EXRS – 2018
European Conference on X-Ray Spectrometry
Ljubljana, Slovenia, 24–29 June 2018

BOOK OF ABSTRACTS

`https://exrs2018.ijs.si/`

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Contents

1 Welcome to EXRS 2018 in Ljubljana, Slovenia!

EXRS is a biennial conference series that started in 1984 in Goteborg. It has become a traditional meeting for scientists from around the world working in x-ray spectrometry or using one of its several techniques: X-ray fluorescence, electron microprobe, PIXE, XRD, etc. It represents an exciting discussion forum for basic research and applications of x-ray spectrometry in a rich variety of fields like materials science, chemistry, radiation physics, medicine, biology, environment, cultural heritage, technology and industry.

The 2018 EXRS will take place in the university city of Ljubljana, Slovenia. It is known for its lovely old town, the curving Ljubljanica River and an abundance of green spaces. It is also home of Slovenia's biggest research institute — the "Jožef Stefan" Institute, which is hosting the conference. The scientific programme of the conference will take place at the Ljubljana Exhibition and Convention centre, situated near the city centre and in the vicinity of many hotels.

A variety of social activities will allow the visitors to explore the city as well as the rest of the country. Some of the highlights include Wednesday's afternoon trip to the coast and the conference dinner in the heart of Ljubljana — at the Ljubljana castle..

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2 Venue

Address:
Gospodarsko Razstavišče, Dunajska cesta 18, Ljubljana

Ljubljana Exhibition and Convention Centre is situated within a walking distance of many hotels. The nearest bus station is located right in front of the entrance. The station is called "Razstavišče" and is served by lines 6, 7, 8, 11, 12, 13, 14, 19 and 20.

The scientific programme will be held at the Marmorna hall and the industrial exhibition will be located in the foyer just outside the hall. Poster sessions will take place in the halls one level lower than Marmorna hall.

3 Exhibitors

Booth	Exhibitor	Booth	Exhibitor
1	**Moxtek, Inc** www.moxtek.com	12	**SUNJE** www.sunstat.com
2	**Sinerlab S.r.l.** www.sinrx.eu	13	**RaySpec Ltd** www.rayspec.co.uk
3	**Brightspec NV/SA** www.brightspec.be	14	**Micro X-Ray** www.microxray.com
4	**Amptek Inc.** amptek.com	15	**SPEX Europe** www.spexeurope.com
5	**BRUKER** www.bruker.com/micro-xrf	17	**PNDetector** www.pndetector.de
6	**XGLab** https://www.xglab.it/x-and-gamma-ray-electronics.shtml	18	**Specac Ltd.** www.specac.com

Booth	Exhibitor	Booth	Exhibitor
7	**Excillum AB** www.excillum.com	19	**Micromatter Technologies Inc.** www.micromatter.com
8	**KETEK GmbH** www.ketek.net	20	**Rigaku Europe SE** www.rigaku.com
9	**Malvern Panalytical** www.malvernpanalytical.com	21	**XOS, Inc.** www.xos.com
10	**Canberra Packard Central Europe GmbH.** www.cpce.net	22	**SPECTRO Analytical Instruments GmbH** www.spectro.com
11	**ELVATECH** elvatech.com	23	**XIA LLC** www.xia.com
*	**DECTRIS Ltd** www.dectris.com	24	**Hitachi High-Technologies Science America** https://www.hitachi-hightech.com/hhs-us/

4 Social events

WELCOME RECEPTION (SUNDAY, 18:00 – 21:00)
After picking up your welcome bag at our registration counter, you are invited to join us for a welcome reception. Food and drink will be served in the foyer outside the lecture halls, which gives you an excellent opportunity for the first introductions and discussions at EXRS 2018.

TOWN HALL RECEPTION & LJUBLJANA SIGHTSEEING (MONDAY, 19:00)
The mayor of the city of Ljubljana *Mr. Zoran Janković* will address the guests of the EXRS 2018 conference at the Town Hall, which is located in the center of the old town. After a short reception, you are invited to join a guided walking tour through the old town of Ljubljana.

PUBLIC LECTURE (TUESDAY, 20:00)
We are very happy to announce that the public lecture on Tuesday evening will be given by *prof. dr. Alexander Föhlisch* from Helmholtz-Zentrum Berlin and University of Potsdam. In his expose titled "Beating the complexity of matter by the selectivity of X-rays", he will talk about how using X-rays helps us to obtain answers to some crucial scientific questions.

EXCURSION (WEDNESDAY, 13:00)
On Wednesday afternoon we will visit the coast of Slovenia. The buses will leave from the venue at exactly 13:00. First, we will visit Sečovlje Salina Natural park, where we will learn about the salt-making and the environment there. Our next stop will be the beautiful town of Piran. We will take a short guided walk through the old town and after that there will be plenty of time for exploring on your own, trying the local specialities or even for a swim.

CONFERENCE DINNER (THURSDAY, 20:00)
Conference dinner will be held in the yard of the Ljubljana Castle (or inside the castle in case of rain) on Thursday evening. You are invited to come to discuss and reflect back on the conference in a more relaxed setting.

The Ljubljana castle is one of the main attractions of the city and offers an amazing view. As it lies on top of a hill we recommend using the funicular from the old town or a taxi. The funicular starts from Krekov trg in the old town, just behind the open market. You can reach it on foot or using bus lines 2, 13 or 20. One way ticket for the funicular costs 2.20 € (1.50 € for students), and return 4.00 € (3.00 € for students). It departs every 10 minutes with the last run at 23:00. There are several pathways leading up the hill. A hike to the castle takes about 10–15 minutes with 80 m ascend.

5 Program overview

Sunday 24. 6. 2018	18:00–21:00	Registration and welcome reception
Monday 25. 6. 2018	8:00–9:00	Registration
	9:00–9:30	Welcome address
	9:30–12:30	Scientific programme
	14:00–16:30	Scientific programme
	16:30–18:00	Poster session
	19:00	Town hall reception & Ljubljana sightseeing
Tuesday 26. 6. 2018	9:00–12:30	Scientific programme
	14:00–15:15	Scientific programme
	15:45–16:45	Industrial session
	16:45–18:00	Poster session
	20:00	Public lecture
Wednesday 27. 6. 2018	9:00–12:00	Scientific programme
	13:00	Excursion
Thursday 28. 6. 2018	9:00–12:30	Scientific programme
	14:00–15:15	Scientific programme
	15:45–16:30	Industrial session
	16:30–17:00	EXSA general assembly
	16:30–18:00	Poster session
	20:00	Conference dinner
Friday 29. 6. 2018	9:00–12:15	Scientific programme
	12:15	Closing ceremony

6 Invited lectures

W. B. Doriese, NIST Boulder, USA: High-efficiency X-ray-emission spectroscopy with arrays of transition-edge-sensor microcalorimeters

P. Glatzel, ESRF Grenoble, France: In-vacuum tender X-ray emission spectrometer with eleven cylindrically bent Johansson crystal analyzers

S. Huotari, University of Helsinki, Finland: X-ray Raman spectroscopy

Y. Kayser, PTB Berlin, Germany: Grazing X-ray fluorescence techniques applied to nanometer-scale characterization applications

F. Lucarelli, INFN Florence, Italy: 25 years of aerosol studies by PIXE and complementary techniques at LABEC

M. Manso, University of Lisbon, Portugal: Contribution of X-ray fluorescence spectrometry in graphical documents characterization

F. Salvat, University of Barcelona, Spain: Physics interaction models and applications of PENELOPE in XRS and EPMA

G. Seidler, University of Washington, USA: Benchtop Analytical XAFS and XES: Applications from Sulfur to Uranium

J. Szlachetko, Institute of Nuclear Physics PAN, Krakow, Poland: Off-resonant X-ray spectroscopy: from synchrotron to Xray Free Electron Laser science

P. Van Espen, University of Antwerp, Belgium: Evaluation of large x-ray spectral datasets from macro-scanning XRF

G. Vankó, Wigner Research Centre for Physics, Budapest, Hungary: X-ray spectroscopy at extreme low and high brilliance

K. Vogel-Mikuš, University of Ljubljana, Slovenia: X-ray spectrometry in plant biology

H. Yoneda, Institute for Laser Science & RIKEN Spring-8, Japan: New type of hard x-ray lasers pumped by X-FEL

7 Call for X-Ray Spectrometry papers

Selected contributions will be published in a special issue of the scientific journal X-Ray Spectrometry (Wiley Online Library).

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 by 1 September 2018.

Detailed instructions for submission will be available on our website:
`https://exrs2018.ijs.si/index.php/call-for-x-ray-spectrometry-papers/`

8 Monday program

	Marmorna Hall 1	Marmorna Hall 2
9:00	Opening session Chairs: M. Kavčič, M. Žitnik	
9:30	Invited: **New type of hard x-ray lasers pumped by X-FEL** *H. Yoneda* (p. 21)	
10:00	Invited: **X-ray spectroscopy at extreme low and high brilliance** *G. Vankó* (p. 22)	
10:30	Coffee Break	
	Session I: Interactions of X-rays with matter and fundamental parameters Chair: M.-C. Lépy	Session II: Microbeam techniques, confocal XRF and X-ray imaging Chair: K. Tsuji
11:00	**High valence metal center molecule creation with high intensity XFEL pulse** *W. Blachucki* (p. 24)	**Multimodal imaging of biological samples: correlation of μXRF with MALDI-MSI and with LA-ICP-MS** *A. Turyanskaya* (p. 36)
11:15	**Cascade Ge-L X-ray emission enhanced by Resonant Raman Scattering** *A. Karydas* (p. 25)	**High Speed Simultaneous XRD-XRF Mapping with the Color X-ray Camera** *J. Davis* (p. 37)
11:30	**Chemical state sensitivity of Cr K$^{h}\beta$ hypersatellite** *J. Hoszowska* (p. 26)	**Analytical X-ray Microscopy in the Soft Energy Range with Very Large Solid Angle of Detection** *B. Kanngießer* (p. 38)
11:45	**Theoretical Calculations of Atomic Fundamental Parameters for X-Ray Methodologies** *M. Guerra* (p. 27)	**Confocal Micro-X-ray Fluorescence Spectroscopy with a Metal Jet Source** *L. Bauer* (p. 39)
12:00	**Determination of the L-fluorescence yields of bismuth** *J. P. Santos* (p. 28)	**Elemental Analysis of Human Hair by Confocal Micro-XRF Analysis** *T. Furusato* (p. 40)
12:15	**X-ray cascades emitted in interaction of slow highly charged Xe ions with metallic foils** *M. Pajek* (p. 29)	**A Compact Vibration Compensating Set-up for Scanning nm-XRF and STXM** *B. Beckhoff* (p. 41)
12:30	Lunch Break	

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	Chair: J. E. Fernández	Chair: J. Osán
14:00	Invited: **Off-resonant X-ray spectroscopy: from synchrotron to X-ray Free Electron Laser science** *J. Szlachetko* (p. 23)	
14:30	**Determination of fundamental parameter for the L-edges of gallium in GaSe with low uncertainties** *R. Unterumsberger* (p. 30)	**The ID21 beamline at ESRF: Sub-micron spectroscopy under cryo conditions for life and environmental sciences** *H. Castillo Michel* (p. 42)
14:45	**Monte Carlo simulation of an EDXRF setup with triaxial geometry: using Rayleigh to Compton ratio to evaluate the mean atomic number of unknown samples** *L. Martins* (p. 31)	**Laboratory confocal micro-XRF on cryo-fixated biological specimen** *F. Förste* (p. 43)
15:00	**Improved value of rhodium K fluorescence yield by direct measurement and using the decay scheme of ^{103m}Rh** *M.-C. Lépy* (p. 32)	**Elemental imaging of biological tissue in frozen hydrated state by micro-PIXE** *P. Vavpetič* (p. 44)
15:15	Coffee Break — sponsored by DECTRIS detecting the future	
	Session III: QUANTIFICATION METHODOLOGY AND METROLOGY – IN MEMORY OF PROF. H. EBEL Chair: C. Streli	Session IV: PIXE AND ELECTRON INDUCED XRS Chair: Ž. Šmit
15:45	**Developments of Quantitative software packages from RFA_WIN to ATI-Quant** *P. Wobrauschek* (p. 33)	**Ion micro-beam analyses of dust particles and co-deposits from JET with ITER-like wall** *S. Fazinić* (p. 45)
16:00	**Partial L-Shell Photoionization Cross Sections for fundamental parameter determination and XRS quantification models** *M. Kolbe* (p. 34)	**Study of complex samples using High Energy PIXE** *A. Subercaze* (p. 46)
16:15	**X-ray mass attenuation coefficients: a comparison of available tables and new measurements** *Y. Ménesguen* (p. 35)	**Qualitative study of Fe-Mn crust samples by High Resolution and High Energy PIXE** *M. Reis* (p. 47)
16:30	Fundamental Parameters Initiative	
⋮ 18:00	Poster Session I.	
19:00	Town hall reception & Ljubljana sightseeing	

New type of hard x-ray lasers pumped by X-FEL

Hitoki Yoneda

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Ultra-high intensity of hard x-rays produced by recent x-ray free electron lasers makes it possible to begin a new field of science in hard x-ray region. Specially, nonlinear optical and quantum optical phenomena in hard x-rays are only observed in high intensity focusing of x-rays. For example, at several 10^{19}W/cm^2, we observe high gain Kα emission in many solid density materials. In addition, by using several XFEL techiques to produce various x-ray pulses, we succeeded, using an injection-seeded Kα laser, to achieve ultra-narrow line width lasers with $h\nu/\Delta h\nu > 10^4$. [1]

Comparing to optical laser configurations, it is very difficult to use a cavity resonator for hard x-ray lasers. That is due to limitation of life time of the upper level of the laser transition and limited angle of reflection for hard x-rays. Comparing to various control methods of cavity resonators for optical lasers, this seems to be a drawback for hard x-ray lasers. To solve this difficulty, we consider distributed feedback lasers. The wavelength of the hard x-rays is similar to the lattice constant of solid crystals. In our experiment, $CuSO_4\ 5H_2O$ single crystal is used as a x-ray laser medium. After adjusting the crystal axes to a phase-matching condition between Kα laser and crystal lattice constant, cavity-controlled x-ray lasers are obtained. In some configurations, a narrower spectrum is observed without external seeding. This is the first evidence of emission control with the standing wave for hard x- ray lasers. We believe this technique will open new photonics in the hard x-ray region (~ 1 Ångstrom).

[1] H. Yoneda, et al., Nature, 524, 446 (2015).

X-ray Spectroscopy at Extreme Low and High Brilliance

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The development of X-ray sources, monochromators and detectors have been continuously enriching our research opportunities in the past decades. Dispersive setups have found their place beside the triple-axis spectrometers, multiple-analyzer instruments became wide spread, pushing X-ray spectroscopy techniques to very high performance at synchrotron beamlines. However, the oldest and newest type of sources in the laboratory and at the X-ray free electron lasers present very different research opportunities, and this talk concerns experiments with such sources.

In addition to frontier research, there is high demand for routine characterization of concentrated samples with the simplest high-energy resolution X-ray spectroscopies including XANES, EXAFS or XES, but such measurements have been hindered by the slow access to synchrotron radiation facilities. Recently, a few groups have started to work on overcoming this by developing novel laboratory spectrometers. Our group has been developing a laboratory von Hámos X-ray spectrometer, which offers rapid transmission experiments for X-ray absorption and is also capable of recording X-ray emission spectra. The use of a small-radius cylindrical analyzer crystal and a position sensitive detector enabled us to build a robust but flexible setup with low operational costs, while delivering spectra with good signal to noise ratio in reasonably short acquisition times. An illustrative example of the applications of laboratory XANES will be presented.[1,2]

In principle, all X-ray spectroscopy tools can be utilized to probe the ultrafast dynamics in pump-probe experiments.[3] However, synchrotron-based studies make use of picosecond-long pulses, and thus lack the necessary time resolution to unveil many of the details of electron and structural dynamics in photo-induced transformations. The very intense femtosecond pulses of X-ray free electron lasers permit us to exploit X-ray spectroscopy tools with the appropriate time resolution, offering direct access to the changes in the charge, spin and nuclear degrees of freedom during the elementary physical processes of a chemical reaction, photophysical transformation, or biological function. Results obtained on light-excited transition-metal-based model systems for photoswitchable or light-harvesting model functional molecules will be reported.[4]

[1] Z. Németh, J. Szlachetko, É. G. Bajnóczi, G. Vankó, Rev. Sci. Instrum., 87, 2016, 103105.

[2] É. G. Bajnóczi, Z. Németh, G. Vankó, Inorg. Chem. 56, 2017, 14220.

[3] G. Vankó *et al.*, J. Phys. Chem. C 119, 2015, 5888; A. M. March, *et al.* J. Phys. Chem. C 121, 2017, 2620.

[4] W. Zhang *et al.*, Nature 509, 2014, 345; S. E. Canton et al., Nat. Commun. 6, 2015, 6359; E. Biasin *et al.*, Phys. Rev. Lett. 117, 2016, 013002; K. Haldrup *et al.*, J. Phys. Chem. B 120, 2016, 1158.

Off-resonant X-ray spectroscopy: from synchrotron to X-ray Free Electron Laser science

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Many different X-ray spectroscopy techniques aims to study structure and functioning of matter. By examining the energy distribution of inner- and outer-shell atomic electrons quantum states, X-ray spectroscopy allow for elemental identification, determination of the atomic data and chemical analysis. The interaction of an X-ray photon with atomic electrons may induce different atomic excitation and decay processes. In the case of off-resonant X-ray approach the incident beam energy is fixed below the absorption edge of interest and the resulting decay transitions are measured with the high energy resolution [1, 2]. In this manner the off-resonant spectra directly reflect density of unoccupied states of scattering atom. The incidence beam energy for the high energy resolution off-resonant experiments has to be set low enough below ionization threshold to not induce normal fluorescence but possibly high enough to maintain sufficient scattering cross section for the inelastic scattering process. Thanks to the combination of off-resonant excitation processes with wavelength dispersive setups, the unoccupied electronic states of matter are probed in a scanning-free approach, spectral shape is independent on initial-state broadening as well as not affected by self-absorption effects [3, 4].

In this presentation we provide a general description of the high energy resolution off-resonant spectroscopy approach with a special focus on the derivation of the X-ray emission and X-ray absorption correspondence relation at off-resonant excitation conditions. A number of off-resonant experimental reports are reviewed in the field of chemistry and material science [5, 6]. We emphasize the applicability of the methodology to pulsed X-ray sources, like X-ray free electron lasers, and discuss experimental examples obtained at XFELs [7]. Finally, importance of off-resonant scattering process to study nonlinear interactions, like two-photon absorption, will be discussed [8, 9].

The work was partially supported by National Science Centre (Poland) under grant nos. 2015/18/E/ST3/00444 and 2015/19/B/ST2/00931.

[1] J. Szlachetko et al., Chem. Comm., 48, 2012, 10898.

[2] M. Kavčič et al., Phys. Rev. B 87, 2013, 075106.

[3] W. Błachucki et al., Phys. Rev. Lett. 112, 2014, 173003.

[4] W. Blachucki et al., Spectrochimica Acta B, 136, 2017, 23-33.

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[6] J. Szlachetko et al., J. Am. Chem. Soc. 135, 2013, 19071.

[7] J. Szlachetko et al., Struct. Dyn. 1, 2014, 021101.

[8] J. Szlachetko et al., Scientific Reports 6, 2016, 33292.

[9] K. Tyrala et al., Applied Sciences 7, 2017, 653.

High valence metal center molecule creation with high intensity XFEL pulse

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Studying the structure of complex systems by means of the 3rd and 4th generation radiation sources have been always associated with concern about the harmful influence of the probe beam on the target sample. The so called *probe-before-destroy* approach allows to profit from the high peak brightness of the pulsed X-ray sources without losing the information sought [1]. In this approach the system is probed before the damage occurs with an X-ray pulse shortened to tens of femtoseconds. The radiation damage is typically described as the Coulomb explosion and occurs after time of more than 50 fs [2]. It is, however, much faster when one takes into account the electronic structure modification [3].

