intent is to upgrade the MA-XRF scanner allowing the addition of other X-ray based techniques for cultural heritage applications using a single tuneable X-ray source. For this scope, two techniques planned to be added are X-Ray Luminescence (XRL) and Radiography (RX). The potentiality of XRL in cultural heritage field was recently tested to study the provenance of lapis lazuli [2]. The usefulness of RX technique is well established, for instance to study the conditions of panel paintings and wooden statues [3].

According to the purpose, another bench-top device, starting from the INFN-CHNet MA-XRF scanner, is under development within the collaboration. For the device, a Silicon-Drift Detector will be used for XRF. For XRL measurements, a CCD spectrometer, with a bandwidth between 250 nm and 1000 nm, will be installed. For RX, in the framework of the NEXTO project funded by the Compagnia di San Paolo, a flat-panel detector with an active area of 11.4x14.6 cm_2 and a pixel size of 50 µm was tested and is now in use. A motorised system similar to the one installed on the INFN-CHNet scanner will allow elemental mapping and radiographies for objects with a size up to 30x30 cm_2. Tests of components are ongoing, and first results will be presented.

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Figures of merit and first applications of a prototype benchtop TXRF spectrometer with GIXRF capacities

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Information of lateral elemental distributions can be gained by scanning the exciting x-ray beams incident angle relative to the reflector plane. The procedure is commonly referred to as Grazing Incidence X-Ray Fluorescence analysis (GIXRF). For sufficiently small samples (approx. 100 nm and smaller) an angle-dependent oscillation in the XRF signal intensity can be observed for angles smaller than the reflectors critical angle. This allows for the analysis of nanoscopic samples above a reflector and shallow implants underneath the reflector plane.[1]

Angle scanning has been quite common in Si-wafer analysis with TXRF to distinguish film-like and particle-like surface deposits. GIXRF, however can be applied beyond this to characterize nano-particulate matter, layered structures and implants, if the angle resolution is sufficient. The angle scan capabilities in TXRF instrumentation *e.g.* the Atomica 8030C were often inadequate. Besides at synchrotron facilities, dedicated GIXRF instrumentation is not widely available to researchers. In 2010 INGERLE *et al*. already reported the development of a dedicated laboratory device, but it is not commercially available.[2] The Nanohunter II is advertised having GIXRF capabilities (Rigaku Corporation, Tokyo, Japan). The S4 T-Star (Bruker Nano GmbH, Berlin, Germany) is equipped with angle scanning capabilities to automatically optimize the angle of incidence in TXRF, and can be extended to enable GIXRF analysis. In this work, a S4 T-Star prototype was equipped with a collimator-monochromator optic for this purpose.

Here we present first figures of merit and first GIXRF applications of the benchtop spectrometer S4 T-Star. The work includes the angle calibration of the spectrometer by measurement of the critical angle of reflector materials with known chemical composition and physical properties. Furthermore, the angle resolution of the spectrometer is determined. The GIXRF capacities of the spectrometer are demonstrated by angle-scans of gold nanoparticles with sizes ranging from 5 nm to 50 nm.

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Reference-free high spatial resolution XRF analysis of individual nanoscaled objects

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As functional devices in many areas of application steadily get smaller and require material systems not only at the microscale but nanoscale, the demand for analytical high spatial resolution methods is increasing in the same manner. X-ray spectroscopy (XRS) is a nondestructive technique widely used to qualitatively and quantitatively characterize material systems. For spatially resolved measurements in the regime of a few nanometers to a few hundred nanometers, any vibration caused from the surrounding environment with an amplitude of the same order of magnitude or larger will deteriorate the resolution achievable. We present a novel instrumentation for synchrotron radiation based scanning XRS, where all relevant optical elements, including a Fresnel zone plate, are mounted on a single platform. This compact setup minimizes vibrations, enabling a spatial resolution in the regime of 100nm with scanning transmission X-ray microscopy (STXM) and scanning X-ray fluorescence analysis (XRF). Both emitted fluorescence radiation and transmitted radiation are detected with calibrated X-ray detectors. We demonstrate a reference-free quantification method based on XRF on a nanostructured germanium sample. To determine the spatially resolved mass deposition of germanium, the lateral dimension of the incident beam has to be known. In initial experiments we achieved a beam with full width at half maximum of about 100 nm, which is in line with the probed sample dimensions.