In this work a solution of 0.1 moles of $Fe(CN)_6$ and 60 moles of H_2O was exposed to X-ray free-electron laser (XFEL) beam of 30 fs-short X-ray pulses. The photon energy was 7200 eV (88 eV above the Fe *K*-edge binding energy) and the photon flux was changed from 5.8×10^{30} to 2.4×10^{32} photon/(s×cm^2). The Fe *K*β emission spectrum was measured for each photon flux in shot-to-shot mode by means of a von Hamos geometry-based X-ray spectrometer equipped with an InSb(444) crystal and a CS-PAD 140K detector.

For increasing photon flux the obtained Fe *K*β emission spectral curve shifted to higher energies and the main line's intensity decreased. Detailed analysis of the electronic processes showed that this effect resulted from the Fe atoms' outer-shell ionization caused mainly by the photoelectrons and Auger electrons ejected from the O atoms.

In this study an aqueous solution of $Fe(CN)_6$ complex was exposed to an XFEL beam which caused Fe atoms' multiple ionization and braking of the Fe-C bonds. This process was observed with the element-specific X-ray emission spectroscopy method at 30 fs time scale when the structure integrity of the complex was preserved but the bonds between Fe and C were ruptured, resulting in a unique high valence state on the Fe site.

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[2] J. Kern *et al.*, Proceedings of the National Academy of Sciences 109(25), 2012, 9721–9726.
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Cascade Ge-L X-ray emission enhanced by Resonant Raman Scattering

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The cascade X-ray emission dominates the intensity of characteristic X-rays emitted after the relaxation of less-inner shell vacancies in the presence of deeper lying ones. Characteristic examples with relevance to X-ray Fluorescence (XRF) analysis are the cases when the exciting X-ray beam is adequately energetic to ionize the K or L atomic shells of an element, and thus the cascade emission of L or M lines takes place manifesting the contribution from the direct photoionization process. On the other hand, the Resonant Raman Scattering (RRS) is an inelastic scattering process that exhibits a resonant behavior as the energy of the incoming photon approaches from lower energies an absorption edge (K or L) of the target element. The final state of the RRS process includes a scattered photon with continuous spectrum, an inner-shell electron ejected in a continuum state and a higher shell (L or M) vacancy. This vacancy is actually the result of a 'virtual cascade' process that occurs through the RRS intermediate states, when an electronic transition from the L- or M-shells fills a virtual hole created in the K- or L-shells, respectively. There are rather few experimental studies which have been individually devoted to quantify and reveal systematics of these two phenomena [1-3].

In the present work we demonstrate that the cascade X-ray emission takes place and it is actually enhanced following a resonant behavior within the energy regime that the RRS evolves towards full X-ray fluorescence. This phenomenon is presented in the study of Ge-L X-ray emission with tunable monochromatic synchrotron radiation (3.7-14 keV) at the XRF beamline of Elettra Sincrotrone Trieste, operated using a Si(111) double crystal monochromator at 2.4 GeV electron beam energy [4]. As a target, a ~9.6 nm thin Ge deposited onto 200 nm silicon nitride membrane was used and the Ge characteristic (K, L) and RRS radiation were recorded by a silicon drift detector equipped with a polymer thin window [4]. Apart the individual studies of Ge-L cascade X-ray emission and of the KL-, KM- RRS scattering processes, the RRS enhanced Ge-L cross-section is quantified. Furthermore, it is proposed a photon-in photon-out method to deduce the fluorescence yield of the RRS process.

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Chemical state sensitivity of Cr $K^h\beta$ hypersatellites

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We report on the chemical sensitivity of Cr $K^h\beta$ ($M\rightarrow K^{-2}$) hypersatellite transitions induced by single-photon double K-shell ionization. The experiment was carried out at the Stanford Synchrotron Radiation Lightsource (SSRL) using the 7-crystal Johann-type hard x-ray spectrometer [1]. The $K^h\beta$ hypersatellite, $K\beta$ ($M\rightarrow K^{-1}$) diagram and valence-to-core (VtC) x-ray spectra were measured for Cr in four nominal oxidation states: Cr (Cr^0), Cr_2O_3 (Cr^{3+}), CrO_2 (Cr^{4+}), and $K_2Cr_2O_7$ (Cr^{6+}). The $K\beta$ diagram and VtC transitions of 3d transition metals are well recognized for chemical speciation. Numerous works have shown that the line energies, energy shifts, and relative intensities provide information on the oxidation state, ligand type and metal-ligand bond length, and the effective spin state. eg., [2-4]. In contrast, the $K^h\beta$ hypersatellite transitions induced by photon impact were reported only for elemental samples, Fe [5] and Ti [6], and hitherto the influence of the chemical state on the $K^h\beta$ hypersatellite transitions has not been explored.

For the $K\beta$ diagram and VtC transitions the present study confirmed the general expected trends with the oxidation state for the line energies, energy shifts, relative intensities and line widths. The $K^h\beta$ ($M\rightarrow K^{-2}$) hypersatellite transitions were found to exhibit complex spectral line shapes and a characteristic low energy shoulder whose relative energy and intensity varied with the oxidation state. Furthermore, the energies and energy shifts of the $K^h\beta$ to $K\beta$ transitions were determined and compared to recent MCDF calculations. An excellent agreement was obtained for the Cr metal energy shift. Most interesting was the finding of a linear relationship with the nominal oxidation state, with a slope of -0.109(6) eV per oxidation increment, of the energy differences of the main $K^h\beta$ component to the centre of gravity of the main $K\beta$ line for Cr and Cr compounds. The obtained results demonstrate the potential of the $K^h\beta$ hypersatellite transitions for chemical speciation and stringent comparison with electronic structure calculations.

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Theoretical Calculations of Atomic Fundamental Parameters for X-Ray Methodologies

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X-ray based techniques form an ever-increasing set of analytical applications in areas as varied as medical technology, renewable energy, semiconductor fabrication, law enforcement, planetary exploration, cultural heritage studies, just to name a few. However, in order for the scientific and technological boundaries of X-ray techniques to expand, we need to reassess the available data expressing the interactions of X-rays with matter, which we label Fundamental Parameters (FP). Most of the commercial and research software for spectra fitting and Monte-Carlo simulations, are based on sets of X-ray/matter interaction data that were measured and calculated several decades ago, with very high uncertainties. For *L*- and *M*-shell, especially in mid to low atomic number, the results are scarce, and most of the databases extrapolate from higher Z data.

In our group, we have calculated a large set of FP, ranging from fluorescence yields, transition rates, photoelectric cross sections, etc., for selected elements across the whole periodic table. For this purpose, we use a MultiConfiguration Dirac-Fock (MCDF) package developed by Desclaux and Indelicato [1] that allows us to include self-consistently first-order retardation terms of the Breit interaction and the Uelhing contribution to the vacuum polarization terms.

Most of our calculations are checked against state-of-the-art experiments performed by metrology and research laboratories from all over the world [2-4]. It is our goal that, through the benchmarking of our method, in the cases where experiments are hard to perform, our results could act as low uncertainty standards and interpolation points on extensive experimental databases.

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Determination of the *L*-fluorescence yields of bismuth

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The knowledge of atomic fundamental parameters, such as fluorescence yields or mass attenuation coefficients with low uncertainties, is of decisive importance in elemental quantification involving X-ray fluorescence analysis techniques. Frequently, discrepancies are found in the available databases, calling for further theoretical and experimental studies. For example, fluorescence yields databases show different values for the majority of the elements.

In this work, we calculated the fluorescence yields of the three *L*-subshells of bismuth using the MultiConfiguration Dirac-Fock (MCDF) package developed by Desclaux and Indelicato [1], which allows us to include self-consistently first-order retardation terms of the Breit interaction, and the Uelhing contribution to the vacuum polarization.

The theoretical results obtained in this work were compared to the experimental ones determined by means of a reflection geometry setup at SOLEIL (France). The relative agreement was found to be better than 11%.

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X-ray cascades emitted in interaction of slow highly charged Xe ions with metallic foils

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In interaction of slow highly charged ions (HCI) with matter the "hollow atoms" are formed as a result of ultrafast neutralization of HCI at the surface [1]. The X-rays emitted in deexcitation of hollow atoms carry information about *formation*, *structure* and *relaxation* of such exotic atoms. In this work we report on the measurements of X-rays emitted from ~8 keV×q Xe^{q+} ions (q=26-35) interacting with metallic Be foil. The ion beams were produced in the Dreebit EBIS-A facility [2]. The X-rays were measured with XFlash silicon drift detector (SDD) having a resolution of about 80 eV in 1-2 keV photon energy range studied.

The M-X-rays measured for different charge states of Xe^{q+} ions were interpreted in terms of dominating electric dipole nf→3d transitions with a small contribution of overlapping nl→4,l-1 transitions (see Fig. 1). The energies of these transitions, including their x-ray *satellites* and *hypersatellites*, were calculated using MCDF method implemented in the GRASP code [3]. The structure of measured M-X-rays generally support a picture of radiative X-ray cascade following fast neutralization of HCI at a metallic surface. However, we found a strong contribution of the internal dielectronic excitation (IDE) process [5] responsible for creation of additional vacancies in the core of Xe^{q+} ions. In particular, the IDE process is crucial for interpretation of observed M-X-rays for Xe^{26+} ions having no initial vacancies in the M-shell.

Generally, the measured M-X-rays can be explained in terms of the radiative deexcitation cascade involving n-states with $n \leq 16$ (see Fig.1). For estimated critical Rydberg state for resonant neutralization of Xe^{35+} ions at Be surface $n_c \sim 30$ the observed X-rays seems to be insensitive to early, very fast stage of the deexcitation process, which was recently proposed to be explained by the interatomic Coulombic decay (ICD) mechanism [6]. We found that the lifetimes of observed X-ray transitions set the time scale for the deexcitation process, which is of order of ns in our case. Additionally, we found that the radiative deexcition cascade developes for Rydberg states below $n \sim 15$, which is in qualitative agreement with the prediction of ICD model [6].

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Determination of fundamental parameter for the L-edges of gallium in GaSe with low uncertainties

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The determination of fundamental parameters (FP) is an important part of reliable, reference-free quantitative X-ray fluorescence analysis (XRF) [1, 2]. In order to reduce the uncertainties of the FP, transmission measurements of the samples have to be performed thus allowing to experimentally determining self-absorption correction factors. For reference-free quantitative XRF with lower excitation energies, the uncertainties of the fundamental parameter associated with L-edges are crucial for the total uncertainty of the quantification, especially for excitation energies above the L1-edge of the respective element. In this work, the fluorescence yields and Coster-Kronig transition probabilities for the L-edges of Ga were determined with considerably reduced uncertainties.

Due to the high absorption of radiation in the soft x-ray range, it is necessary to reduce the thickness of the samples for transmission measurements. Here, a nominal 300 nm thin GaSe layer was deposited on a thin silicon-nitrate window for measuring both the transmission and the fluorescence intensities simultaneously in order to perform absorption correction without having to rely on literature database values of the mass attenuation coefficients. In order to reduce the uncertainty of the spectral deconvolution, a silicon-drift-detector (SDD) with an optimized energy resolution was employed. The measurements were carried out at the plane-grating monochromator (PGM) beamline in the PTB laboratory at BESSY II using monochromatized undulator radiation and calibrated instrumentation [3, 4].

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Monte Carlo simulation of an EDXRF setup with triaxial geometry: using Rayleigh to Compton ratio to evaluate the mean atomic number of unknown samples

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Energy Dispersive X-ray Fluorescence spectrometry is a non-destructive analytical technique that allows multi-element analysis of a large variety of materials in a relatively fast and simple way. The analysis of the fluorescence peaks in the EDXRF spectrum allows elemental identification and quantification. Additional information can be obtained from analysing the Compton and Rayleigh scattering peaks. Since Compton and Rayleigh scattering cross sections are both dependent on the atomic number Z, the Rayleigh-to-Compton intensity ratio, R_{RC}, can be used to evaluate the mean atomic number Z_{ef} of the matrix.

The calibration curve $R_{\mathrm{RC}} = f(Z_{\mathrm{ef}})$ can be obtained by measuring the Rayleigh-to-Compton intensity ratios of several reference materials with known composition and Z_{ef} for a given experimental setup. This method permits the determination of the Z_{ef} of unknown samples [1, 2]. Due to high variation of Rayleigh scattering cross section in the low Z range, this method is highly sensitive for low Z_{ef} matrices and allows to perceive variations in the matrix that wouldn't be possible from the spectral lines. In a typical setup, where the sample is excited by polychromatic source, this method is affected mainly by the additional background under the scattering peaks and the additional Compton broadening, which may lead to high deviations.

In this work, the method is implemented using a spectrometer in a triaxial geometry between the X-ray source, a secondary target, the sample and the detector. In parallel we simulated the curve through the implementation of Geant4 simulations of the same spectrometer [3].

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Improved value of rhodium K fluorescence yield by direct measurement and using the decay scheme of ^{103m}Rh

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A first experiment to determine K fluorescence yield of rhodium was performed at SOLEIL synchrotron facilty, resulting in a value with 5 % relative uncertainty [1]. It was decided to iterate the measurement with improved experimental conditions to refine this result. Thin foils of rhodium in metallic state were first used to provide accurate values of the mass attenuation coefficients of rhodium in the 4 keV to 35 keV energy range. These were measured in a transmission mode, at the METROLOGY beamline of SOLEIL, in a dedicated goniometer, CASTOR [2] equipped with calibrated photodiodes and energy-dispersive detectors.

The fluorescence yield was determined using a reflection configuration where the rhodium target is at 45° from both the incident beam and the energy-dispersive detector. In parallel, the intensity of the beam transmitted through the target is recorded with a photodiode. The measurement was performed for several incident energies in the 24 to 30 keV energy range. The peaks of interest were processed using the COLEGRAM software, which allows detailed fitting of the peak shape [3]. The new resulting value of the niobium K fluorescence yield, 0,795 (20), is consistent with the older measurement (0,809(50)) and the uncertainty is twice lower.

Complementary measurements were performed with a solution of ^{103m}Rh, which is a radioisotope decaying by gamma transition and emitting mainly rhodium X-rays. The absolute intensity of KX-rays was measured by a high-purity germanium detector, accurately calibrated with radioactive standards in the 10 to 120 keV energy range. The radionuclide activity was determined by liquid scintillation counting using the Triple-to-Double Coincidence Ratio which provides results with about 0,2 % relative standard uncertainty [4]. The resulting KX-ray emission intensities are derived with about 2 % relative combined standard uncertainty. These are directly linked to the rhodium K fluorescence yield through the ^{103m}Rh conversion coefficients.

Both approaches, leading to consistent results, will be presented and discussed.

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Developments of Quantitative software packages from RFA_WIN to ATI-Quant

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Part of the valuable scientific work of Horst Ebel was leading to a user friendly version of a software package named RFA_WIN developed by S.REZAI AFSHAR, R. SVAGERA , H.EBEL, which was based on a fundamental parameter data base by M.Mantler. It was useful to achieve quantitative results applying fundamental parameters and used results from experimental data for the spectral distribution of x-ray tubes done at the Institute for Technical Physics TU Wien. Based on the experiments, theoretical tube spectra with all influence parameters as HV, mA, angle of incidence of the electrons, photon emission angle, anode material, Be window thickness were used to create best theoretical calculation of the experimental setup [1]. Data were also compared with theoretical results from other researchers e.g. Kramers, Wiederschwinger, Love, Scott and Pella. The complete corrections for absorption and secondary excitation are considered. Calculation of the detector efficiency completes the input options and allows the determination of concentrations of the elements in a sample. Input starts with net counts and serves as basic input information for the quantitative results. In continuation of Ebel´s work a new software package named ATI-QUANT was developed at Atominstitut, TU Wien as a result of several Master's theses [2], [3]. The software is taking similarly into account all experimental data of source, sample and detector. In particular the following tube parameters are considered: anode material, details of the tube design, e.g. electron incident/photon emission angle, window material and thickness, solid angle for the emission/detection, finally data of high voltage and current - thus allowing the calculation of the source photon flux on the sample. Further, the originally calculated tube spectra can be corrected according to the usage of spectral modification devices. This typically includes filter materials of any material and thickness or spectral modifiers as mirrors for a high energy cut-off, multilayers or crystals resulting in a quasi- or sharp monochromatic beam. Moreover, changes in the spectral distribution by using polycapillaries can be simulated by applying mathematical functions. The detector parameters are requested to calculate the efficiency, and even a filter in front of the detector can be added. User can choose between thin films, intermediate and thick samples for further fundamental parameters calculations. ATI-QUANT is correcting for absorption and inter-element effects. The software factors in various experimental conditions, e.g. analysis in total reflection geometry with internal standard; thick/thin samples, or presence of oxides. Results from standard reference materials measured under different conditions are presented to show the applicability of various excitation conditions.

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Partial L-Shell Photoionization Cross Sections for fundamental parameter determination and XRS quantification models

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In memory of Prof. Dr. Horst Ebel

The Sherman equation approach for quantification in X-ray spectrometry is dependent on reliable knowledge of the fundamental parameters (FP) involved in the photon-matter interactions inside the samples. The need to know these parameters very accurately is even more evident as the development of new materials is progressing faster than the availability of appropriate reference samples. In this regard, a reference measurement method, such as SI traceable X-ray Fluorescence analysis, is crucial for supporting both material developments and the related understanding of the correlation of materials' functionality with their chemical and physical properties.

The provision of well-known FP data including their respective uncertainties is indispensable for quantification in XRF algorithms, which is an important task to ensure the characterization of materials. *Horst Ebel* et al. provided, for instance, a *numerical description of photoelectric absorption coefficients for fundamental parameter programs* [1]. Meanwhile the energy dependent slope of these coefficients could be confirmed experimentally [2]. These coefficients were calculated theoretically by Scofield [3], and carefully evaluated and implemented by Ebel et al.

Employing a reference-free XRF approach for FP determinations, new data of L-subshells of high and medium Z elements, such as Coster-Kronig probabilities, fluorescence yields as well as subshell photoionization cross sections, have been experimentally determined [4] and compared to the available theoretical calculations [3]. The understanding of the diverging energetic behavior of the three L-subshell photo ionization cross sections [1,2,5], leads to significant improvements in quantitative analysis, as compared to the IUPAC recommendation of using constant jump ratios. This confirmed the high relevance of careful FP-data compilations as performed by Horst Ebel for the XRF community.

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X-ray mass attenuation coefficients: a comparison of available tables and new measurements

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To the memory of Prof. Dr. Horst Ebel

X-ray applications based on fluorescence analysis for quantification with or without reference specimens require an accurate knowledge of fundamental atomic data to provide reliable results associated with low associated uncertainties. For example, mass attenuation coefficients are basic parameters characterizing the interaction of the incident beam in the sample and also the attenuation of the emitted fluorescent radiation. Users of attenuation coefficients can find these collected in databases made accessible through the internet on websites such as the National Institute of Standards and Technology (NIST) one (http://www.nist.gov/pml/data/index.cfm), which provides the compilation made by Hubbell, under the name XCOM. Certain measurements and calculations carried out by Chantler are also made available by NIST under the name FFAST. The database from the Center for X-Ray Optics (CXRO) calculates filter transmission, mirror reflectivity etc. based on Henke’s compilation. Another accessible database called EPDL97 [1] has been assembled by the AIEA. Ebel’s table can be found in the literature [2].

Although very practical for the user, some of these tables are based on rather old measurements or on theoretical calculations where measurements were missing. However, the associated uncertainties are often rather quite large, especially for low photon energies, i.e., below 1 keV. Indeed, the smaller the photon energy, the more difficult the measurement of mass attenuation coefficients with reliable uncertainties becomes. The estimated uncertainties of existing values below 1 keV are a few % for all elements and certainly above 25 % for photon energies below 500 eV [3]. Recent measurements have also revealed significant differences of a few % above certain K-edge absorption thresholds [4] for transition metals.

New measurements of mass attenuation coefficients carried out by the Laboratoire National Henri Becquerel took the advantage of using tunable monochromatic radiation at SOLEIL synchrotron, on the METROLOGIE beamline and using a specific procedure. Within the frame of different institutional and industrial metrology research projects, the LNHB & partners studied several elements from photon energies as low as 100 eV up to 35 keV, special care was taken to ensure reliable uncertainties.

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Multimodal imaging of biological samples: correlation of µXRF with MALDI-MSI and with LA-ICP-MS

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The combination of the various imaging methods, although challenging, breaks new ground in the investigation of biological samples. X-ray fluorescence analysis (XRF), due to its distinctive advantage of being non-destructive technique, is a desired candidate for coupling with other elemental and molecular imaging methods. The PhD program “Molecular and Elemental Imaging in Biosciences (MEIBio)” of TU Wien, Vienna, provided an ideal opportunity for combining µXRF with other cutting-edge imaging techniques, such as matrix-assisted laser desorption/ionisation mass spectrometry imaging (MALDI-MSI) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

For this project the in-house built µXRF spectrometer of Atominstitut (ATI) was employed. The spectrometer is equipped with a Rh-anode low power tube (20 W), the tube settings used were: voltage - 50.0 kV, current - 0.4 mA. The system features a 30 mm2 Si(Li) detector (LN2-cooled) with a 300 nm ultrathin polymer window (UTW). A polycapillary optic (full lens) was used to focus the primary beam on the sample surface; the beam size determined for Cu-Kα (8.047 keV) was 50 µm× 50 µm. All the measurements were performed in vacuum conditions.

The capabilities of the spectrometer for measurements of biological samples were recently demonstrated in imaging of bone tissue [1].

MALDI-MSI is a molecular imaging method, therefore, if combined with µXRF analysis, can provide the comprehensive coverage of both molecular and elemental structure of the sample. The samples used for MALDI-µXRF analysis were thin cuts (~20 µm) of chicken finger, containing both soft tissues and calcified tissue (bone).

LA-ICP-MS provides elemental information with lateral resolution comparable to µXRF. For this part of the project sample of human femoral head was prepared in thin cuts (below 50 µm).

The approach to the combination of µXRF with other imaging methods, including the sample preparation requirements will be discussed, and the results of combined µXRF-MALDI and µXRF-LA-ICP-MS projects will be presented.

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High Speed Simultaneous XRD-XRF Mapping with the Color X-ray Camera

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The Color X-ray Camera (CXC) [1] is a unique imaging spectrometer capable of measuring both the position and energy of each X-ray event on the detector, both with high resolution. This enables the simultaneous collection and analytical separation of both X-ray fluorescence and X-ray diffraction [2]. When combined with a micro focused X-ray source, the CXC can create X-ray maps of materials with mapping dwell times as low as 10 ms per point. In this relatively short measurement time, a full X-ray spectrum with an energy resolution of 145 eV at Mn Kα is recorded along with a diffraction pattern with an angular range of approximately 150° 2θ. This new imaging technique, enabled by the CXC, is useful for a variety of both compositionally and crystallographically heterogeneous samples. One example application is in the analysis of steel, which is compositionally consistent, but contains large crystals in a variety of orientations. To create the images shown in Figure 1, a 100 µm X-ray beam was scanned over a sample area measuring 30 mm x 50 mm. In the 200 ms per point dwell time (total mapping time = 13 hours), a diffraction pattern and fluorescence spectrum were recorded. As the sample contained over 99 wt% Fe, the apparent compositional heterogeneity identified in the uncorrected Fe fluorescence image was due to crystal structure changes, not compositional changes. Using the diffraction data, a machine learning algorithm was able to identify 25 different classes of crystals present in the material.

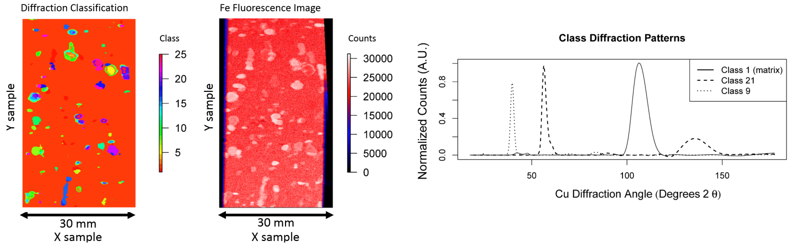

Figure 1: Results from the analysis of a steel sample (X,Y) using the simultaneous XRD-XRF mapping technique with the CXC. The apparent compositional heterogeneity seen in the uncorrected Fe image (middle) is identified as diffraction using our method. Diffraction patterns (left) from each of the grains were classified using a machine learning algorithm and the diffraction patterns from three of those classes are plotted (right).

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Analytical X-ray Microscopy in the Soft Energy Range with Very Large Solid Angle of Detection

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Scanning transmission X-ray microscopy (STXM) in the soft energy range, especially in combination with X-ray fluorescence detection, is becoming an increasingly important tool for life sciences. Biomedical material has generally a low fluorescence signal. Hence, high detector efficiency (e.g through a large solid angle) is indispensable to avoid long measurement times and radiation damage.

A novel STXM endstation has been installed at the P04 beamline at PETRA III, profiting of its high brilliance [1]. Recently, a 4-channel fluorescence detector offering a solid angle of detection of up to 1.2 sr was integrated (see Fig 1). Since biomedical research often involves samples prone to radiation damage, this unique combination of a high brilliance beamline and the high detection efficiency of the endstation offers new analytical possibilities for this field.

As a first biological application and in collaboration with Prof. Heeren from the University Medical Center of Hamburg-Eppendorf, our endstation was employed to investigate the lipid metabolism in mice cells with respect to the iron distribution in cold-activated brown adipose tissue (BAT). Under cold conditions brown adipose tissue produces heat by burning huge amounts of lipids correcting hyperlipidemia and atherosclerotic plaque progression [2]. With measurement times of down to 50 ms per pixel we could carry out fast scans for the investigation of trace elements in these biomedical samples.

The principal of the setup, especially with respect to the unique 4-channel SDD, will be presented. In addition the challenges of the huge solid angle of detection for analytical quantification approaches will be discussed and first applications will be shown.

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Confocal Micro-X-ray Fluorescence Spectroscopy with a Metal Jet Source

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Confocal micro-X-ray fluorescence spectroscopy (CMXRF) enables three-dimensional elemental analysis with a spatial resolution in the micrometer range. Because of its non-destructiveness, the method is applicable in many different fields such as biology, art, archaeology or geology.

For CMXRF an excitation beam is focused with an X-ray optic onto a sample and the view of the detector is limited using a second optic. This is typically realized by two polycapillary lenses due to their broadband transmission and efficiency. This confocal arrangement creates a small probing volume, from which information is in first approximation exclusively derived. For 3D elemental analysis, the sample is moved stepwise through the probing volume and in each position a fluorescence spectrum is detected.

Due to the reduced efficiency compared to MXRF caused by the second optic and the necessity of moving the sample in three dimensions, measurement times are long. To widen the applicability of the technique independent on large-scale facilities, more efficient setups are desirable.

We demonstrate a CMXRF setup using a metal jet X-ray source, which is currently one of the brightest X-ray sources for laboratory setups. Characterization measurements will be presented and with the help of the 3D imaging of a millet seed the performance is compared to measurements obtained with a state-of-the-art X-ray tube setup [1].

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Elemental Analysis of Human Hair by Confocal Micro-XRF Analysis

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XRF analysis enables the compositional analysis nondestructively. In particular, confocal micro-XRF analysis is effective as a method of acquiring the element distribution inside the sample. Meanwhile, minor components such as Ca and Zn are included in the hair. Therefore, by analyzing the hair, it is possible to evaluate excess or deficiency of these elements and examine harmful metals in the body. In this study, we aimed to clarify element distribution information on the hair cross section by confocal micro-XRF analysis.

Micro-XRF analysis was carried out in 1 cm steps from the root to the tip of a single hair. The areas of analysis on the cross section orthogonal to the hair was 180 μm × 180 μm. The spatial resolution of the apparatus used in this study was 56.0 μm at 1.49 keV [1]. The mapping results obtained by confocal micro-XRF analysis are shown in Fig. 1. As shown in Fig. 1, the intensity of Ca Kα strongly appeared in the upper left part. However, since the detector is in the upper left direction in Fig. 1, the fluorescent X-ray generated from the lower right part is absorbed by the hair itself until it reaches the detector. Therefore, we considered that the Ca is uniformly distributed. Since S Kα is lower in energy than Ca Kα, it seems that absorption effect appears more strongly. It is necessary to consider the influence of such self-absorption in hair analysis [2, 3].

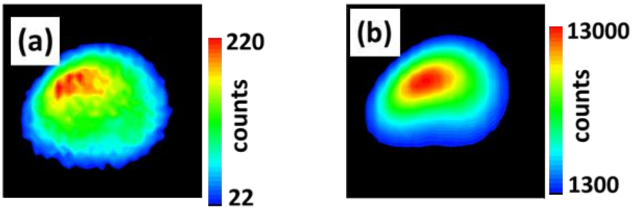

Fig. 1 XRF elemental maps of human hair.
(a) Ca Kα (b) S Kα (areas of analysis : 180 μm×180 μm)

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A Compact Vibration Compensating Set-up for Scanning nm-XRF and STXM

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Synchrotron radiation (SR) based scanning X-ray spectroscopy (XRS) can determine both elemental concentrations and chemical binding states with high spatial resolution down to the nanoscale. At SR facilities there are currently only a few dedicated scanning X-ray microscopes that offer XRF analysis in combination with scanning transmission X-ray microscopy (STXM).

A novel kind of vibration compensating XRF set-up have pushed the spatial resolution towards the 100 nm regime. With the advent of UHV-compatible piezo stages with nanometer resolution, it became possible to mount optical elements in a compact manner on a single platform. Relevant parts of any external vibrations can be compensated for by such a single platform. The lay-out of its stages and related holders is to ensure amplitudes of relative vibrational movements to be smaller than the absolute ones by avoiding any resonance frequencies. We realized this approach in a compact set-up to align diagnostics, zone plates, order sorting apertures (OSA) and samples on a single mounting plate. This plate was mounted on a sample manipulator of an UHV XRF instrument [1]. Its overall size offers versatile areas of operation as the compact set-up can be readily inserted in a wide range of XRF chambers [2] through their load-locks. The optical elements of the scanning X-ray microscope consist of an Au zone plate with an 50 µm integrated central stop and an independent 50 µm OSA. All measurements were carried out with photon energy of 1500 eV at PTB’s plane grating monochromator beamline for undulator radiation at BESSY II.

Two objects were used to examine the performance of the novel type of scanning nm-XRF microscope. The test object for STXM was a Siemens star on a Si3N4 membrane completely covered with a 133 nm thick layer of W, while for the fluorescence experiments we chose a silicon wafer with an alternating Ge-Si-wafer bar test structure. The smallest structures (approximately 100 nm) were clearly resolved in transmission while the resolution was slightly larger in XRF mode. Here, the Ge-Si-sample was measured at an angle of incidence of 60° with an energy-dispersive silicon drift detector (SDD) calibrated by PTB. The highest spatial resolution achieved in initial experiments was in the range of 130 nm to 140 nm which is in line with the probed sample dimensions. Follow-up experiments are going to be focused at traceable XRS of appropriate and even smaller test structures.

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The ID21 beamline at ESRF: Sub-micron spectroscopy under cryo conditions for life and environmental sciences

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The ID21 beamline at the European Synchrotron Radiation facility (ESRF) is dedicated to micro X-ray fluorescence (µXRF) and micro X-ray absorption spectroscopy (µXAS) in the tender X-ray range (2-9keV). It has an important scientific activity in the fields of life and environmental sciences, in particular for studying the fate of metals in the environment. Indeed, metal bioavailability and toxicity in the environment is speciation dependent. Metal speciation determines the distribution at tissue and cellular level, and ultimately the various mechanisms of toxicity and detoxification. The chemical form and distribution of a metal are also important to environmental risk assessment. This type of questions can be tackled thanks to the ID21 X-ray microscope.

Improvements have been done to offer a reliable and easy-to-operate passively cooled cryogenic stage, as well as the required auxiliary equipment for sample transport, storage and preparation. Thus, cryo-fixed samples are better preserved under intense X-ray beams and the elemental distributions, chemical states, and sample morphologies are close to the *in-vivo* state under frozen-hydrated conditions [1].

Software developments have also been done to automatize acquisition of sub-micron scale XANES 2D maps (in XRF mode). The acquisition of 2D µXRF maps is repeated a hundred times, for varying energies of the incoming beam. 3D image stacks, the third dimension being the incoming beam energy, are created for all detectable elements and several counters (incoming/transmitted signal). The so-called “Spectrocrunch” python software library includes all the routines needed for data processing: dead-time correction, normalization by I_0, fitting using PyMca[2] software and image realignment based on feature detection or optimization of mutual information between maps. This tool also offers a real-time realignment of maps, to correct possible sample or beam drift over time and/ or energy, during the acquisitions.

This presentation will highlight experiments performed at ID21 taking full advantage of these beamline capabilities to investigate the distribution and speciation of engineered nanomaterials in complex biological samples (plant [3] and animal tissue [4], and cells [5]). Finally, the future capabilities expected with the refurbishment of ID21 in the context of ESRF-EBS upgrade will be presented.

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Laboratory confocal micro-XRF on cryo-fixated biological specimen

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The non-destructive imaging of elemental distributions in specimen is of high interest in many fields of research as for example in biology, art, geology or archaeometry, when sectioning or sampling is undesirable. In biology, specimen have a high content of water, which leads to the challenge, that specimen must be fixated to stop a change in elemental distributions due to drying or shrinking during measurements. Most commonly specimens are either freeze-dried or cryo-fixated, the latter being the method of choice regarding the maximal sample integrity.

X-ray fluorescence (XRF) techniques like micro-XRF (up to 2D) or confocal micro-XRF (up to 3D) can be combined with a cryogenic sample environment, thus, fulfilling the above-mentioned requirements for elemental imaging of biological specimen.

In this work, a modified commercial micro-XRF spectrometer (M4 Tornado, Bruker Nano GmbH) is used [1]. The instrument enables micro-XRF as well as confocal micro-XRF with high speed acquisition and lateral resolutions of 25 μm at Cu Kα. We present the addition of a liquid nitrogen Cryo-Jet (Oxford Instruments) which cools the specimen to 120 K rendering longtime measurements of biological specimen feasible. Characterization and stability measurements show the feasibility for cryo-measurements in the laboratory. Measurements on various biological sampling systems will be presented.

In addition to compensate absorption effects inside the sample during confocal measurements an absorption correction procedure was developed[2]. The applicability will be shown on confocal cryo measurements performed on sunflower roots, which show different uptake of heavy metals.

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Elemental imaging of biological tissue in frozen hydrated state by micro-PIXE

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Within the efforts to optimally preserve the biological tissue morphology for elemental imaging by micro-PIXE, we developed the instrumentation and the sample preparation protocols in frozen hydrated state [1]. We installed a cryostat to the micro-PIXE chamber and carefully designed new sample holders, which enable the primary proton beam transmission. In this configuration, we are applying five detection systems simultaneously during the measurement: low- and high-energy X-ray detector, elastic backscattering detector (EBS), on-off axis STIM [2] and a detector measuring the backscattering protons from rotating chopper positioned in the primary beam. The combined information on the light matrix composition and the sample thickness, obtained by EBS and STIM, combined by proton flux information from the chopper system, enables fully quantitative elemental mapping by micro-PIXE.

The tissue slices are shock-frozen, cryotome-cut, mounted to the dedicated sample holders within two ultra-thin pioloform foils, transported and stored in liquid nitrogen for the forthcoming measurements. The frozen hydrated sample capability is especially beneficial in the cases, where lyophilisation results in sample disintegration, i.e. in the case of plant or animal samples containing large fraction of water [3]. The system enables us to analyze various types of tissue, ranging from plant samples to the animal and human tissue, with a lateral resolution of 600 nanometers [4].

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Ion micro-beam analyses of dust particles and co-deposits from JET with ITER-like wall

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Plasma-surface interaction processes in devices for controlled thermonuclear fusion cause erosion of plasma-facing components (PFC). A certain part of material eroded from the walls is converted into dust. Plasma dynamics in a tokamak includes transport of dust down toward the divertor. Its formation in present-day machines does not pose operation issues, because quantities are small, especially in the presence of metal walls. However, in International Thermonuclear Experimental Reactor (ITER), which is under construction in France, generation of large quantities of loose particles could create serious problems. Therefore, studies of metal dust generation, composition, size and morphology of particles in the Joint European Torus (JET) tokamak with the ITER-like wall (ILW), is a topic of vital interest to next-step fusion devices because of safety issues in plasma operation.

In this presentation we report about simultaneous use of Nuclear Reaction Analysis (NRA) and Particle-Induced X-ray Emission (PIXE) with focused 4 MeV ^{3}He micro-beam to study composition of dust particles related to the JET tokamak operation with the ITER-Like Wall, with the focus on 'beryllium rich particles' and their main constituents like beryllium, deuterium and heavier metals like Cr, Fe Ni, Mo, W.

Dust sampled after the second ILW campaign (2013-2014) using a sticky carbon pad from the divertor was studied. The particles found are composed of a mix of co-deposited species up to 100 x 120 µm in size with the thickness of 30-40 µm. The main constituents are: deuterium from the fusion fuel, beryllium and tungsten originating from the main plasma-facing components, nickel and chromium from Inconel grills of antennas for auxiliary plasma heating. Elemental concentrations of major and minor elements have been estimated by quantitative iterative NRA-PIXE analysis. NRA-PIXE data acquisition and analytical procedures are presented and main results elaborated.

Study of complex samples using High Energy PIXE

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High Energy Protons Induced X-ray emission (HEPIXE) is a well-suited method to analyze thick samples and heavy elements [1]. The protons range is larger than the thickness of the investigated sample, and the detection of the energetics K X-rays of heavy elements is possible thanks to the large production cross-section [2]. In many investigated samples, the elemental concentration is not evenly distributed [1]. The inhomogeneity can be in the bulk, such as layers of different composition in paintings, and on the samples surface of soils or rocks. Therefore analysis method based on the X-rays detection such as PIXE can be biased due to non-homogeneous surface or bulk. However, the low energy loss of high-energy protons, combined with a smooth variation of the K X-ray production cross sections [3], induce a low variation of this cross section during the experiments. The data analysis is therefore simplified and HEPIXE could be a well-suited method to study non-homogeneous objects.

In our previous works, on thick multi-layers samples, we have demonstrated that it is possible to provide the thicknesses and the sequences of the layers using the differential effect on the X-rays absorption induced by the variation of the detection angle [4]. In this work, a complementary method to analyze complex multi-layers objects like paintings is developed. It is based on the differential effect by using different incident energy proton beam between 17 MeV and 68 MeV delivered by the cyclotron ARRONAX. To study the effect of the surface homogeneity, some irradiations of samples with different grain sizes and chemical compositions, using 68 MeV protons, have been performed.

A description of the experimental setup and the results provide by our experiments on various samples will be presented. The contribution of the HEPIXE method for the analysis of non-homogeneous objects (in-depth and surface) will be discussed.

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Qualitative study of Fe-Mn crust samples by High Resolution and High Energy PIXE

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Samples from the Portuguese continental self were irradiated at High Resolution High X-ray Energy (HRHE)-PIXE setup of C2TN [1] using proton and oxygen beams at various energies. Simultaneous spectra were collected using both the CdTe and the X-ray microcalorimeter spectrometer (XMS) detectors of the facility. Spectra acquired at various energies and using different ions beam provide different views upon the same sample. In this study, samples from two Fe-Mn nodule samples collected in the Portuguese continental self were irradiated and analysed qualitatively using the DT2 code [2]. Various interesting as well as puzzeling results are discussed. Advantages and drawbacks from both the XMS and the CdTe detector, as well as of the use of different types of beams and different energies will be discussed in detail. It will be shown that even non-quantitative PIXE, can provide very interesting results when a wide range of energies and various beam conditions are used.