Poster presentation preferred

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Application of portable benchtop X-ray fluorescence analyzer for non-destructive analysis of stone artifacts

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Stone artifacts such as hammerstones, flakes, cores are often the only source of information for studying the culture and manufacturing processes in the Stone Age due to the destruction of wood, leather and bone artifacts under the effect the environmental conditions. The study of the chemical composition of the stone materials that were found on the archaeological sites are used to identify the source of lithic raw material, assess transportation and trade routes between people living in different regions. Stone artifacts are unique finds, therefore we considered the possibility of non-destructive analysis. Stationary laboratory-based X-ray fluorescence spectrometers are usually equipped with sample holders with a diameter of not more than 40 mm, which does not allow measuring the large-sized samples.

In this study, to determine the composition of stone archeological materials, we used a CTX portable benchtop energy-dispersive analyzer (Bruker, Germany), equipped with the sample chamber sized 12 cm x 13.5 cm x 8.5 cm. In order to calculate the concentrations of elements represented as oxides (MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, MnO, TiO_2, Fe_2O_3), were used software based on the method of fundamental parameters.

The objects of research were selected artifacts made from argillite, basalt, rhyolite, and quartz. For measurements, we selected a surface close to flat and free from the influence of the post-depositional processes. To account for the heterogeneity, the sample was irradiated at several points from different sites. To check the accuracy of the results of non-destructive analysis, several samples were milled and prepared as 40 mm glass disks and measured using an X-ray fluorescence wavelength-dispersive spectrometer S8 Tiger (Bruker, Germany). The discrepancies between the results of non-destructive analysis and analysis of glass disks were 10-30 % rel. for Al_2O_3, SiO_2, K_2O, CaO, Fe_2O_3. For low contents of MgO, P_2O_5, MnO, TiO_2, discrepancies between the obtained results are more significant (> 30% rel.). Non-destructive analysis of stone axes allowed us to identify the composition of the stone geological raw materials used for their manufacture.

The work was carried out using the equipment of the RAS Joint Use Centers "Geodynamics and Geochronology" and "Isotope-Geochemical Research" with the financial support of the Russian Science Foundation (project No. 19-78-10084).

Exploring possibilities and drawbacks in the analysis of Pb loaded reference samples by using TXRF spectrometers

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Particulate matter (PM) is a prominent air pollutant responsible for negative health effects. Environmental monitoring procedures include the determination of PM composition and related-concentration in order to assess the presence of potentially toxic elements such as Pb, As, Ni, Cd, and Hg [1]. Recent works showed the applicability of total reflection X-ray fluorescence (TXRF) spectrometers for this purpose. Exploiting the geometrical configuration of TXRF spectrometer, enhanced elemental sensitivities can be obtained. Further, for samples thin enough, a linear relationship between the intensity of the analyte emission line and its concentration can be retrieved [2].

In this work we describe such method for the measurement and analysis of lead in PM filter samples. This process makes use of the SMART STORE® sample handling procedure which sandwiches the sample between two polymeric foils. Plasticized lead-loaded reference samples with masses ranging from 0.028 to 10.169 μg/cm^2 were analyzed with three TXRF spectrometers, namely the Nanohunter II (Rigaku), the S2 Picofox (Bruker) and the Horizon (GNR), all equipped with Mo X-ray tubes. All these instruments allow for the detection of Pb in the test samples, confirming the suitability of the sandwiching procedure for qualitative analysis. For quantitative analysis, challenges remain to be tackled, as for TXRF a linear calibration curve needs to be built, which compensates for eventual matrix effects.

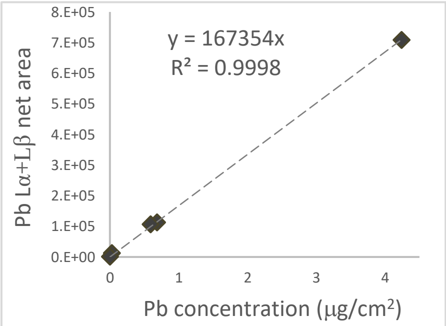

Fig. 1: Calibration curve obtained analytically

Both analytical and theoretical approaches were implemented for retrieving the calibration curve. A direct linear relationship between the Pb net area and its concentration was obtained (Fig. 1), of better precision and limit of detection than the ones previously published [2]. In addition, a calibration curve including the sample with the highest mass deposition, exceeding the acceptable Pb critical mass, was implemented theoretically, considering the angular dependency of the mass attenuation coefficient.