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8.1 Poster session I

8.1.1 Interactions of X-rays with matter and fundamental parameters

8.1.2 Microbeam techniques, confocal XRF and X-ray imaging

23 **Evaluation of the Structural Characteristics and the Fading Effects of Image Plates**
Aline Silva, Davi Oliveira, Célio Gomes, Alessandra Machado, Joseilson Nascimento and Ricardo Lopes (p. 77)

24 **Characterization of Carbonate Rocks Through X-ray Fluorescence and Computed Microtomography**
Alessandra Machado, Ramon Santos, Amanda Rodrigues, Leonardo Borghi, Davi Oliveira, Marcelino Anjos and Ricardo Lopes (p. 78)

25 **Elemental distribution by synchrotron X-ray microfluorescence of prostate 3D cell culture**
Karolynne Rocha, Roberta Leitão, Eliane Barros, Maria Oliveira, Catarine Canellas, Marcelino Anjos, Luiz Nasciutti and Ricardo Lopes (p. 79)

26 **What's hidden for X-Ray? An archaeological plant study**
Cristina Marilin Calo, Marcia De Almeida Rizzutto, Carlos S. B. Dias, Sandra M. Carmello-Guerreiro and Eduardo Góes Neves (p. 80)

27 **Effects of angiotensin II receptor blockers in coronary arteries of hypertensive rats: analysis of elemental distribution using LEXRF**
Arissa Pickler, Delson Braz, Andrea Mantuano, Carla Lemos Mota, Samara Ferreira-Machado, Cláudio Lau, Camila Salata, Carlos Eduardo Dealmeida, Gabriela Sena, Gabriel Fidalgo, Marcos Vinicius Colaço, Regina Cely Barroso and Alessandro Nascimento (p. 81)

28 **Sensitivity improvement for identifying gadolinium distribution in planar XRF images by means of optimized low dose EDXRF system**
Mauricio Santibañez, Matias Vasquez, Antonieta Silva, Mauro Valente and Rodolfo Figueroa (p. 82)

29 **Synchrotron X-ray phase-contrast micro-CT to morphometric study of the Thoropa Miliaris tadpole**
Gabriel Fidalgo, Marcos Vinicius Colaço, Liebert P. Nogueira, Delson Braz, Gustavo Colaço, Helio R. Silva and Regina C. Barroso (p. 83)

30 **Hidden foreign matter analysis using EDXRF and Transmission X-ray in Labo instruments**
Tomoki Aoyama and Patrick Chapon (p. 84)

31 **Combined microanalytical study of U(VI) uptake capability of argillaceous rocks from Boda Claystone Formation, Hungary**
Janos Osan, Margit Fabian, Felician Gergely, Istvan Rigo, Miklos Veres, Rainer Daehn, Daniel Grolimund and Szabina Török (p. 85)

32 **Iron, copper and zinc analyze in of human neuroblastoma cell spheroid by microXRF technique**
José Eduardo Rosa, Roberta Leitão, Gabriel Ferreira, Davi Oliveira, Célia Palmero, Eliane Oliveira-Barros, Maria Aparecida Oliveira, Luiz Nasciutt, Ricardo Lopes and Marcelino Anjos (p. 86)

33 **In Situ Observation of the Corrosion Process of Steel Sheets under Bending Stress by Confocal Micro XRF Technique**
Momotaro Nakanishi, Ryohei Hosomi and Kouichi Tsuji (p. 87)

8.1.3 PIXE and electron induced XRS

34 **Standardization of Proton Induced X-Ray Emission for Analysis of Trace Elements**
Johar Zeb, Shad Ali and Jehan Akbar (p. 88)

35 **A PIXE Facility at the 2-MV Kist Tandem Ion Accelerator: Design and Simulations**
Sy Minh Tuan Hoang, Gwang Min Sun and Tran Hoai-Nam (p. 89)

36 **Ionic Exchange Resins as ^{14}C filters: SEM/EDXRS study**
Stefania Bruni, Alessandro Gessi, Giuseppe Marghella, Lorenzo Moretti, Antonietta Rizzo and Chiara Telloli (p. 90)

37 **Recent archaeometric investigation with PIXE-PIGE – selected problems from Iron Age**
Žiga Šmit (p. 91)

38 **An Assessment of the Atmospheric Impact of Construction Work on Fine Particulate Matter in The University of Jordan: A PIXE Study**
Hanan Sa'Adeh and Sara Aburugia (p. 92)

39 **PIXE analysis of barbarian imitations of Late Roman period coins**
Oleksandr Buhay, Volodymyr Bilyk, Kyrylo Myzgin, Aleksander Bursche and Ruslan Shulipa (p. 93)

40 **Monitoring of non-destructivity of PIXE analysis on cultural heritage objects**
Zoltán Szőkefalvi-Nagy, Imre Kovács, Bogdan Constantinescu and Daniela Cristea-Stan (p. 94)

41 **A TES probe for PIXE applications in the frame of the AHEAD Project**
Paolo Bastia, Vadim Burwitz, Massimo Chiari, Jan-Willem den Herder, Ioannis Georgantopoulos, Lorenzo Giuntini, Franco Lucarelli, Claudio Macculi, Diana Martella, Gabriele Minervini, Lorenzo Natalucci, Paul O'Brien, Luigi Piro, Laura Reginato, Monia Rossi, Salvatore Sciortino, José Miguel Torrejón and Peter von Ballmoos (p. 95)

42 **Five Year PIXE Study of Elemental Content in FAPM Collected in Seven Sites During Fireworks Burning Events**
Francisca Aldape, Javier Flores, Javier Flores-Aldape and Olivia Rivera-Hernandez (p. 96)

43 **Sulfur Contents in FAPM in Days with Relevant Events in Comparison with Normal Days in the MCMA**
Javier Flores, Francisca Aldape, Javier Flores-Aldape and Olivia Rivera-Hernandez (p. 97)

44 **Multiple ionization X-ray satellites of magnesium, aluminum and silicon in alpha particle PIXE**
Christopher M. Heirwegh, Marko Petric, Stjepko Fazinić, Matjaž Kavčič, Iva Božičević Mihalić, Jordan Schneider, Ivana Zamboni and John L. Campbell (p. 98)

45 **Use of micro-beam PIXE and NRA in postmortem analysis of samples exposed in plasma devices**

8.1.4 Quantification methodology and metrology

8.1.5 XRS applications in advanced materials and nanoscience

X-ray nanophotonic development from simples to composite planar air waveguide-resonator

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Peculiarities study of X-ray flux total external reflection phenomenon formed the basis of X-ray polycapillary optics [1] and allowed to built X-ray slitless collimator [2]. Theoretical description of these devices function rested on the multiple total reflection mechanism. It was enough for the features analysis of policapillary units. But the multiple total reflection mechanism use for the slitless collimator work explanation was failed. Our systematic investigations of planar extended slit clearance features for the quasimonochromatic X-ray fluxes transportation showed that the alternative mechanism of X-ray flux propagation is permissible by nature. This mechanism was called the radiation waveguide propagation one, and the device functioned in frame of the mechanism got name the planar X-ray waveguide-resonator (PXWR) [3]. This device forms X-ray beam with nanosize width and enhanced radiation density. But its emergent beam is characterized by noticeable angular divergence depreciated of its chief advantages. For this imperfection overcoming we elaborated the composite waveguide-resonator (CPXWR), which involves two simplest PXWR positioning one after another with mutual aligning.

Experimental investigations of the this device functioning showed that it captures X-ray quasimonochromatic flux in the angular range φ_1, which can not exceed double magnitude of the total external reflection critical angle, transports the radiation almost without attenuation and forms the emergent beam with the angular divergence φ_2 smaller as φ_1. It is known that the Liouville theorem postulates the phase volume invariability for the any statistical ensemble in the process of its reorganization. So, the variation of one ensemble parameter must be accompanied by the other parameter changing. Our diffractometric measurements showed that the angular divergence decreasing is accompanied by the deterioration of X-ray radiation monochromatism and decreasing of its coherence length, accordingly. On base of these results we elaborated the model of emergent beam formation by CPXWR. X-ray fluxes generated by laboratory sources are characterized by the mean wavelength magnitude λ_0 and the monochromatization degree $\Delta\lambda$. The mean wavelength magnitude in CPXWR emergent beam is unchanged and its monochromatization degree will be described by the sum $\Delta\lambda_2=\Delta\lambda+\delta\lambda$. Our model allowed to get the function connection between angular divergence decreasing $\Delta\varphi=(\varphi_1-\varphi_2)$ and the deterioration monochromatization degree $\delta\lambda$ in the form:

$$\delta\lambda=\varphi_1\lambda_0(\varphi_1-\varphi_2)$$

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XMI-MSIM: a general Monte Carlo simulation of energy-dispersive X-ray fluorescence spectrometers

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Since their inception during the Manhattan project, Monte Carlo simulations have been used for a variety of applications in physics, mathematics, engineering, finance and more. When applied to X-ray fluorescence spectroscopy, it is well known that Monte Carlo simulations are useful for predicting the spectral response of samples irradiated with an X-ray beam of given characteristics. This requires the development of a dedicated computer code that simulates the histories of a large number of individual photons, whose trajectories in the system are modeled as a number of straight steps. At the end of each step, an interaction occurs, leading to a change in direction, energy and polarization state. A photon's trajectory is terminated when it leaves the system, or when the detector captures it. If detection occurs, one count is added to the appropriate channel of a virtual multichannel analyzer.

We have developed a software package *XMI-MSIM* [1], based on the Monte Carlo code by Vincze et al[2], enhancing and extending it with numerous new features. These include an update of the essential physical data such as cross sections, fluorescence yields and transition rates through linking with the *xraylib*[3] package. Through this dependency, it is now possible to simulate M-lines and cascade effects (radiative and non-radiative). From a software viewpoint, the use of advanced programming techniques such as OpenMP, OpenCL and MPI has led to a significant increase in computational efficiency and allows for the deployment on computer clusters, which is recommended when operating in brute-force mode.

Optionally, the code can be called as a plugin from *PyMca*[4], an open-source tool for XRF spectral analysis, where it serves as an alternative to the default fundamental parameter based quantification procedure. This is accomplished by means of an iterative algorithm in which the simulated line intensities are compared with those experimentally observed, while at every iteration step the simulation input concentrations are adapted until convergence of the line intensities is reached. The code itself is written in C and Fortran 2003, and makes extensive use of several open source packages. *XMI-MSIM* is available at `https://www.github.com/tschoonj/xmimsim` and is distributed under the GNU General Public License (GPL).

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[3] T. Schoonjans et al. Spectrochimica Acta B, 66(11-12), 2011, 776-784.

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The *xraylib* library for interactions of X-rays with matter

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X-ray based analytical techniques have seen a surge in popularity over the last decades. This had led to an increased interest in interaction cross sections and other atomic parameters, which are of fundamental importance in both quantitative and qualitative analysis. In X-ray fluorescence (XRF), for example, quantification using either the fundamental parameter method or Monte Carlo simulations is only possible if accurate data of X-ray interactions with matter are available. Such data can be obtained in two ways: experimental and computational through quantum mechanical calculations. Several authors have published databases and tabulations in the literature, but none of them are presented in the form of freely available library functions, which can be easily included in software applications for X-ray techniques.

In an effort to solve the problem of interfacing the data to the user, Brunetti et al.[1] designed a software package called xraylib based on a shared ANSI C language library. The physical data included in the package is a compilation of several popular datasets including for example photoionization-, Rayleigh-, and Compton cross sections as well as absorption edge energies, fluorescence line energies and fluorescence yields.

In this work we will present the features offered by the most recent release of the xraylib package (version 3.3.0), such as partial photoelectric effect cross sections, cascade effect corrected X-ray fluorescence production cross sections, atomic level widths, Compton broadening profiles, diffraction related functions etc. Furthermore, in order to increase the library's usability, we have added bindings to several popular programming languages such as IDL, Java, Fortran, Python, Perl, Ruby, Lua, PHP and .NET, and have created versions compatible with all major operating systems and architectures[2].

We have constructed a website, hosted at `http://lvserver.ugent.be/xraylib-web`, that relies on xraylib's newly added PHP bindings in order to provide convenient access to all of its databases while simultaneously also giving developers assistance on how to extend their software with the xraylib API.

The xraylib development occurs at `https://www.github.com/tschoonj/xraylib` where the source code, prebuilt binaries as well as comprehensive documentation can be found. xraylib is released under the BSD license.

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[2] T. Schoonjans et al. Spectrochimica Acta B, 66(11-12), 2011, 776-784.

Calculation of the X-Ray Absorption Coefficients for nMnHAp

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Manganese substituted hydroxyapatite nanoparticles (nMnHAp) were produced with using ultrasonically assisted wet chemical method [1].The values of absorption coefficients were calculated with using narrow beam geometry. The specimens were absorbed with using 59.6 photons emitted from an ^{241}Am radioisotope source with 50 mCi activity. The photons transmitted from the specimens were counted with an Ultra-Low Energy Germanium detector with resolution 150 eV at 5.9 keV. The absorption coefficients of the samples (including hydroxyapatite without any substituted metal and real bone powder) were compared with each other. This study has been dealt with as a guide to medical field. Also the results have been evaluated in terms of the electron density.

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Determination of Valance Electronic Structures of Cu and Zn in $Cu_{1-x}Zn_x$ alloy thin films by using Kβ-to-Kα X-ray Intensity Ratios

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In this study, Kβ-to-Kα X-ray intensity ratios of Cu and Zn in $Cu_{1-x}Zn_x$ alloy thin films were measured using 59.5 keV gamma-rays from a ^{241}Am annular radioactive source and an Ultra-LEGe detector with a resolution of 150 eV at 5.9 keV. The Kβ-to-Kα X-ray intensity ratios of these films were compared with pure Cu and Zn. The valance electronic structures of Cu and Zn in $Cu_{1-x}Zn_x$ alloy thin films were obtained by comparing of the measured Kβ-to-Kα X-ray intensity ratios with the results of multiconfiguration Dirac–Fock calculation for various valence-electron configurations.

X-ray Tube-based RIXS: Synchrotron-free Atomic Local Environment Determinations

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During the last few years, several works have been shown different applications of Resonant Inelastic X-ray Scattering (RIXS) for the discrimination, determination and characterization of chemical environments in a variety of samples and irradiation geometries. So far, this RIXS tool had been applied using synchrotron radiation facilities in an exclusive way, due to the main requirement of a monochromatic exciting beam and the convenience of the high flux.

This work presents results of the first measurements of this novel RIXS tool for chemical characterization using a conventional X-ray tube source.

The experimental experience was carried out at the Non-Conventional XRF Laboratory of the Atomic and Nuclear Spectroscopy Group at the National University of Córdoba, Argentina. The preliminary setup designed for these measurements is mainly composed by an X-ray tube (Mo anode), a Si(111) crystal as monochromator, a versatile sample holder, a couple of slits and a Si-pin diode X-ray detector AMPTEK-XR100T (180 eV @ Mn-Ka line, 3mm front lead collimator).

The studied samples were three pure compounds of iron: a steel, a Fe(III) (Fe_2O_3) and a Fe(II,III) (Fe_3O_4) oxide. Several RIXS spectra of each sample were acquired using an incident energy of ~7050 eV (i.e. below the Fe-K edge) in air atmosphere and in the conventional 45°-45° geometry. RIXS peaks were analyzed by Multivariate Methods (as Principal Component Analysis (PCA)) in order to properly discriminate the fine structure of each spectrum.

The PCA procedure revealed that the fine structure of each RIXS peak clearly depends on the studied compound. This result open the possibility of local environment characterization by means of RIXS using an energy dispersive system combined with a conventional X-ray tube. This promising RIXS tool, where synchrotron radiation is no needed, would offer an unique opportunity to study chemical states in different kinds of samples at a local X-ray tube based laboratory; characterization nowadays difficult or impossible to achieve by other methods.

Taking into account these encouraging results, the next step consists in the improvement of the experimental setup, as a new channel cut monochromator, for the ulterior study of a variety of samples of interest by using the presented RIXS methodology.

Polycap: a Monte Carlo based ray tracing simulation of polycapillary optics

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Polycapillary optics consist of arrays of small hollow glass channels, which guide the X-ray photons by multiple instances of total reflection, analogous to the way fiber optics guide light [1]. Polycapillary optics are regularly used in the field of (micro-)X-ray fluorescence (XRF) spectroscopy to focus the X-rays, and thus increase the flux density of the beam, down to a microscopic spot. Additionally, a second polycapillary optic can be implemented on the detector side in order to limit the field of view in a so-called confocal detection scheme [2].

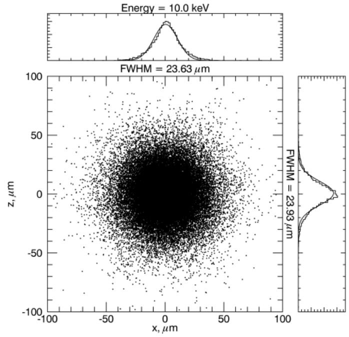

Figure 1: Simulated focal spot size at 10 keV of a 9 cm long ellipsoidal polycapillary optic with focal distance 5 mm, entrace and exit diameter of 4.13 and 1.17 mm, and 200k capillaries with diameter from 7 to 2 µm.

Besides the polycapillary shape, length and start and end diameter, several other factors influence that polycapillary optic performances as well (e.g. the capillary material, surface roughness). Next to these, the size, divergence and X-ray source distance and energy distribution also strongly influence the performance of said optics. Due to these restrictions, quantification of XRF data obtained by these methodologies remains difficult and is usually restricted to a fundamental parameter based approach [3]. Here, a Monte Carlo based ray tracing code, named polycap [4], is presented in order to simulate photon trajectories through polycapillary optics.

This code, written in C, is based on the previous work of Vincze *et al.* [5]. Besides ray tracing of photons in ‘ideal’ straight, conical and ellipsoidal shaped polycapillary optics, it also allows for the simulation of arbitrarily shaped optics to account for small deviations from the ideal shape as is often the case in real world examples. Additionally, the current code allows for multi-core processing and is developed as an API under the GPLv3 license to permit incorporation in other programs such as XMI-MSIM [6] for quantification of (con)focal XRF applications. Future versions of the program will incorporate X-ray polarization effects, Fortran and Python bindings, as well as a structured output provided in a HDF5 file format to allow for straightforward data evaluation.

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Reliable x-ray fundamental parameter determinations at PTB

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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) and optical constants 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.

The PTB operates two laboratories at synchrotron radiation facilities in Berlin, Germany, for metrological aspects. Therefore radiometrically calibrated instrumentation for photon detection is available over a broad spectral range from harder X-rays down to EUV and VUV spectral ranges.. The available calibrated instrumentation allows for performing reference-free XRF [1], which provides SI traceable quantitative results without the need for any calibration samples. In addition, our instrumentation can also be used for the experimental determination of atomic fundamental parameters [2-7].

In this presentation, we will summarize recent results of our activities on the experimental determination of X-ray fundamental parameters, covering examples for the determination of low-Z fluorescence yields, subshell photoionization cross sections and Coster-Kronig factors.

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Monte Carlo simulation of electron tracks for assessment of dependence x-ray generation on size of inclusion

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To estimate the intensity of the analytical signal under EPMA, the Monte Carlo method has become widespread, which allows modeling of electron trajectories, both in bulk samples and inclusions, whose size is smaller than the region of X-ray generation.

This work is based on the Monte Carlo model [1], previously used to construct the distribution function of X-ray radiation along the depth of the target (z-coordinate). Model [1] involves only one spatial coordinate z in modeling of the trajectories of electrons into the sample depth. We supplemented the model [1] and took into account all three spatial coordinates of the electron trajectory in the medium with regard to the formulas selected from description by Penelope-2011 Code System [2].

The algorithm of calculations was recorded in the language C+ for Windows OS. The electron trajectory was split into 50 intervals. From 2 500 to 20 000 electron trajectories were sampled depending on middle atomic number of the medium, that provided the error of counting to assess the backscattering factor at the level 1 % and less.

The Monte Carlo method was used to calculate the dependences dependences of relative intensity of X-ray radiation Au$L_{\alpha1}$- and Fe$K_{\alpha1}$-lines on the size of gold inclusion in the matrix of pyrite mineral for the model of cubic particle and long thin layer of gold perpendicular to the flat sample surface with probe diameter 0.5 μm.The intensities are normalized for the intensity of "bulk" gold sample for Au Lα1-line and «bulk» pyrite sample for Fe Kα1-line. It was found that, that the character of relative intensity differs essentially from the size of cubic particle and layer.

The research was performed using the equipment at the Center for Collective Use: Isotope-Geochemical Research Center at IGC SB RAS. This work was supported by the Russian Foundation for the Fundamental Research (project № 18-33-00369).