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Spectromicroscopy analysis of toilet paper

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Allergy to bleach and/or moist toilet paper has been reported in the literature [1-2]; Allergies can be attributed to formaldehyde, lanolin, and benzocaine composites which are commonly found only in moist toilet paper. On the other hand, chlorine bleach is used to produce bleach toilet paper. However, since it disperses as a gas during the time, the probability to find it in "at the shelf" products are very low. Spectroscopy (X-ray fluorescence – XRF, Fourier transform infrared spectroscopy – FTIR) and X-ray diffraction – XRD have been used to study paper mostly in the forensic sciences for documents and banknotes counterfeit purposes [3-4]. In this work we extend these spectroscopy techniques to try to figure out if "at the shelf" toilet papers can present allergic components in their chemical composition. Since the most white and stiffness toilet papers, in principle, have more chemical products than the cheap "grayish" brands [5] we have selected four different brands of bleach toilet paper available in the Brazilian market. XRF, FTIR, Scanning Electron Microscopy with Energy Dispersive Spectroscopy – SEM / EDS, crystallographic analysis (XRD), and imaging analysis (X-ray phase contrast imaging and SEM) have been carried out in the four different toilet paper brands. Formaldehyde and chlorine composites were not found. In spite of that, EDS measurements show the presence of calcium in one of the samples, which can be attributed to different components (e.g. calcium carbonate or calcium oxalate) which, in principle, are not considered allergic. Although, since calcium oxalate can be associated with paper biodegradation [6] such sample is being closely examined by biological microscopy analysis. Also, calcium additives are used to improve the physical/mechanical properties of the paper [7]. For that, shear and tension stress/strain measurements [8] in the different sample brands are envisaged. At last, for comparison, measurements in cheap unbleached brands are being carried out.

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Determination of the Content of Selected Metals in Croatian wines by Total Reflection X-ray Spectrometry – the chemometric approach

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The elemental composition of wine depends on soil properties, climatic conditions, cultivation and winemaking practices and is directly related to the quality, organoleptic characteristics and health safety of wine [1].

The aim of this study was to examine the impact of geographical origin and type of wine on the content of selected metals such as K, Ca, Fe, Cu, Zn, Mn, Sr, Rb, Ba, Pb, Ni, Cr and V in 70 red and white wine samples from different regions of Croatia (continental and Adriatic part) using total-reflection X-ray spectrometry (TXRF). TXRF was chosen as the method of choice since it does not require complicated and time-consuming sample preparation methods such as acid digestion, which makes it simpler and greener analysis approach in comparison to other more commonly used techniques [2]. Basic statistical tests and unsupervised and supervised classification methods were used to present statistically significant differences between the studied groups, to indicate if there are any patterns or trends, to explore possible wine and variable classes, or to reduce the number of variables in order to explain the data variation as much as possible.

Significant differences were found in the contents of Mn, Ni, K, Rb, Sr and Ba between categories. Principal component analysis and cluster analysis showed that the variables used had sufficient explanatory power to group them according to geographical origin and the type of wine. It was found that Mn, K, Ni and Sr were the most important variables differentiating by type of wine, while Rb and Ba were the most important variables related to origin. Finally, linear discriminant analysis showed good recognition and prediction abilities using these selected elements. The recognition ability was 100%, while the prediction ability was 96.43%.

The contents of almost all of the analyzed metals were below the maximum permissible contents (MPC) set by the Croatian legislation and also below the MPC in wine set by the Office International de la Vigne et du Vin (O.I.V).

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Preliminary elemental characterization of various types of muscles by means of SR-XRF

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Among the neuromuscular diseases, myopathy which is characterized by direct damage to muscle tissue, can be distinguished. The origin of this disease can be either congenital, which is called dystrophie, or acquired.Pathogenic processes taking place in the muscle fibers can lead to changes in the elemental composition. These differences may also arise from the presence of two types of muscle fibers: type I - slow (oxidative metabolism) and type II - fast (glycolytic metabolism).

The aim of this experiment was the quantitative, chemical imaging of minor and trace elements in various types of human muscle fibers affected by neuromuscular diseases. In order to obtain information about the types of fibers, a comparison of the tissue with the histopathological staining was used.