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High resolution X-ray spectroscopy of two-vacancy states in Ar

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For a Rydberg series converging to a core-hole ionization threshold, the emission spectrum is dominated by the spectator-type transitions [1]. After the emission process the core-hole electron most probably remains in the initially populated outer orbital and the final state is generated by a single electron jump of some other electron into the inner shell vacancy. In other words, the configuration mixing of singly excited core-hole states is weak. The interference effects are practically absent in the emission spectrum even if the initial core-hole broadening is large enough to generate ambiguities about which intermediate state exactly was excited by photon absorption. The lack of such knowledge does not upgrade to a sizeable interference effect precisely because each final state is predominantly populated by emission from a single intermediate state [2].

The situation changes dramatically when two electrons are excited into unoccupied orbitals. Since spectral density of two-electron-two-hole states is large, there are many overlapping resonances that are strongly mixed in the configuration space due to electron-electron correlations. A change of the potential, caused by the electron jump in the core, redefines the active orbital set but still, many final states may each have a considerable dipole matrix element with different intermediate states. This means that several absorption-emission paths from the ground to the specific final state may have comparable amplitudes, making the emission probability strongly dependent on path interference. Technically, in Kramers-Heisenberg equation the contribution of interference terms becomes important and photon-in–photon-out cross section cannot be factorized into the photoabsorption and photoemission part. The situation gets further complicated if the emission dynamics involves an additional electron jump – the radiative Auger decay.

The use of high resolution x-ray spectroscopy is mandatory to study interference effects in the emission spectra. It is well-known that when the experimental resolution in the photon-in-photon-out experiment is tighter than spectral width of the observed core-hole, the resonant part of the absorption spectrum is narrower because the width of the intermediate state is bypassed. While the so-called HERFD technique is efficiently implemented in the point-to-point focusing configuration, a parallel accumulation of a given emission spectrum over a full range of emission energies [3] is needed to study modulation of emission spectra due to interferences. We will present experimental and theoretical aspects of K-M emission from doubly photo-excited $K^{-1}M^{-1}V^2$ states in argon considering also the corresponding $KM - M^3$ radiative Auger decay [4].

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M_i (i=1-5) sub-shell X-ray production cross sections at photon energies across the L_j (j=1-3) sub-shell absorption edges of $_{66}$Dy

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The present work embodies measurements of the M_k (k = ξ, αβ, γ, m) x ray production cross sections for $_{66}$Dy at incident photon energies across its L_j (j=1-3) sub-shell absorption edge energies ranging 7.8-9.2 keV [1]. By probing the M_k x ray emission, this study aims to investigate, for the first time, the evolution of probability for the cascade L_j sub-shell vacancy decay as the tunable energy incident photons progressively ionize different L_j sub-shells of $_{66}$Dy. Earlier, the experimental studies have been carried out to evaluate systematically the attenuation coefficients, the photo-ionization [2] and production cross sections across the L_j (j=1-3) edges of $_{66}$Dy [3], as well the respective sub-shell fluorescence and Coster-Kronig yields [4].

The present measurements have been performed under vacuum at the IAEA end-station of the x ray fluorescence beam line of Elettra synchrotron radiation facility [5]. A pure thin target of DyF_3 (nominal thickness ~ 5.9 μg/cm^2) deposited on a 6.3 μm thick Mylar backing (Micromatter, USA) was irradiated with the tunable energy 7.8 to 9.2 keV photons and the M_k emission lines of $_{66}$Dy were recorded using a Silicon Drift Detector (SDD) equipped with a thin polymer window [5].

The experimental X-ray production cross sections have been compared with the theoretical ones calculated using the non-relativistic Hartree-Fock-Slater (HFS) model based photoionization cross sections; three sets of the X-ray emission rates, fluorescence and Coster-Kronig (CK) yields based on the non-relativistic Hartree-Slater (NRHS) model, Dirac-Hartree-Slater (DHS) model and Dirac-Fock (DF) model; the L_j (j=1-3) sub-shell to the M_i (i=1-5) sub-shell vacancy transfer probabilities evaluated in the present work. The presently measured M_k XRP cross sections are found to be significantly lower than the theoretical ones evaluated using physical parameters based on the relativistic DF / DHS model calculations, whereas a much better agreement is observed with respect to the NRHS model-based calculations, however the measured XRP cross sections are still systematically lower than the NRHS values.

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K-edge absorption spectra of gaseous hydrides

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X-ray absorption spectra in the energy region of absorption edges reveal fine details of the mechanism of inner-shell photoexcitation: in particular in spectra of free atoms or simple molecules, the simplest being gaseous hydrides [1-2]. In a collection of data from consecutive and homologous elements, analyzed by a common procedure, the reaction channels can be identified with better precision and reliability than in analysis of individual spectra.

Absorption spectra of the hydrides of 3*p* elements (PH_3, H_2S in HCl) were measured at the XAFS beamline of the Elettra synchrotron in Trieste: a new type of adjustable absorption cell for measurement of noxious gases at room temperature and at low photon energies was developed for the purpose. For the analysis, data from an earlier experiment on 4*p* hydrides (GeH_4, AsH_3, H_2Se, HBr), and published data of 2*p* hydrides (CH_4, NH_3, H_2O, HF) [3-4] as well as SiH_4 and the noble gases concluding the isoelectronic series (Ne, Ar, Kr) were adopted. The spectra are compared to respective calculated spectra, obtained by atomic HF86, GRASP codes and molecular DFT (Density functional theory) ORCA code [5].

Our analysis of the pre-edge structures showed that the energies and probabilities of single-electron transitions into the lowermost orbitals with the molecular character were strongly affected by the symmetry of the molecule, essentially in the same way in 3*p* and 4*p* homologues, but not in 2*p* homologues with a stronger influence of the core charge. In transitions to higher orbitals with prevailing atomic character the influence of the molecular field is negligible.

The fine structure immediately above the *K* edge stems from the coexcitation of valence electrons. These coexcitations can be explained as a two-step process: the inner-shell photoeffect followed by the shake-up of a valence electron predominantly to a free atomic orbital. The process is markedly different from coexcitations of more tightly bound electrons [3]. The results of relative shake-up probabilities can be compared to results of emission spectroscopies, the probabilities of double excitation to bound states show a correlation with the dissociation probability of the molecule.

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New measurements of $M_{\alpha\beta}$, M_{γ} and M-shell X-ray production cross sections induced by carbon ions on Bi and Pt targets.

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In the present work, the $M_{\alpha\beta}$, M_{γ} and M shell X-ray production cross sections for the elements Pt and Bi have been measured by $C^{4,3+}$ ions in the energy range 1.5 MeV to 5 MeV. X-ray and elastic backscattered spectra from thin Pt and Bi targets were simultaneously measured and X-ray production cross sections were extracted from collected spectra.

The obtained results have been compared with the theoretical calculations based on Semi-classical Approximations (United Atom – Separated Atom) model [1], the PWBA (Plane Wave Born approximation)[2] and the ECPSSR [3] model including the effects of the binding energy, relativistic, colomb deflection and energy-loss. The ISICS code is used for PWBA and ECPSSR calculations [4].

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Line shape study of L$\gamma_{2,3}$ and Lγ_4 transitions in barium metal and compounds

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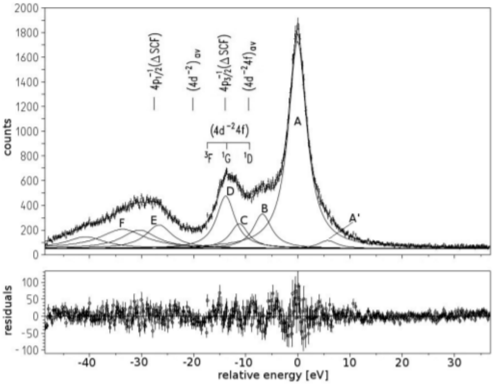
Barium L$\gamma_{2,3}$ and Lγ_4 X-ray transition were measured with a high-resolution Johann spectrometer. Chemical speciation is examined comparing the line-shapes of metallic barium and the Ba compounds $BaSO_4$, $BaCO_3$, $BaCl_2$, and $Ba(OH)_2$. Line parameters like transition energies, natural widths, and relative intensities are extracted and compared with the literature values. The L$\gamma_{2,3}$transition smears out, independently from the Barium chemical environment, as the pure quasi-particle picture of the Ba $4p_{1/2}$ core hole no longer holds due to strong dynamical effects. In the case of the Lγ_4 transition, however, chemical effects appear. Furthermore, evidence for the $L_1N_{6,7}$ transition was found. In addition, the L$\gamma_{2,3}$ transition of Xenon was measured to be compared to the corresponding Barium spectrum.



L$\gamma_{2,3}$ spectrum from $BaSO_4$

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Measurement of the bremsstrahlung cross section for protons between 15 and 70 MeV in C and Al

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High energy PIXE is under development at the ARRONAX facility [1]. The bremsstrahlung cross section measurements are necessary for quantitative analysis using high energy incident beam. At low energy ion beam < 4 MeV, experimental values for several elements exist, and are in good agreement with the theoretical models [2]. At higher ion beam energy, there are only few experimental data [2].

Therefore, at our facility, we have started an experimental campaign to measure bremsstrahlung cross sections, differential in photon energy and angle, with a HPGe detector and a Silicon Drift Detector (SDD), for carbon and aluminium targets impinged by proton beams between 15 and 70 MeV. An attention has been paid in order to afford a good control of the experimental parameters. Particularly, an effort has been given to determine the efficiency of the detectors (the HPGe X-ray detector in the energy range 3 to 100 keV and the silicon detector in the energy range 1 to 30 keV). In the same vein, a study of the theoretical model has been performed to check its validity at high energy.

During this talk, a review on the theoretical model of bremsstrahlung will be presented, followed by a description of our experiment (beam, detector and target). Our experimental data will be shown in comparison with the theoretical model and the existing scarce data for the same proton energy.

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Identification of free lime in slag using scanning electron microscope-cathodoluminescence analysis

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The reuse of slags, which are by-product of steel making process, is promoted for the environmental conservation. Thirty percent of the steelmaking slag is reused for road construction. The steelmaking slag contains a few weight percent of calcium oxide (CaO), termed as free lime. The free lime doubles its volume by the hydration reaction, which leads to the expansion and the collapse of the roads. The steelmaking slag is misted with water vapor to covert the free lime to calcium hydroxide ($Ca(OH)_2$) before being reused for the road construction. Therefore, detection of free lime in the steelmaking slag is important for its reuse. The analysis of the free-lime is conventionally conducted by a method combining ethylene glycol extraction, inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis, and thermogravimetric analysis (TG)[1]. This analytical method is time-consuming and required complicated steps. In the present study, we apply cathodoluminescence (CL) analysis, that is light emission from materials as a result of electron bombardment, to rapid and simple identification of free lime in the steelmaking slag. A model sample of the steelmaking slag was prepared by heating mixture of calcium carbonate ($CaCO_3$), silica (SiO_2), and ferrous oxide (FeO) powders in an iron crucible at 1300 °C for 1 h in an argon atmosphere and quenching to room temperature by blowing argon gas. CL image of the sample was captured with a digital single-lens reflex camera (α7RII, Sony Corp., Tokyo, Japan) equipped with a zoom lens (LZM-06075A, Seimitu Wave Inc., Kyoto, Japan) through a quartz viewport of a customized SEM-CL system (TECHNEX, Mighty-8DXL)[2] for 60 s. We detected orange luminescence in the sample as shown in Fig. 1(a). The areas emitting orange luminescence were confirmed to be free lime phase by EDX point analysis. CL spectrum of the areas agreed with that of previously reported CL spectrum of CaO[3] as shown in Fig 1(c). Therefore, we can identify free lime by capturing CL image of the steelmaking slag for 60 s.

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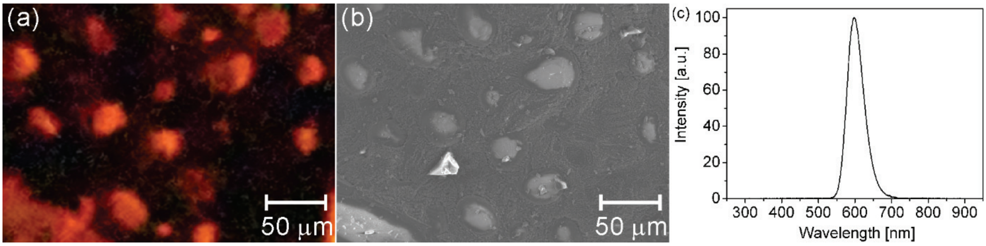

Figure 1 (a) CL image and (b) SEM image of the sample. (c) CL spectrum of illuminated area in (a).

Experimental assessment of effective probed volume in confocal XRF spectrometry using micro-particles.

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Current approaches for assessing a confocal µ-XRF probing volume involve the use of sharp knife edges, thin films or wires that are moved through this volume. The fluorescence radiation excited in the material of the object is measured, and profiles are built that determination of the full width at half maximum in any of the three axes. Naturally, these approaches do not provide information on the shape of the volume, and the consequent alignment of both the used lenses is made using the maxima of the registered intensity measurements.

The use of particles that are smaller than the interaction volume (isolated enough to prevent the influence of nearby particles) and translated through the interaction volume (3D scan) is presented as an alternative to determine the confocal probing volume. Spherical shape Uranium particles with diameter of 1 - 3 □m, originally produced for SEM-EDS calibration purposes were used in this study.

The methodology includes: Finding and characterizing the particles by SEM-EDS (Fig. 1), relocation to CXRF sample stage, 3D scan and further rendering in 3D maps (Fig. 2).

Herein, we shall present the preliminary results of the study.

Fig.1 SE image of U particle

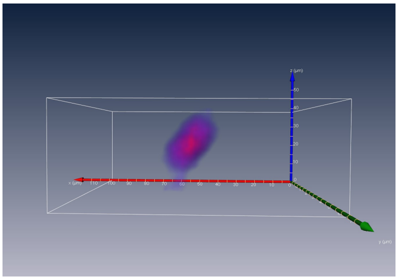

Fig.2 3D representation of measured U-La intensity

Calibration of a Laboratory Confocal Micro X-ray Fluorescence Setup for a Quantitative Analyses of Stratified Samples

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Depth profiling using confocal micro X-ray fluorescence analysis (confocal micro-XRF) has become a significant instrumental method for qualitative and quantitative composition analyses of stratified samples. Contrary to the conventional XRF analysis, with the confocal arrangement it is possible to obtain depth-resolved information on the elemental distribution. However, the acquired depth profiles of individual elements contained in the analyzed sample do not directly reflect their concentration profiles, because they are modified by absorption effects and sensitivity function of the spectrometer. For a quantitative evaluation of the measured depth profiles, i.e. restoring the elemental concentration profiles and thicknesses of the layers, a reconstruction procedure needs to be applied that is based on a proper calibration of the setup.

This work describes a calibration procedure of a laboratory confocal micro-XRF setup designed recently at the Czech Technical University (CTU) in Prague [1]. The setup contains an X-ray tube (Mo, 50 kV, 1 mA), FAST SDD™ detector from the Amptek company, and is equipped with polycapillary X-ray optics both in excitation and detection channel. The calibration consists in determination of energy-dependent depth resolution and sensitivity of the setup. Based on the calibration results, an algorithm for a quantitative reconstruction of measured depth profiles has been created. The procedure considers the direct deconvolution approach [2] and consists of two major steps: deconvolution of the depth profiles with the sensitivity function of the spectrometer and correction for absorption effects. As the confocal micro-XRF setup constructed at the CTU in Prague is primarily dedicated to the investigation of historical paintings, the quantification algorithm was tested on a hypothetical multilayered sample consisting of two overlapping paint layers.

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Micro-XRF analysis of zinc and lead accumulation in the tidemark of articular cartilage

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The tidemark as the transition zone between non-calcified and calcified articular cartilage is an active or resting calcification front. It is still ill defined but is suspected to play a role in some cartilage diseases such as osteoarthritis.

Previous studies using confocal synchrotron radiation induced micro-XRF have shown higher Zn and Pb accumulation in the tidemark [1, 2], compared to the bone tissue. However, as the tidemark was suspected to be thinner than the diameters of the used X-Ray beams (about 20 µm x 14 µm); the results would be smeared over a larger volume. Therefore, the true element levels in the tidemark would be underestimated.

To gain a better insight into the accumulation of Zn and Pb in the tidemark, its structure and different element levels compared to the mineralized cartilage, we now measured the elemental distribution in six 3 µm thin femoral head samples from 5 different patients with a monochromatic (17 keV) sub-micrometer beam (about 500 nm x 800 nm) at the B16 bending magnet Test Beamline of the Diamond Light Source synchrotron. The spectra were recorded with a 4-element Vortex detector. Scans were performed with a 1 µm x 1 µm step size. Measurement time per pixel was 20s.

Tidemark regions were identified and measured in areas of all six samples. In two of the measured areas the elemental map of Zn revealed a double tidemark. Tidemark thickness (FWHM) varied between 3 and 11 µm for Zn and between 3.5 and 14.5 µm for Pb.

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Soft X-ray STXM at the Swiss Light Source

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Scanning transmission X-ray spectro-microscopy (STXM) in the soft X-ray regime (250 eV - 1600 eV) has been demonstrated to be an excellent tool for the study of a wide range of nanostructured materials due to its high spatial resolution (less than 30 nm) and strong contrast mechanisms based on soft X-ray spectroscopy. In addition to quantitative elemental mapping, STXM can also map molecular composition and oxidation states, based on image contrast achieved through near-edge X-ray absorption fine structure spectroscopy (NEXAFS) [1]. More sophisticated material properties such as molecular orientation and magnetic domains can also be imaged with the aid of (linear or circular) polarised X-rays, which generate orientation sensitive dichroism effects in the materials [1, 2].

We present the basic concepts and operation modes of the PolLux STXM instrument installed at the X07DA beamline of the Swiss Light Source at the Paul Scherrer Institut, Villigen, Switzerland [3]. A selection of recent research projects will be presented including examples of molecular orientation mapping in an annealed conjugated polymer film (with application to organic opto-electronic devices [4]), composition mapping of a thin blend film of conjugated polymers (with application to polymer solar cells and LEDs), quantifying iron oxidation state in aerosol particles exposed to humidity and oxidising trace gasses in an environmental cell (with application as a marker for radical chemistry), and time-resolved imaging of magneto-dynamical processes (e.g. magnetic vortex gyration dynamics under an applied mechanical strain [5] and spin-wave generation by topological defects in synthetic antiferromagnetic materials [6]).

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Detection of Gadolinium accumulation in bone by XRF

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Gadolinium-based contrast media are routinely used in magnetic resonance imaging (MRI). Until recently gadolinium-based contrast media were considered to be rather safe in diagnostical applications, though in patients with kidney disease it could cause nephrogenic systemic fibrosis [1]. However, some studies revealed that gadolinium (Gd) is not cleared from the body completely and that some tissues and organs retain gadolinium for a very long time [2,3]. Free gadolinium is extremely toxic for the human organism, and, if released from depot, might pose a serious health threat.

The recent findings showed that the contrast agent is not fully excreted, and the accumulation of gadolinium in brain tissue even in subjects without renal dysfunction was observed [3,4]. The other possible depots of gadolinium are bone and cartilage tissue.

To prove this assumption, various samples of bone tissue from patients, who previously received MRI, were analyzed using 2 D imaging with high resolution (> 1 µm). Our aim was to investigate the distribution of gadolinium in human bone, and the obtained results will be demonstrated. To the best of our knowledge these measurements are the first attempt of imaging of Gd accumulations in the bone tissue, which is of exceptional interest for understanding of mechanisms of such accumulations and, further, for predictions of safety of Gd-based contrast media in different bone diseases and associated conditions.

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Evaluation of the Effects of Azadirachtin on Internal Structures of *Rhodnius prolixus* Head Using Low-Energy X-Ray Microfluorescence

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This work uses Low-Energy X-Ray Microfluorescence to evaluate the distribution of Mg, Na, Al and Fe in the structures *Rhodnius prolixus* head, to understand the effects of Azadirachtin treatment on the development of the nervous system. This insect is the main insect vector of Chagas Disease, which affects between 6 and 8 million individuals, with approximately 12,000 deaths per year in Latin America. Azadirachtin is a drug that causes changes in the neuroendocrine system in several species of insects, including triatomines, thereby inhibiting your development [1].

In this study, 8 specimens of fifth-instar nymphs of *Rhodnius prolixus* were taken from the colony of the Laboratory of Biochemistry and Physiology of Insects (Oswaldo Cruz Foundation (FIOCRUZ), Brazil) and were divided in two groups. In the first group, the insects were fed with defibrinated rabbit blood containing azadirachtin and the other group only with simply defibrinated rabbit blood. Both groups were measured at TwinMic beamline, (ELETTRA sincrotrone, Trieste, Italy) [2]. The beamline was operated at 1.7 keV in scanning mode, where the sample was raster scanned across a microprobe delivered by a zone plate diffractive optics. The transmitted X-rays provided absorption and differential phase contrast images constructed by the transmitted photons collected by using a fast readout CCD camera providing morphological information on the scanned areas [3].

The results obtained with Low-Energy X-ray fluorescence allowed to compare the differences in important structures of *Rhodnius prolixus* head obtaining distribution maps of important light elements and providing new insights on the nervous system. As the composition of insects' structures is basically the same, understanding how Azadirachtin affects the respiratory and nervous system of *Rhodnius prolixus* is very important in the studies of prevention of other vector diseases.

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Evaluation of the Structural Characteristics and the Fading Effects of Image Plates

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Image plate (IP) is a type of ionizing radiation detector used in Computed Radiography (CR). After radiographic exposure of IP, latent image is formed. Scanning the IP in a CR system with laser beam enables photostimulated luminescence (PSL) and thus transforming the latent image into visible light for further digital image formation [1,2]. PSL decreases exponentially with the increasing of the elapsed time between the exposure and the IP scanning (t_f) and consequently there is a fading of the digital image [3].

The purpose of this paper is to investigate the relationship between IPs physical structure and elemental composition and the fading behavior. Three different types of image plates were analyzed: Blue plates (Blue IP) with the highest resolution, high resolution plates (HR IP) and standard resolution plates (ST IP). The IPs characterization were performed by determining the thickness of the sensitive layer, and evaluating the grain size and the elemental composition of this layer, with the aid of a scanning electron microscope (SEM), equipped with a Energy Dispersive X-ray (EDX). As a result, the elements C, F, Br, Ba and I were found. For measuring the fading rates as function of the elapsed time t_f, several exposures of the IPs were performed using a constant potential X-Ray source. Figure 1a shows the behavior of the PSL normalized intensity as function of t_f for the Blue plate, Figure 1b shows the SEM image obtained with a 1,000x magnification rate and Figure 1c shows the EDX spectra of the sensitive layer for this IP.

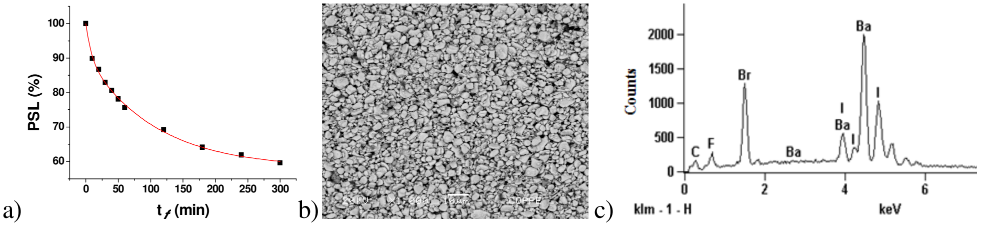

Figure 1 - a) Fading curve, b) SEM image and c) EDX spectra of the Blue plate.

The results showed that the blue plate has lower thickness and grain size and lower concentration of Br and I. In addition, the fading is less intense for this type of plate. The knowledge of the structural characteristics of image plates allowed a better understanding of the PSL process and the difference in the fading effect for each IP.

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Characterization of Carbonate Rocks Through X-ray Fluorescence and Computed Microtomography

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Carbonate rocks play an important role in petroleum geology by acting as reservoir rocks, generators and even hydrocarbon sealants, accounting for about half of the oil and gas reserves known in the world. In the search for new analysis techniques aimed at complementing and adding new data on carbonate rock structural behavior, X-ray Computed Microtomography (microCT) appears as a non-destructive and fast analytical technique. Studding a rock by microCT means obtaining knowledge, in microscale, on shape, size, distribution, volume, area and pore connectivity and have a 3D visualization of the facies that structure it [1,2]. The micro X-ray fluorescence (µXRF) analysis has become a complementary tool for carbonate rock examination as it provides information on the elemental composition distribution of the samples [3]. Thus, the objective of this research was to use µXRF and microCT techniques to characterize samples of carbonate rocks to identify their elemental composition distribution and provides a morphological analysis of its heterogenic internal structure.

The samples studied were 04 plugs of carbonate rocks. The analyses of microtomographic images allowed the identification of the many structures that made up the rock samples. Figure 1a shows the microCT image of a carbonate stromatolite of parallel lamination and many fracture zones. Occasionally, these fractures are filled by thick calcite mosaic and iron oxides/hydroxides (approximately 1.23%). The distribution of these elements could be identified in the µXRF images of iron and calcium (figures 1b and 1c). The results showed that both techniques are complementary and of great potential in the characterization of carbonate rocks, where the structural and elemental composition of the samples could be evaluated and correlated.

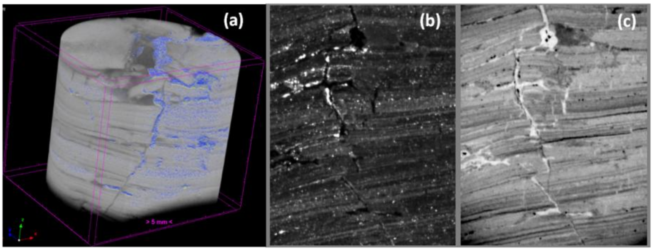

Figure 1 - (a) 3D model of sample A, (b) µXRF of the sample highlighting iron oxides/hydroxides (in white color) and (c) µXRF of the sample highlighting the fractures filled by calcite (in white color).

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Elemental distribution by synchrotron X-ray microfluorescence of prostate 3D cell culture

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The global estimate shows that, in 2012, there were 14.1 million new cases of cancer (except for nonmelanoma skin cancer) and 8.2 million deaths. Prostate cancer is a highly prevalent disease and ranks second among malignant neoplasms that affect men around the world, behind lung cancer alone [1]. Trace elements are very important and are involved in many cellular processes. The X-ray microfluorescence technique (µXRF) is an advanced tool of high spatial resolution, sensitivity, multielement analysis and non-destructiveness for trace element study [2]. This study aimed to investigate the levels of trace elements in spheroids obtained through the following human prostate cell lines, tumor cell line androgen independent (DU145), tumor cell line androgen dependent (LNCaP) and normal cell line (RWPE- 1), using synchrotron X-ray microfluorescence (µSRXRF). The measurements were performed with a standard geometry of 45° of incidence, excited by a white beam using a pixel of 25 µm and a time of 300 ms/pixel at the XRF beamline at the Synchrotron Light National Laboratory (Campinas, Brazil) The results by µSRXRF shows for some elements intensity levels were different between the cancerous and normal groups. The results of this study showed that further studies should be performed to understand the relationship of these trace elements with the progression and development of the prostate cancer.

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What's hidden for X-Ray? An archaeological plant study

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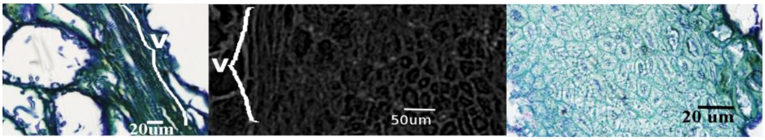
X-Ray MicroCT analyses are an ever growing and appropriate technique to study pieces of historical, artistic and cultural value [1], due to the non-destructive characteristic of the technique. Archaeological plant remains have a biological origin and a low-contrast for typical x-ray Absorption-Contrast imaging [2][3]. However, synchrotron-based Microtomography, using X-Ray Phase-Contrast, is an alternative way to enhance contrast of biological samples [1][2] that is, as for today, still scarcely tested for ancient non-fossil plants.

Within this context, archaeobotanical samples recovered at Monte Castelo archaeological site (RO, Brazil) [4] were studied and imaged, revealing evidences on the similarities and differences of morpho-anatomical data obtained by mean of X-Ray Phase-Contrast MicroCT and High Resolution Light Microscopy techniques. Comparative analysis took into account morphometric and morphological description of plant organs, tissues, cells, cell walls, vascular bundles and crystals. Most of them were observed and measured by both techniques. The figure below exemplifies how thick walled cells and vascular bundles (V) are visualized in X-Ray and Light Microscope images.

High detailed histological information is obtained from Light Microscopy, but current preparation procedures irreversibly damage the samples. Likewise, microtomed slices preserved single-plane information and inhibit the study of other dimensional planes. By opposite, X-Ray virtual slicing of microtomograms compensates these disadvantages of the histological slices. It provides 3D models which could be digital handled, analyzed and reproduced, preserving archaeological plant evidences in a complete non-destructive way.



At center, X-Ray Phase-Contrast MicroCT: Pink Beam Energy = 4keV to 14keV; Pixel Size 0.82, Objective = 10x (IMX Beamline, LNLS, CNPEM), longitudinal section using ImageJ 1.51w. At sides, High resolution Light Microscopy, Olympus DP71 digital camera coupled to an Olympus BX51 microscope, longitudinal sections 8 µm thick (Biology Institute, Unicamp).

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Effects of angiotensin II receptor blockers in coronary arteries of hypertensive rats: analysis of elemental distribution using LEXRF

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Hypertension is one of the major public health problems worldwide due to its strong impact on cardiovascular (CV) morbidity and mortality. The hypertension can cause damage in target organs such as arteries [1]. Angiotensin II (Ang II) has been linked to vascular dysfunction and target organ damage. Previous studies showed that blockade of the angiotensin II type 1 receptor (AT1) with an angiotensin II receptor blocker (ARBs) may reverse vascular pathology independent of blood pressure lowering. Antihypertensive agents ARBs have demonstrated some vascular and cardiac benefits [2]. The efficiency of ARBs to protect organs that may be affected has been increasingly studied. However, its efficiency was not be verified at an elemental level in the literature. Knowledge about elemental distribution in tissues have a great importance in the study of diseases, since chemical imbalance can alter biological functions. The aim of this work was to assess the distributions of selected elements (O, Na, Mg, Fe, Cu and Zn) in the coronary arteries of hypertensive rats, in comparison with healthy specimens, in order to evaluate the effects of the ARBs (losartan and olmesartan).

Elemental semi-quantitative microanalysis was performed using Low Energy X-Ray Fluorescence (LEXRF) maps acquired on TwinMic X-ray spectromicroscopy station, located at the ELETTRA synchrotron radiation facility. Morphological changes in coronary samples were also investigated. Six healthy rats from the Kyoto (WKY) lineage and eighteen spontaneously hypertensive rats (SHR) were used for this study. SHR rats were divided into three groups (n = 6): the group treated with losartan (25 mg/kg/d – SHR+L), the group treated with olmesartan (30 mg/kg/d – SHR+O), and the hypertensive control group (SHR). The results revealed changes in the preferential location of important elements after treatment using the ARBs. Copper and zinc contents in the coronary from SHR+L group were comparable to the values obtained for normotensive rats. On the other hand, the group treated with olmesartan presented similar contents of iron to those expected for coronary arteries of normotensive rats.

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Sensitivity improvement for identifying gadolinium distribution in planar XRF images by means of optimized low dose EDXRF system

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Nowadays, gadolinium is used in medical practices, like magnetic resonance imaging (MRI) or neutron therapy. The assessment of Gd spatial distribution and concentration is a key issue for these medical procedures. This work presents a study on the sensitivity improvement for identifying the Gd distribution in planar EDXRF images and incrementing the signal-to-noise ratio (SRN), while keeping lower doses, by means of an optimized in vivo EDXRF system [1,2]. The optimization of the measuring system was experimentally performed in tissue equivalent phantoms, implementing two different configuration criteria: Firstly, the Lowest-Limit-of-Detection setting (Lowest-LoD), which was determined by LoD assessment for a specific acquisition time evaluating different experimental narrow spectra of equal FWHM (2.5 keV) with central energy above the energy L edge. Secondly, the Lowest-Dose setting consisted of evaluating the surface dose for a given LoD corresponding to the different incident spectra. Surface (2D) scanning of the Gd-doped tissue-equivalent phantom were performed according to the following optimized scenarios: Lowest-LoD (central energy of 10.9 keV) and Lowest-Dose (central energy 12.9 keV) [1,2]. 625 pixel images were acquired in two different conditions: a pre-defined time (5 seconds) per pixel was set in the first approach, whereas a pre-defined total surface dose (4mGy) was set for the second approach. According to the obtained results for the first approach, 58 times reduction was observed comparing SNR between Lowest-LoD and Lowest-Dose settings. On the other hand, for the second approach pre-defining total dose during the whole examination, the better SNR was obtained for the Lowest-Dose configuration exhibiting a 42% of increment with respect to the Lowest-LoD configuration and 47 times higher when compared with limit case of no optimization.

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Synchrotron X-ray phase-contrast micro-CT to morphometric study of the *Thoropa Miliaris* tadpole

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Micro-CT is the most powerful 3D imaging technique to study morphology of the small animals, such as annelids [1], insects [2] and amphibian embryos [3]. Commercial lab-based X-ray micro-CT system is the most used to study anurans, however it presents some limitation when compared with synchrotron micro-CT techniques that offers significant advantages over such as a wide energy range, high flux and small source size and beam divergence. [4,6]. In this work, we performed the first morphometric study of internal structures of *Thoropa miliaris* tadpoles, using synchrotron phase-contrast micro-CT.

A tadpole is the free-living aquatic larva of an anuran. As a larva, it is non-reproductive and undergoes radical changes in morphology and ecology between life stages. About three-quarters of 7,537 species have a tadpole for some period during their development, and tadpole descriptions are available for about a third of those. Most of tadpole structure is composed by low attenuation tissue, becoming an interesting specimen for phase-contrast micro-CT analysis [7, 8].

High resolution phase-contrast micro-CT scans were performed at the SYRMEP beamline. In this set-up, the outcoming beam from the ring is restrained before the monochromator and in a devoted end-station, absorption and phase contrast radiography and tomography set-up are available. The phase contrast effect provides appropriate edge enhancement of tadpole structures. It was possible to distinguish structures to apply virtual segmentation process and volume quantification for different organs.

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Hidden foreign matter analysis using EDXRF and Transmission X-ray in Labo instruments

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Foreign matter identification and analysis is important to reduce failures of thin film products. For instances, the presence of foreign matter could cause dramatic failures of final products in battery industry. Similarly high value thin films are used for packaging industrial products to keep products safe or clean and the presence of embedded particles could severely harm the products.

The classical procedure for finding foreign matter (particle) is to observe the specimen with optical image or transmission x-ray image. Although operator will find particles from these images, no analysis is provided and it is not possible to identify which part of the process is responsible for the presence of these particles in the film in order to correct/improve the process.

Most metallic foreign matter materials are from stainless steel, brass or aluminum alloys. EDXRF could easily detect most transition elements in depth but Al is challenging: it is a low Z element - its fluorescence energy is low and can therefore be easily absorbed by the film - and so micro EDXRF measurement could therefore miss to detect embedded Al particles.

On the opposite Al can be seen in transmission X Ray images. Therefore the combination and simultaneous measurement of optical image, transmission X Ray image and micro EDXRF Image within a single X Ray microscope is extremely valuable for total analysis of metallic foreign matter in thin films.

Combined microanalytical study of U(VI) uptake capability of argillaceous rocks from Boda Claystone Formation, Hungary

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Argillaceous rock formations, due to their high clay content and low permeability, have significant radionuclide retention/retardation capacities, and are therefore in the focus for high level radioactive waste (HLW) repositories in several countries. In Hungary two geological sites (Gorica Block and Boda Block) of the Boda Claystone Formation (BCF) have been selected for the study of potential host rocks for HLW. The aim of the measurements was to obtain information on the U(VI) uptake mechanism on the micrometer scale, in order to complete molecular scale sorption results and understand the behaviour of uranium dissolving from HLW and to identify the possible differences in uptake capacity between the two possible sites.

Synchrotron radiation microscopic X-ray fluorescence (SR μ-XRF) has sufficient sensitivity to study the metal uptake on the microscale. In order to identify the mineral phases responsible for the uptake, SR μ-XRF elemental mapping was combined with simultaneous microscopic X-ray diffraction (μ-XRD) mapping. Scanning electron microscopy energy dispersive X-ray analysis (SEM/EDX) was performed on identical sample areas in order to obtain quantitative information on the rock-forming light elements (e.g. Na, Mg). In addition, micro-Raman spectroscopy was applied for identifying newly formed phases during the uptake process. The oxidation state of U was verified with microscopic X-ray absorption near-edge structure spectroscopy. Measurements were performed on thin sections subjected to uptake experiments involving U(VI). The thin sections were prepared on high-purity silicon wafers from geochemically characterized cores of BCF.

Our results revealed that in the sample, taken from Boda Block, where dolomites have ankerite rims and U-bearing rings, newly formed goethite precipitations were observed, which partly replaced the ankerite at near neutral pH (6.8). Goethite can easily bind U(VI) due to the enhanced specific surface area and high adsorption capacity. The oxidation of Fe(II) required to the formation of goethite is caused by partial reduction of U(VI) to U(IV). Eighty percent of uranium was taken up by clay minerals and 20% by goethite although the ankerite concentration is as low as 6% in Boda Block of BCF. The study demonstrated that the different mineralogy of Gorica Block and Boda Block significantly influences the U retention capacity of BCF.

Iron, copper and zinc analyze in of human neuroblastoma cell spheroid by microXRF technique

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Neuroblastoma is the most common extracranial solid tumor of childhood is responsible for approximately 15% of paediatric cancer deaths and has high potential for metastasis [1-3]. The trace elements are extremely important in biological processes, such as in participation in reactions involving metabolic enzymes. An important fact is that all studies of healthy and diseased tissue elements levels report that there is an increase in concentration for most elements in tumor cells. Zinc plays an important role in the proliferation and differentiation of neural cells, it plays an important role in the function of several regulatory proteins and it is crucial for activation and functional integrity of several metallothioneins. In this study, elemental distribution in 3D cell culture (spheroid model) of neuroblastoma cells (SHSY-5Y) was investigated after supplementation with zinc chloride by 24 hours with the objective of analyzing the iron, copper and zinc using X-ray microfluorescence (µXRF). The measurements were performed using the state-of-the-art spectrometer M4 Tornado, from Bruker. The results by µXRF showed non-uniform elemental distributions in all the spheroids analyzed. It was possible observed that intensity of Fe, Cu and Zn were changed with the Zn supplementation. Therefore, the Zn supplementation changes the metabolic of neural cell.

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In Situ Observation of the Corrosion Process of Steel Sheets under Bending Stress by Confocal Micro XRF Technique

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Steel sheets have been widely used as construction material such as blidges and buildings, and it is important to prevent rust by surface treatment such as plating and painting. However, when these materials are used in sea water or in river water, the corrosion of the steel is accelerated. This corrosion occurs at the solid-liquid interface, and analytical method for directly investigating the solid-liquid interface is required to understand the reaction mechanism[1][2]. In addition, if we use steel sheets for a long time under bending stress, it can be a cause of characteristic corrosion such as stress corrosion cracking. Therefore, it is important to observe the corrosion process of the steel sheete in the solution under bending stress. In this research, we observed the corrosion process of the steel sheets using confocal micro-XRF method. This method can detect only fluorescent X-rays generated in a specific small space as compared with the conventional XRF[3].

Figure 1 shows the sample cell with the steel sheet sample attached. A small piece (15 × 35 × 0.16 mm) of a galvanized steel sheet having a surface scratched was immersed in the NaCl solution. The region of elemental imaging acquired is perpendicular to the steel plate, and the region is 1500 μm × 400 μm. The measurement time per point was set to 60 seconds, and the time required for one imaging was set to about 24 hours, and the measurement was carried out continuously for 5 days. As a result, it was confirmed that Zn was eluted into the NaCl solution but Fe was not eluted in the measurement for 5 days. It was found that the corrosion process of a steel sheet under bending stress was accelerated.

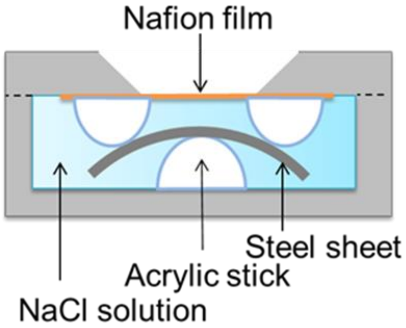

Figure 1 Schematic diagram of sample cell.