The samples designed to the elemental analysis were prepared and diagnosed at the Department of Pathomorfology of Collegium Medicum Jagiellonian University. The tissue material came from a surgical biopsies and has been prepared by shock freezing in liquid C_3H_8. For each specimen two adjacent tissue slices were cut into 8 micrometers on the cryo-microtome and placed on the microscope slide and Silicon Nitride Window (membrane thickness: 200 nm, window size: 2x2 mm), respectively. The experiment was carried out at the I18 beamline, DIAMOND Light Source. The beam size used was 5x5 μm^2 with excitation energy of 13.5 keV. Different size sample areas were recorded with a step size of 5 µm. The acquisition time was 1s per pixel. The fluorescence radiation was detected with the use two SDD detectors – one in front of and second one behind the sample. All measurements were carried out in helium atmosphere.

Preliminary data analysis showed differentiation of both types of fibers: type I and type II, based on elemental analysis.

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A preliminary comparative study of the metal content of mobile phones over the last 15 years, using EDXRF

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Abstract

Energy Dispersive X-Ray Fluorescence is used at the Nuclear Engineering Department of NTUA (NED-NTUA) for qualitative and quantitative analysis of environmental samples. The facility consists of an X-ray Chamber with Mo target and a SiLi detector. The collected spectra are analyzed by b-AXIL software. Our last work is about the metallic elements in mobile phones. Mobile phones are a large industry all over the world which produces million of new models and on the other hand millions of old models are already obsolete for our over-consuming way of living. A mobile phone except plastic parts mainly consists of printed circuit board with metal components, magnets and metal contacts often gold plated. Recycling and environmental impact of used mobile phones differ according their metal substances. The directives about the use of hazardous elements like Pb have changed, since the first mobiles were produced, so mobile phone companies had to adjust their products accordingly reducing the quantity of the Pb or replace it with other metals. Therefore, it is important to establish a quick screening method to analyze the different parts of mobile phones (electronic circuits, metal contacts for SIM cards or batteries etc) in order to categorize them according their elemental concentration. For this purpose the above mentioned EDXRF facility was used and indicative mobile phones from three different periods (2004, 2010, 2014) were dismantled and their parts were analyzed to detect the metals on them. From the analysis results obtained so far, it may be concluded that Lead which was used in metal contacts of SIM cards in early mobile phones was replace by Bismuth because of health precautions and Gold (Au) was also reduced maybe due to cost reasons and better production procedures. Additionally, EDXRF spectra analysis concluded that mobile phones consist of a variety of metals and other elements (Cu, Ni, Cr, Fe, Br, Sn, Ag, La, Sr, Ba) so right disposal of used mobile phones is recycling and special care for all the remaining waste.

Characterization by Total Reflection X-Ray Fluorescence of Particulate Matter Collected on Air Filters in Sale City, Morocco

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Total reflection X-ray fluorescence spectrometry (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 [1].

Particulate matter (PM) is a complex mixture of extremely small particles and liquid droplets. Particles are usually characterized by their size diameter. PM size is important because of the adverse health effects associated with particles in certain size ranges. Basically, the smaller the particle, the more likely it will penetrate deeper in the lung. Particles much greater than 100 µm are typically not inhaled, while smaller particles, typically less than 4 µm, can interfere with oxygen gas-exchange in the lung alveolar region [2].

In the present study, air particulate matter was collected in Sale City (located in North-Western Morocco). Fine (PM2.5) and coarse fractions (PM2.5-10) were sampled during 1 year (from July 2018 to July 2019) using dichotomous sampler. Samples were collected on a weekly basis (one day per week) with 24-h sampling time. By studying the relationship between the two fractions and the meteorological parameters, significant correlations were found between PM2.5 and PM10 and negative correlations were observed between PM10 and humidity on the one hand and between PM2.5 and wind speed on the other hand. The observed average concentrations of both fractions were higher in winter as compared to summer and other seasons. This may be due to low wind speed and high humidity during the winter season in comparison to other seasons. The analysis of the measured PM10 concentrations during the studied period showed that 33% of PM10 contents exceed the limit value fixed by the World Health Organization (WHO) and the Moroccan Standard (50µg/m^3 over 24 hours). For PM2.5, there is not yet a standard setting the limit value in Morocco so we adopted that of the WHO which is equal to 25µg/m3. For the present study, 17% of the recorded PM2.5 concentrations were above this WHO standard value.

For elemental compositions, we have noted that the concentrations of soil-related elements were higher in the coarse than the fine fraction. However, the elements supposed from anthropogenic sources were more present in the fine fraction. Source apportionment was carried out using enrichment factor (EF), spearman's correlation and Principal Component Analysis.

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Ultrasoft X-Ray Bremsstrahlung in electron scattering by xenon clusters

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Bremsstrahlung (BS) [1] arising from the scattering of electrons by atoms, molecules, or clusters is formed by two mechanisms. In one of the mechanisms, the emission of photons is caused by the incident electron when it is decelerated in the static field of the target particle (ordinary BS). In another method, continuous-spectrum photons are emitted by electrons of the target particle due to its dynamic polarization, namely polarization bremsstrahlung (PBS).

For detailed studies of bremsstrahlung radiation originated from the scattering of electrons by atoms and clusters, we used a supersonic gas jet flowing into the vacuum as a dense target. This unique method allowed us to place the electron beam in immediate proximity to the target and study the ultrasoft X-ray bremsstrahlung over a broad range of incident electron energies.

BS processes (including PBS) have been well studied using the scattering of intermediate-energy electrons by xenon atoms and clusters [2]. In particular, the absolute differential cross sections of BS were determined for the scattering of 0.6 keV electrons by Xe atoms [3], and a change in the PBS spectrum was found at the transition from atoms to clusters [2].

In this work, for the first time, the absolute differential cross sections of BS were experimentally measured by the bombardment of Xe clusters with electrons with energies of 0.3–1 keV. Additionally, the contribution of the polarization mechanism to the BS cross section is separated and the dependence of the BS cross section on the energy of the incident electron is established. Xenon clusters with an average size of 400 to 12000 atoms per cluster were obtained via the adiabatic expansion of a gas through a supersonic nozzle into a vacuum [2]. The size and number of interacting with electrons Xe clusters were measured according to the original approach [4]. The emission spectra of the Xe cluster jet were recorded in the 70–240 eV region with an X-ray spectrometer using a proportional counter.

The results obtained can be used for X-ray spectroscopy of clusters and for development of the theory of bremsstrahlung at low energies of interacting particles.

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Electrochemical reactions in organic-metal batteries studied by X-ray Raman spectroscopy

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Lithium-ion batteries currently dominate energy storage market and are most commonly used in various commercial applications. Because of high cost of production, low volumetric capacity and environmental concerns, a search for other alternatives is underway. Metal-organic batteries are a promising candidate for next generation of sustainable and efficient energy storage solutions [1]. Redox polymers with high energy storage capacity were shown to have a high cycling stability [2], but not much is known about electrochemical reactions due to a lack of suitable analytical bulk sensitive characterization methods.

In this work, redox reactions were studied in batteries containing polyanthraquinone (PAQ) and poly(anthraquinoyl sulfide) (PAQS) organic cathodes with Li and Mg counter ions. A reduction of carbonyl bond from O=C to O-C^- by attaching a corresponding metallic ion was suggested as the mechanism of electrochemical activity [3]. Oxygen (O) atomic environment is strongly affected by the redox reaction, so X-ray Raman spectroscopy (XRS) [4] was used to measure O K-edge absorption spectra in bulk cathode material. XRS measurements were performed at the PETRA III synchrotron facility on various anode materials (PAQ, PAQS, Li2AQ), which were used to mimic possible chemical environment around O atoms, and several ex-situ samples of pre-cycled cathodes from Li-PAQ and Mg-PAQS organic batteries.

Shape of oxygen K-edge absorption spectra was used to examine local atomic environment during the charge/discharge cycle of a battery. Linear combination fitting of standards to the measured ex-situ spectra was used to determine relative amounts of carbonyl bonds in each cathode sample. Values obtained from the analysis of XRS spectra were in a good agreement with electrochemical information, gained from the individual cathodes during their preparation. Measured XRS spectra were also compared to theoretically calculated absorption spectra, obtained with first principle density functional theory, using Cp2k program package. This confirmed reduction of carbonyl bond as a mechanism for electrochemical activity.