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Standardization of Proton Induced X-Ray Emission for Analysis of Trace Elements

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This paper presents the standardization of Proton Induced X-rays Emission (PIXE) technique for the trace element analysis of standard samples. Standard Reference Materials (SRM's) (Titanium based alloy, Copper based alloy and Iron based alloy) is proposed for the desired PIXE analysis in such a way that it covers the maximum range of elements in the periodic table. In this technique, the accelerated proton beam with three different values of charges (i.e. 0.5 μC, 1 μC, 1.5 μC) is incident on the sample with a maximum energy of 2.57MeV from a source of 5UDH-II tandem Pelletron accelerator. This accelerated proton beam is incident at different positions on target samples, each sample is exposed to the incident proton beam for more than three times in order to get X-rays from almost all the containing elements of the samples. The emitted X-rays is detected by Silicon Sirius Detector (SSD) placed at an angle of 45^0 with a target sample. The obtained raw data from the accelerator is further analyzed by running GUPIXWIN software to determine the trace elements of the desired samples. Finally, the analyzed data is compared with SRM’s data, which are in good agreement.

Key Words: PIXE Standardization, Trace Elements, GUPIXWIN

A PIXE Facility at the 2-MV Kist Tandem Ion Accelerator: Design and Simulations

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Particle induced X-ray emission (PIXE) is powerful yet non-destructive elemental analysis techniques now used routinely by geologists, archaeologists, art conservators and others to help answer questions of provenience, dating and authenticity. The PIXE system has been designed and evaluated the performance and characteristic by using CAD programs and Monte Carlo simulation packages (MCNP6, PHITS, and TRIM). The components of systems as a target vacuum chamber dimension, beam's collimator and beam's nozzle and Si(Li) and HPGe detectors were considered in the design. The design of the PIXE will be turned to appropriate with the requirements of the purpose based on the simulated results before installation at the KIST Tandem Ion Accelerator (Republic of KOREA).

Keywords: PIXE, Simulation, Accelerator, Detector.

Ionic Exchange Resins as ^{14}C filters: SEM/EDXRS study

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Ion exchange resins (IERs) are commonly used in PWR nuclear reactors as filters for ^{14}C impurities: ^{14}C, one of the most concerned radioisotopes due to its life cycle in all the biological systems, is produced during the nuclear reactor cycle and released by the corrosion phenomena of irradiated steels and Zircaloys.

The efficiency of both cationic and anionic resins, as filters or as waste containers, is strictly connected to their morphology: the preservation of their spherical shape in time is one of the key parameters for a quality assessment and for the evaluation of the potential release of radioisotopes during the storage condition.

The present work is a systematic study on two reference IERs, LEWATITT® S100 KRH and LEWATITT® MonoPlus M500 KR, manufactured by Bayer Chemicals. Both new and aged specimens were taken into account in order to assess the quality of the resins after 10 years of disposal.

Scanning Electron Microscopy (SEM) allowed the observation of the specimens' morphology and, thus, their eventually degradation cause to the ageing. Image analysis tools were also used in order to define and possibly quantify the degradation rate of the materials. EDXRS quantitative microanalysis was coupled to the SEM to investigate the principal elements concentration and the amount of possible impurities inclusions.

The comparison between the results obtained on new and on aged specimens could provide information on different production methods and the effect of the natural ageing.

Recent archaeometric investigation with PIXE-PIGE – selected problems from Iron Age

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Is there any continuation in material culture from the Bronze Age into the Iron Age? Our analyses involve two important materials, glass and bronze that were collected from the archaeological sites in Slovenia. Glass beads are easily transportable and traded over great distances, so they are mark of technology over a broad area. The production of glass during the Bronze Age relied on the alkalis from the ash of plants; these we halophytic plants in Bronze Age Egypt and Mesopotamia, and potassium-reach plants in Northern Italy. In the beginning of the first millennium BC, mineral sources of alkalis known as natron started to be exploited first in Egypt, and by 800 BC spread to the rest of Mediterranean and central European world. The oldest glass beads excavated from Slovenia are from 9th-8th c. BC. Measurements with PIXE-PIGE suggest they are made of mixed alkalis with a significant admixture of magnesium. It is still disputed whether this glass was made of plant ash or it represents the earlies form of natron-type glass. The production of bronze continued into the Iron Age. Intriguing objects are fragments of the so-called shaft-hole axes that contain significant amount of lead. As the material composition makes them useless for practical work, it is supposed they represent the earliest monetary forms. The high lead that was obviously added prevents tracing the origin of copper according to the lead isotopes. Our analysis involved raw bronze and objects from two sites in Julian Alps. The trace element pattern as obtained from the discriminant analysis suggests two sources of copper, one of them being Alpine, while the other is still a matter of speculation.

An Assessment of the Atmospheric Impact of Construction Work on Fine Particulate Matter in The University of Jordan: A PIXE Study

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The School of Science at the University of Jordan, Amman, Jordan, has recently conducted an intensive construction work to build a new building for the department of chemistry. The construction process in about two years went through various stages including digging the foundation, lifting the bases, pouring the concrete, etc. Impacts of construction work to air quality have negative effects on the university campus on both human health and local climate. To investigate these impacts, PM2.5 samples were collected for selective periods that cover the different seasons during the construction process. The samples were collected using an ISAP® 1050e sampler located just a few meters away from the department of chemistry and overlooking the construction site. Gravimetric measurements and PIXE analysis have been performed for the selected samples in order to determine the total aerosols mass and the elemental composition, respectively. Additionally, the black carbon (BC) content was measured with a light reflectance technique. In this contribution, the obtained results will be presented and discussed.

PIXE analysis of barbarian imitations of Late Roman period coins

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Archaeological samples of various nature are being characterized at analytical accelerating facility at Institute of Applied Physics NAS of Ukraine [1].

A series of barbarian imitations of Late Roman period coins (54 coins) found on the territory of Ukraine were analyzed by PIXE. The study has been performed in the framework of international project “IMAGMA: Imagines Maistatis”. Coins were manufactured by barbarian population of East Europe in III- IV centuries A.D. as imitations of official Roman coins (I - IV centuries A.D) of various denomination. Coins production was carried out by stamping, moulding and, sometimes, plating.

A part of the analyzed coins constituted silver alloys, another part was a bronze alloy with various ratio of copper and tin and the other one was gold-plated coins. The plating materials and the core of the coins were analyzed with uPIXE. The base material of the core is copper with zinc, tin and other impurities, plating material consists of gold with trace elements: copper, tin and, sometimes silver.

One sample was presented by a fractured gold coin, that enabled 2D mapping of its cross section with uPIXE technique. The mapping results are shown in fig. 1.

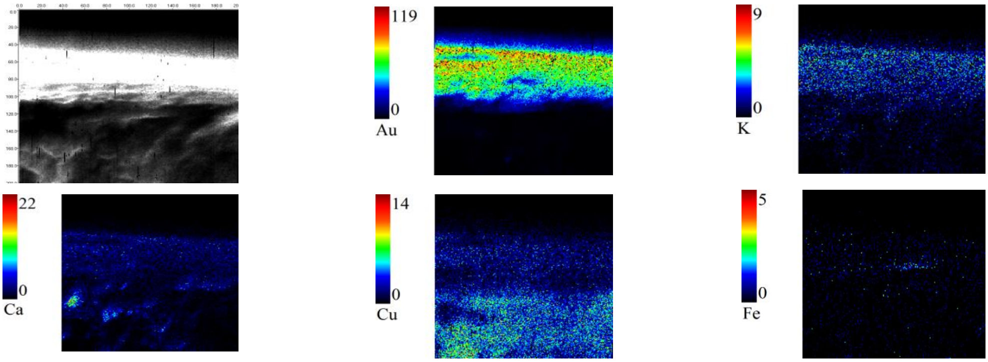

Fig. 1. 2D mapping of the cross section of the fractured gold-cladded coin

Array of data obtained in the course of elemental analysis was analyzed with principal component analysis, PCA. Basing on the analysis results, the coins may be divided into groups by their specific elements or their concentration.

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Monitoring of non-destructivity of PIXE analysis on cultural heritage objects

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Non-destructivity could be a very important requirment in studying unique, sometimes very valuble art and archaological objects. Methods using invasive mechanical or chemical intervention hardly satisfy this criteria. Some sophisticated physical techniques, however, where the delicate objects irradiated by energetic electrons, ions (protons, alpha particles etc.), neutrons, or illuminated by high energy electromagnetic radiations (X-rays or gamma rays) are usually referred to non-destructive or non-invasive ones. But to give a satisfactory definition of the meaning of the word „non-destructive", is not an easy task. This problem is the objective of several international meetings an European projects such as the „IAEA Technical Meeting (F1-TM-47768) on Investigating Heritage Materials with Safer Ion and Photon Beam Experiments", Louvre Museum, Paris, France 7-10 December 2015 or IPERION CH WP6: In-situ and ex-situ methodologies for monitoring radiation damage on CH materials/samples. Among questions to be answered could be for instance whether the non-destructivity does mean that not any clearly visible damage was caused, or the possible latent effects of the microscopic atomic or molecular modifications produced by the irradiation should also be considered? But even the opposite situation is also possible: the promptly observed effect such as discolouration of the irradiated spot will disappear as time goes on. Can we consider this phenomenon as a damage? This possibilty was experimentally demonstrated in our laboratory. To determine the elemental compositions of different pigments on a glazed ceramics external milli-beam Particle Induced X-Ray Emission (PIXE) analysis was performed. After the irradiation of a yellow region of the ceramics by focused proton beam of 2.5 MeV energy and about 1 nanoampers intensity a definite brownish discolouration is clearly visible. But on the picture of the same object taken eight months later, no discolouration can been seen, yet. In addition to ceremics the study of non- destructivity was extended to other cultural heritage materials, such as painted parchments etc.

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A TES probe for PIXE applications in the frame of the AHEAD Project

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AHEAD (integrated Activities for the High Energy Astrophysics Domain) is a collaborative research project carried on by a consortium of 26 institutions from 16 countries within the Horizon 2020 initiative funded by the European Commission.

The focus of the AHEAD research project is to coordinate the advancements in the field of High Energy Astrophysics at many levels, including the development of enabling technologies for state-of-art instrumentation to be used for the observation of astrophysical targets.

The reference frame for the project is the ESA Cosmic Vision L-class ATHENA mission, a large part of the research effort is put in the development of a focal plane array of TES microcalorimeters used as X-ray detectors. The ultimate goal of the project is anyway wider and foresees enabling technologies also in other fields like gamma-ray instruments.

The AHEAD project also includes a dedicated work package devoted to technology innovation with the aim to explore the transfer of technologies developed in the AHEAD project to other applications relevant to the high-tech industrial market, both in the space domain and for “ground” applications.

One possible application which has been selected for further development is the engineering study of a compact laboratory-grade probe using a set of TES detectors for use in a PIXE facility. The spectral resolution of TES is more than an order of magnitude better w.r.t. the SDD detectors used in PIXE nowadays so reducing spectral interference and allowing a better identification of the atomic species and their chemical state within the sample.

The study presented here, carried out in collaboration with the INFN LABEC laboratory in Florence, will be completed in Q1 2019 issuing a final Engineering Design Report which will set the basis for future implementation.

The poster shown at this conference aims to present the AHEAD project to the X-ray community, gives the available details on the ongoing design of the probe and discusses the expected benefits in some typical PIXE study cases like air/soil pollutant analysis and fine art and archeology analysis.

Five Year PIXE Study of Elemental Content in FAPM Collected in Seven Sites During Fireworks Burning Events

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Aerosols play an important role in the atmosphere, the environment and the human health. Depending on their concentrations and composition, the potential health risks of Fine Airborne Particulate Matter (FAPM) in the atmosphere, i.e. $PM_{2.5}$ particles under 2.5 µm of aerodynamic diameter, can provoke from slight to severe consequences. Atmospheric pollution is subject to multiple variables which can make it change quickly in time and space. Diverse events can influence it in short times and lead to pose in serious risk a small community or a densely populated area. Fireworks (FW) burnings are such kind of events, and one of the most common around the world, especially during worldwide celebrations such as New Year's Eve and others. In such cases, large amounts of fumes and particles are put into the atmosphere, changing dramatically the elemental composition and their concentrations in the air. Moreover, it is also common that FW manufacture change from place to place, a fact that can introduce additional variables in elemental and compound composition of fumes and particles introduced to air when FW events happen. In order to assess the influence and effects of FW events, it is very important to characterize the elemental content in FAPM as well as to determine other compounds and by-products.

In this research, systematic observations over approximately five years (2005-2010) were used to determine the elemental content in FAPM. Around 1700 samples were collected in seven monitoring sites located in the Mexico City Metropolitan Area (MCMA). The elemental content of a selected subset of 77 samples was determined by PIXE, choosing for this study those samples collected in days such as December 25th and January 1st of each year (Christmas and New Year's Day events). Fifteen elements were identified in the samples, but only six elements characteristics of FW are reported in the descriptive statistics. Elemental concentrations, temporal variations, and linear correlations were calculated. Elements such as Barium (Ba) was found consistently in the samples. This element is not commonly detected in a typical aerosol sample. Other elements such as K, Ca, Cr and Cu were found with increased abundance. PIXE spectra derived from FW burnings show different characteristics compared to typical aerosol spectra from normal activity days. High mass concentration values associated to FW events were also found in comparison with normal activity days samples.

Sulfur Contents in FAPM in Days with Relevant Events in Comparison with Normal Days in the MCMA

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As it is well known, sulfur contents in the atmosphere are introduced mainly as a primary pollutant (SOx) derived from combustion processes. Further chemical reactions can tranform it, in the highest pertcentage, into a secondary pollutant, mainly in the form of sulfate particles. Sulfate aerosol particles are nowadays considered as one of the main atmospheric pollution species of anthropogenic origin, which are an important constituent of the fine airborne particulate matter (FAPM) fraction, i.e. particles under 2.5µm of aerodynamic diameter. They are also an important contributor of the atmospheric brown clouds (ABCs) [1], which give rise to a dimming effect on earth's surface, affecting the climate and temperature [2] of wide regions around the world. Concerning the sulfur contents in the atmosphere, it usually remains within an averaged interval of values, in accordance with local weather conditions and season of the year. However, whenever any relevant event occurs, the concentrations and composition of local atmospheric pollutants can be changed, suffering alterations in accordance with the intensity of the event. Such is the case of fireworks burning events, large biomass burnings, volcanic eruptions, and others. In particular, FW burnings in the Mexico City Metropolitan Area (MCMA) occur during local celebrations, usually coinciding with non-working days, when local vehicle traffic is very low. During normal days, the sulfate content is mainly due to secondary particles derived from fossil fuel combustions, which can be calculated from the equation: $SO_4^{2-} = 3[S]$, where S is a value determined by PIXE. Nevertheless, this relation may not be applicable in all cases to measure sulfates coming from chemical reactions produced during FW burning events, because in this case sulfate particles come from different chemical compounds produced through different chemical reactions. In this work, a comparison of results and tendencies in both cases is presented and discussed.

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Multiple ionization X-ray satellites of magnesium, aluminum and silicon in alpha particle PIXE

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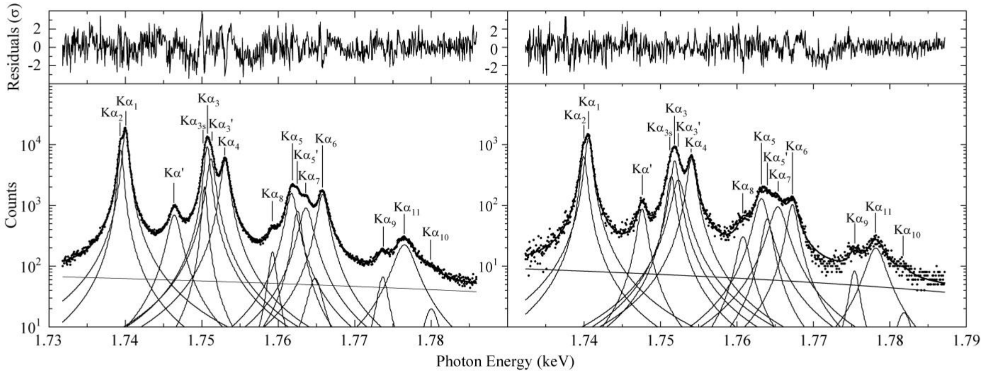
The Curiosity rover's alpha particle X-ray spectrometer employs simultaneous XRF and PIXE to analyze rock and soil samples on the Martian surface. The PIXE is accomplished by alpha particle emission from ^{244}Cm, and the XRF by the L X-rays from the daughter. Recent work [1] has shown that fits to these spectra, which extend over a 23 keV range, are improved by accounting rigorously for both X-ray detector non-linearity and the alpha-induced multiple ionization satellites. This work necessitated the insertion of an interim satellite database into the GUPIX-based fitting code GUAPX. The database was assembled from a rather sparse literature and involved considerable extrapolation and interpolation.

For 3- 5 MeV alphas, the summed intensity in the KL^1, KL^2, KL^3 satellites is of similar order to that of the KL^0 diagram line. It is clear that the accuracy of laboratory-based PIXE with alpha particles can be improved by including these in the spectrum fitting procedure.

We have therefore started an effort to refine and extend the interim satellite database, using WDX spectroscopy at IJS and IRB. Work has been completed on magnesium, aluminum, silicon and their oxides. The spectra below are from Si and SiO_2; all individual Voigtians are shown.



Comparison of our results for individual line energies and intensities with those of the database has enabled small corrections to the latter. The work will now proceed to elements of higher atomic number.

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Use of micro-beam PIXE and NRA in postmortem analysis of samples exposed in plasma devices

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Erosion and deposition of plasma facing material in the inner walls of a fusion reactor are important issues when dealing with plasma facing component lifetime and core plasma performance. The large power loads and particle fluxes on the inner walls especially in the lower part of a fusion device lead to material erosion, lattice damage and fuel retention in the wall material. Migration of impurities influences material erosion and deposition patterns and can be an important contributor to fuel retention.

Usually the postmortem analysis of samples exposed in plasma devices, either tokamak or linear plasma devices, is carried out with ion beam analytical methods in a broad beam configuration (≈1 mm^2). Ion beam methods such as Rutherford Back-scattering Spectroscopy (RBS) and Nuclear Reaction Analysis (NRA), are used to provide the general information on sample composition and trapped impurities or fusion fuel.

In recent years, our group at the Jožef Stefan Institute (JSI) extended the use of RBS and NRA to particle induced x-ray emission (PIXE) spectroscopy, in combination with focused ion beam at our micro-beam experimental chamber [1]. In this chamber, we are able to focus analytical ion beams to dimensions of few μm and compliment the broad beam results with the lateral resolution. The chamber is equipped with two x-ray detectors used to detect x-ray photon emitted from the sample via PIXE [2]. In such configuration PIXE provides an valuable additional information on surface topography and element distribution, as we are working in mapping mode. In combination with RBS and NRA information, we can investigate the influence of surface roughness on fusion fuel retention and erosion/deposition patterns of the inner wall material.

We will summarize and present results obtained on samples exposed in ASDEX Upgrade tokamak and Pilot PSI linear plasma device [2,3]. There PIXE served as a tool for observing the surface topology and detecting the small amounts of metal pollutants originating from plasma devices that were deposited on the sample surface.

Additionally, we will show work done on thin tungsten foils where PIXE performed as a useful method to pin down the sample position by elemental markers produced on the sample for overlaying NRA and scanning electron microscope images.