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Interfacial Interaction study of Adsorbate CuPc with Ferroelectric Polymer Substrates

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Polyvinylidene difluoride-trifluoroethylene P(VDF-TrFE) copolymer and Poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) [P(VDF-TrFE-CFE)] terpolymer were applied as ferroelectric polymeric underlayer for extensive investigations of interactions with molecular adsorbate Copper Pathalocyanine (CuPc) layer. Work Function (WF) and Highest Occupied Molecular Orbital (HOMO) energy level shift observed from UPS spectroscopy for successive deposition of CuPc molecules on ferroelectric polymer surfaces confirms formation of interface dipole at CuPc-ferroelectric interface owing to emptying of tailing states from CuPc HOMO density of states due to electron transfer from CuPc molecules to ferroelectric polymer layer. According to thickness dependent XPS data, CuPc molecules are coupled to the organic ferroelectric surfaces through central metal atom of the CuPc molecules i.e. copper atom and the halogens of underlying ferroelectric polymer surfaces and hence support the charge transfer phenomenon from CuPc molecules to ferroelectric polymer substrate. While polarization dependent NEXAFS results reveal that CuPc molecules retain their tilted geometrical configuration at even submonolayer thickness of the molecular films on both ferroelectric surfaces and further confirm emptying of some of the molecular orbitals states of CuPc molecule corresponding to B peaks because of charge transfer. Therefore, the energy level alignment with increment in the thickness of CuPc films at both the organic semiconductor-ferroelectric polymer interface is controlled by the charge transfer phenomenon from deposited CuPc molecules to the organic ferroelectric substrates.

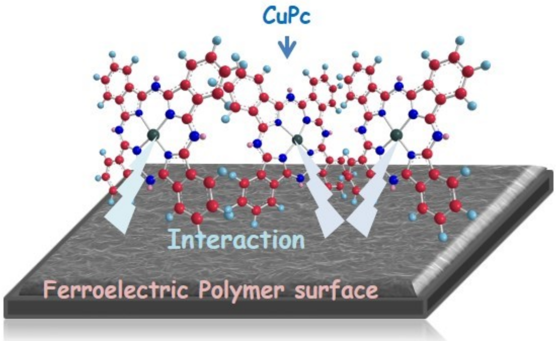

Figure: Schematic presentation of interaction of CuPc molecules with ferroelectric polymer substrates.

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Application of X-ray reflectometry in analysis of Ti and TiO_2 nanolayers implanted with Xe^{q+} ions

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Modification of metal, semiconductor and insulator surfaces by ion irradiation is of great importance for developing new technologies for manufacturing a small functional electronics system with nanometer dimensions. Due to the exhausting potential of currently used technologies, extensive research is carried out around the world to develop a new, repeatable and effective technologies for modifications of various material properties. One from such promising future technologies, which gives possibility for obtaining novel physico-chemical properties of materials is modification of materials surfaces by irradiation with low-energy highly charged ions (HCI) [1-2].

The main aim of this study was to determine the changes in morphology and physico-chemical properties of nanolayers caused by irradiation by low-energy highly charged Xe ions. In order to investigate the changes of nanolayer properties, as a result of the HCI irradiation, in dependence of nanolayer thicknesses and the ions potential energy, synchrotron radiation-based X-ray reflectometry (SR-XRR) was applied [3]. In the presented studies characterization of Ti and TiO_2 nanolayers of thickness of 25 nm, 50 nm and 75 nm, deposited on the Si substrate, nonmodified and modified with xenon ions, was performed. The nanolayers were implanted with low-energy highly charged Xe^{q+} (q = 25, 30, 35) ions at the Kielce EBIS facility (Jan Kochanowski University, Kielce, Poland) [4]. The SR-XRR measurements were performed at Elettra Synchrotron X-ray fluorescence beamline, using synchrotron X-ray beam with energy 6.0 keV [3].

In order to determine the effect of ion irradiation on the surface characteristics of the tested nanolayers, the measured SR-XRR curves were analyzed with X'Pert Reflectivity 1.3a program (PANalytical). In the procedure of fitting theoretical curves to the measured ones, the nonmodified and modified TiO2 nanolayers were modeled using two layers: the main TiO2 layer and, thin top layer consists of amorphous TiO_2 with contaminations. Respectively, the titanium layers were modeled by Ti layer, main TiO_2 layer, and top layer TiO_2 (a) with contamination. As a result of the analysis the thickness, density, and roughness of the nanolayers were determined from the SR-XRR curves depending on the charge state of the ions.

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Keywords: X-ray reflectometry, Synchrotron radiation, morphology, HCI irradiation, Xe ions

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