[1] Pelicon et al, Nucl. Instr. Meth. B 269 (2011), 2317.
[2] Kelemen et al. Nucl. Instr. Meth. B 404 (2017) 179.
[3] Kelemen et al. 2017 Phys. Scr. (2017) 014067

Quantitative Elemental Analysis of Human Hairs by Using Desktop X-Ray Fluorescence Analyzer

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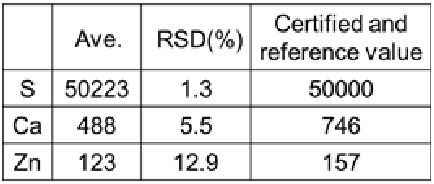
Minerals play a great role in the human body. Therefore, it is important to know the excess or deficiency of minerals for health examination. However, the mineral concentration in the blood is kept constant due to homeostasis, therefore blood tests cannot give us the abnormality. On the other hand, since hair takes in and holds mineral information, it is possible to examine the mineral concentration in the body by measuring the hair. ICP-AES/MS analysis has been mainly used for analysis of hair, however this technique requires a large amount of hair samples, and time and effort for pretreatment of dissolution. Therefore, we decided to study simple element determination method in hair. In the case where the hair sample is not dissolved but is analyzed as it is, the difference in thickness for each hair affects the quantitative value. This is because the fluorescent X-ray intensity increases with thick hair, even if the hair composition and length are the same. Therefore, in this study, scattered X-ray internal standard method was applied.

As shown in Table 1, regarding sulfur(S), we obtained high accuracy with small variation. This is because the S content in the hair is as high as about 50000 ppm. In addition, it has been reported that there is almost no individual difference in S content [1]. Therefore it can also be confirmed that the quantitative value of S analyzed on this time is accurate. In contrast, for Ca and Zn with small content, the dispersion in quantitative value became slightly larger. This is because the fluorescent X-ray intensity obtained from a small amount of hair is small. The above results depend on the sample form. It was found that preparation method of hair sample is important.

Table 1 Concentration(ppm) of elements in human hair.



	Ave.	RSD(%)	Certified and reference value
S	50223	1.3	50000
Ca	488	5.5	746
Zn	123	12.9	157

[1] T. Takeuchi, T. Hayashi, J. Takada, Y. Hayashi, M. Koyama, H. Kozuka, H. Tsuji, Y. Kusaka, S. Ohmori, M. Shinogi, A. Aoki, K. Katayama, T. Tomiyama, Variation of Elemental Concentration in Hair of the Japanese in Terms of Age, Sex and Hair Treatment, Journal of Radioanalytical Chemistry, 70, 1-2(1982)29-55

Rapid detection of uranium in blood extracted from wounds using X-ray fluorescence analysis

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Workers in nuclear handling facilities have a finite risk of injury and contamination in wounds from uranium. Due to their hazardous nature, accidental intake of uranium such as from wounds can lead to a considerable amount of internal exposure. Although an appropriate surgical resection of tissue in the contaminated wound is useful to suppress the additional intake of uranium, rapid quantification of uranium in the wound is required to avoid unnecessary surgeries. For surface contaminations, the rapid detection of uranium is usually performed via the α-particle counting method. However, in case of wound contamination, most of the α-particles emitted from uranium cannot pass through the oozing blood from the wound. Therefore, X-ray fluorescence (XRF) analysis can be an alternative approach to the detection of uranium because X-rays can pass through several millimeters of blood or soft tissue. In this study, we developed a new methodology for the rapid detection of uranium in wounds based on X-ray fluorescence analysis of contaminated blood collected by filter paper.

Mouse blood contaminated with uranyl acetate solutions having different concentrations were dropped on the filter paper and were subjected to XRF using a desktop XRF device (SEA1100 Hitachi High-Tech Science). The X-ray tube voltage was 50 kV, and the tube current was 1 mA. The X-ray accumulation time was 60 sec.

Since the obtained U Lα (13.6 keV) peak from the XRF analysis was overlapping with the Rb Kα (13.4 keV) and Br Kβ (13.3 keV) peaks (Figure 1), a Gaussian fitting was performed in order to separate them. Up to 25 ppm, the net count of the U Lα peak was directly proportional to the uranium concentration, and the obtained detection limit was low enough to detect uranium in emergency situations. These results confirm that the XRF approach is useful for the rapid detection of uranium in oozing wounds at radiation emergency medical facilities.

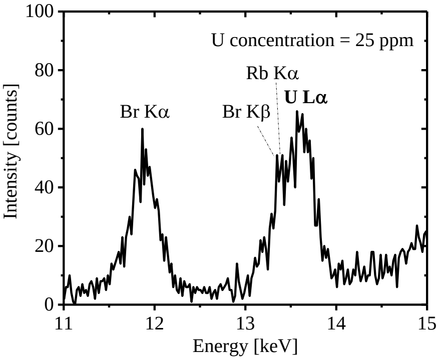

Figure 1. XRF spectrum of the mouse blood with uranium concentrations of 25 ppm.

Quantification of 2D elemental distribution maps of intermediate-thick biological sections by low energy synchrotron μ-X-ray fluorescence spectrometry

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Two fundamental-parameter (FP) based models for quantification of 2D elemental distribution maps of intermediate-thick biological samples by synchrotron low energy μ-X-ray fluorescence spectrometry (SR-μ-XRF) are presented and applied to the elemental analysis in experiments with monochromatic focused photon beam excitation at two low energy X-ray fluorescence beamlines - TwinMic, Elettra Sincrotrone Trieste, Italy, and ID21, ESRF, Grenoble, France. The models assume intermediate-thick biological samples composed of measured elements, the sources of the measurable spectral lines, and by the residual matrix, which affects the measured intensities through absorption. In the first model a fixed residual matrix of the sample is assumed, while in the second model the residual matrix is obtained by the iteration refinement of elemental concentrations and an adjusted residual matrix. The absorption of the incident focused beam in the biological sample at each scanned pixel position, determined from the output of a photodiode or a CCD camera, is applied as a control in the iteration procedure of quantification.

Acknowledgements: The research was funded by the Slovenian Research Agency (program P1-0112 and P1-0212), and the IAEA framework of coordinated research projects RC 13858 “Unification of nuclear spectrometries: integrated techniques as a new tool for materials research” (CSI, Peter Kump), and RC 16796 “Applications of synchrotron radiation for environmental sciences and materials research for development of environmentally friendly resources” (CSI, Katarina Vogel-Mikuš), Access to the synchrotron radiation facilities at ESRF (beamline ID21, projects EC 719, EC 968), and of Elettra (beamline TwinMic, projects 20130375) is acknowledged. We would like to thank Hiram Castillo-Michel of ESRF and Alessandra Gianoncelli of Elettra Sincrotrone Trieste, for support and beamline operation and Alenka Gaberščik for provision of the common red grass leaf material.

EMPIR MetVBadBugs – Reference-free X-ray spectrometry depth profiling studies on the uptake of antibiotics in multi-resistant bacteria and biofilms

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Gram-negative bacteria innately possess resistance to antibiotics as a consequence of the combinatorial effects of two permeability barriers: the outer and inner bacterial cell membranes, their ability to efflux antibiotics out of the cell and their capacity to form antibiotic tolerant biofilms that are up to 100 times more resistant than planktonic bacterial cells.

The objectives of the EMPIR project *Metrology vs. Bad Bugs* is to provide the urgently needed essential metrology to quantitatively measure and image the localization of antibiotics/biocides and to understand the penetration and efflux processes in bacteria and biofilms.

In this contribution, an overview of the ongoing reference-free (soft) X-ray spectrometry studies [1,2] (grazing incidence X-Ray Fluorescence (GIXRF), micro-X-ray fluorescence (µ-XRF), near edge X-ray absorption fine structure (NEXAFS), near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS)) on the penetration of biocides/antibiotics into bacteria and biofilms is given.

A specifically adapted liquid cell is utilized and allows for *in-situ* traceable quantification of the vertical concentration profiles of antibiotics in bacteria- and biofilms. The liquid cell can be applied for X-ray and IR analysis alike and will feature an option for UHV compatibility. Complementary techniques for XRF depth profiling involve line intensity ratio modifications and grazing incidence variations.

The NAP-XPS measurement capabilities have been tested out on both artificial and biological samples, including a biofilm of *E. coli*. Alginate (exopolysaccharide) was characterised and quantified based on measurements performed under near ambient pressure and ultra-high vacuum at the endstation of the HE-SGMbeamline.

The chemical composition and homogeneity of the alginate film was assessed by Fourier-Transform infrared (FTIR) micro-spectroscopy. Different concentrations of biocides embedded in the alginate matrix were probed in order to challenge the discriminatory power of their vibrational spectroscopic fingerprints to the signature of the alginate matrix, enabling quantitative analysis through IR-based calibration.

These studies will have an impact on the wide range of biological and biomedical research as it will enable studies of biological samples by XRF methods, which has not been possible thus far, due to the high-vacuum requirements of these techniques.

Acknowledgments

The authors acknowledge support by the team at the BESSY II synchrotron radiation facility and Dr. A. Nefedov (Karlsruhe Institute of Technology, KIT) from the HE-SGM Collaborate Research Group as well.

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In-line metrology of Tellurium-based materials for advanced memory applications

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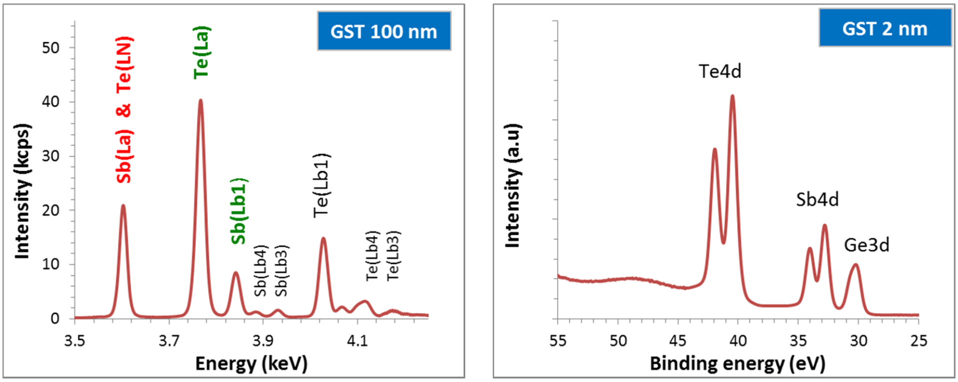
Tellurium-based chalcogenides materials are the core of both the storage element and the selector in innovative phase-change memories (PCRAM) that feature fast and easy storage to capture the exponential growth of data from mobile devices and the Internet of Things. The storage element consists in GeSbTe alloys, which bonding, structure and phase-change properties can be fine-tuned by adjusting the stoichiometry of the film [1]. Hence, production monitoring of GeSbTe thin films and process development of GeSbTe alloys with improved stoichiometry-driven performances require in-fab metrology protocols that must cover large ranges of GeSbTe stoichiometry, film thickness (from 1 to 200 nm) and spatial resolution (from few 10 µm on product wafers to mm on blanket wafers).

In this paper, we report on the accuracy of inline quantitative analysis of the stoichiometry of a large variety of GeSbTe films grown by physical vapor deposition. First, we compare the performances of wavelength-dispersive X-ray fluorescence (WDXRF) strategies with Ion beam Analysis (RBS, PIXE), resulting in ± 1 % overall discrepancy. Then, we demonstrate that WDXRF-based optimization of the relative sensitivity factors in micro-spot X-ray photoemission spectroscopy (XPS) analysis results in ± 2 % agreement between XPS and WDXRF for a large range of GeSbTe composition.



WDXRF analysis (left) is based on unconvoluted Te(Lα) and Sb(Lβ_1) lines whereas XPS quantification (right) lies on Te4d, Sb4d and Ge3d components with related photoelectrons featuring similar kinetic energy

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Gafchromic film dosimetry for *in vivo* bone lanthanum measurements

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Gafchromic films are a powerful 2D dosimeter that have an effective atomic number, Z_{eff} = 6.98, close to that of water, Z_{eff} = 7.3. The sensitive dose range for the films is between 1 mGy and 10 Gy, which is useful for clinical dosimetry and radiation protection purposes. Compared to traditional thermoluminescence dosimeters, Gafchromic films are preferred as they are relatively simple to use, and are self-developing, unlike previously used radiographic films that must be processed.

In this work, we assess the suitability of using Gafchromic EBT3 films for our K-shell X-ray Fluorescence (K-XRF) *in vivo* bone lanthanum system that utilizes a 1.09 GBq ^{241}Am excitation source, which has been shown to be successful for measurements at the tibial site, with a detection limit of 0.7 μg La/g HAp. The source emits 59.5 keV photons sufficient to overcome the 38.9 keV K-edge of lanthanum. The films were irradiated with a 180 kVp beam from an orthovoltage unit (Model D3300, Gulmay Medical LTD, England), calibrated following the Task Group 61 absolute dose calibration protocol [1], with nine doses ranging between 0-800 cGy to produce a calibration curve. The beam has an HVL of 0.56 mm Cu and an effective energy of 61.3 keV, which closely matches the 59.5 keV photons from ^{241}Am. Beam matching was necessary due to the known energy dependence of the films. Measurements were carried out using a plastic bottle filled with water to represent the lower leg and placing a film at the surface of the bottle and a film directly on the source collimator opening. An irradiation time of 28 hours was used to ensure adequate dose was delivered to the film for accurate dose measurements. For a source-to-film distance of 1.57 cm, we report an equivalent surface dose rate of 135 mSv/hr to the film from both experimental and Monte Carlo work. It was found that the largest contribution to dose was from 13.9 keV emissions from the ^{241}Am source decay. These photons do not contribute to the K X-ray signal and can be easily attenuated down to negligible levels with the use of a metal filter. Despite this, the overall equivalent skin dose for a typical 2000 s measurement at a distance of 5 cm without a metal filter was 12 mSv, which is well below the maximum equivalent annual dose limit of 50 mSv to skin for the public [2]. This justifies the ^{241}Am system for routine diagnostic testing of *in vivo* bone lanthanum and demonstrates the usefulness of a simple radiochromic film procedure for verification of entrance dose for *in vivo* X ray fluorescence measurements. Future optimization work is required to determine the optimal filter material/thickness to minimize attenuation of the 59.5 keV excitation photons while nearly eliminating the 13.9 keV photons.

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Optimizing the use of the XMI-MSIM Monte Carlo tool for the simulation of tube excited XRF spectra

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The strict requirement towards non-invasive compositional analysis of cultural heritage materials, has naturally motivated the application and evaluation of advanced modern Monte Carlo tools to simulate complex XRF spectra acquired by portable spectrometers [1-5]. In such cases, the analytical challenge relies on the holistic and accurate description of all spectral features, including the background shape, the intensity and shape of the scattered discrete lines of the tube anode material and of all detected elements emission lines. Each particular spectrum component projects useful analytical information on the sample elemental composition, stratigraphy, roughness etc., usually ignored in conventional quantitative analysis based only on major peaks analysis.

The reliability of Monte Carlo tools, apart the subjective modelling of the sample composition and structure, depends on the embedded databases of the X-ray fundamental parameters (FPs), the adopted model for the analytical description of the X-ray source excitation spectrum, but also from the good knowledge of set-up geometrical parameters, hardware specifications and operational parameters. Obviously, relevant uncertainties and particularly the adaptation of the widely applied semi-empirical model of Ebel [6] to describe the emission spectrum of modern low power X-ray tubes, can propagate inconsistencies in the simulated spectrum.

In the present work, the XMI-MSIM open source Monte Carlo tool [1], is employed for the systematic simulation of XRF spectra obtained from the analysis of certified gold, silver and copper alloys presenting compositional profiles that resemble the ones of the most common relevant archaeological alloys. The measurements were carried out using a portable XRF spectrometer equipped with a Rh anode, side window X-ray tube (50 Watt) and a Si-PIN detector. To optimize the use of the XMI-MSIM tool, scattered spectra from a certified material (PTFE) were measured at different high voltages (10 - 48 kV) and through comparison with the simulated ones, the description of the tube emission spectrum was optimized. The obtained results are critically evaluated and discussed.

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Compton Scattering Polarizes Continuous X-rays

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We report a method of X-ray polarization via Compton scattering for any wavelength of X-rays without changing the optics, and consequently, X-rays should be linearly polarized as continuous X-rays.

By Barkla scattreing [1], X-rays can be polarized, which was first applied to energy dispersive X-ray spectrometry by Young *et al*. [2]. This allowed the use of bremsstrahlung from the X-ray tube without the contribution of background. Although it is well known that scattered X-rays from polarizer includes not only the elastic scattered X-rays but Compton scattering [3], in the present method, we explicitly use the polarization property of Compton scattered X-rays as follows. Based on the Schrödinger's wave picture of Compton scattering, the de Broglie wave of a recoil electron performs as a Bragg crystal [4]. Considering Compton scattering at an angle of 90 degrees, the de Broglie wave of the recoil electron always goes away in the direction of 45 degrees with respect to the incident X-rays, which satisfies 45 degrees Bragg diffraction condition. Here, we regard the recoil electron as a Bragg crystal whose lattice spacing varies with respect to the incident X-ray energy (Figs.1 and 2). Through the method, we need not to prepare polarizers that are designed corresponding to the wavelength of the incident X-rays or to employ large-scale high-power facilities.

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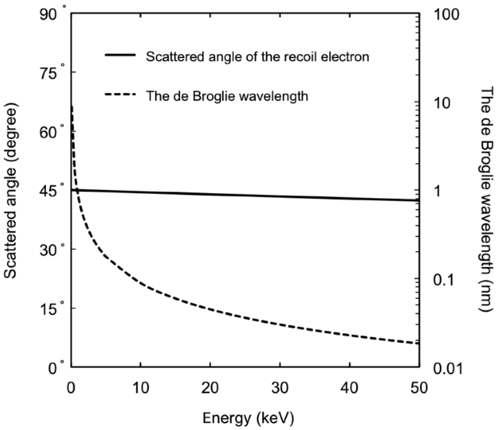

Fig.1. The incident X-ray energy dependence of scattered angle and the de Broglie wavelength of the recoil electron. Scatterd angle keeps 45 degrees with changing the wavelength.

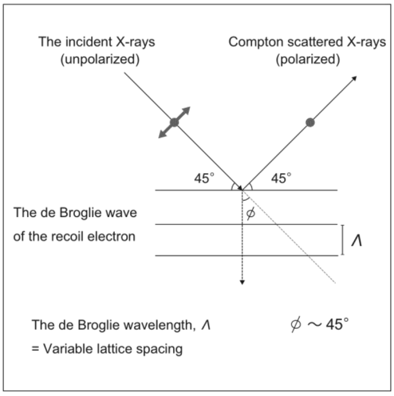

Fig.2. Schematics of X-ray polarization by the de Broglie wave of the recoil electron. The gray colored double-headed arrow and circle represent the *p*- and *s*- polarization direction of electric field, respectively. The dotted arrow is the moving direction of the de Broglie wave.

Software for Quantitative Analysis in X-Ray Spectroscopy

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We present free, open-source and cross-platform software for quantitative analysis of X-ray spectra. In the calibration mode, the software can be used for energy or efficiency calibration on spectra from samples with known elemental composition (standards). In the analysis mode, the software is used to fit spectra in order to obtain peak areas or, if the calibration for the experimental setup is available, to directly provide elemental concentrations. In the latter case, it also includes corrections for absorption and secondary emission in the sample. The fitting procedure can be done manually in which case the user selects peaks that will be included in the fit or automatically with a peak-search algorithm. The software is written in Java with a modular design which enables users with little programming experience to easily make modifications (for example, modify the fitting function). All needed data (fundamental parameters, experimental setup, fit results, etc.) are stored to and retrieved from a database which is provided with the program.

Application of HPGe detectors in X-ray spectrometry to improve counting efficiency

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Standard devices of energy-dispersive X-ray emission spectrometry are Si(Li), Si-PIN, Si.drift detectors. Typical devices of (high resolution) gamma-spectrometry are high purity Germanium (HPGe) detectors. Modern HPGe are equipped with rather thin window (typically carbon-epoxy), which allows the detection downto 5 MeV energy, covering a wide range of X-ray region. Due to the manufacturing technology HPGe crystals are available in definitely larger geometric dimensions compared to Si-based X-ray detectors. However the energy resolution of HPGe detectors are worse than Silicon detectors at identical energy.

The availability of detection of the characteristic X-rays of several elements indicates the idea of application of HPGe detectors in X-ray emission spectrometry. In the case of not too complex spectra, where the moderate energy resolution is enough, the counting efficiency can be increased by application of HPGe detectors, due to the larger crystal sizes.

The efficiency of typical Si(Li) and HPGe detectors will be compared and illustrative applications are discussed.

Angle resolved X-ray fluorescence spectroscopy for in-depth structure identification

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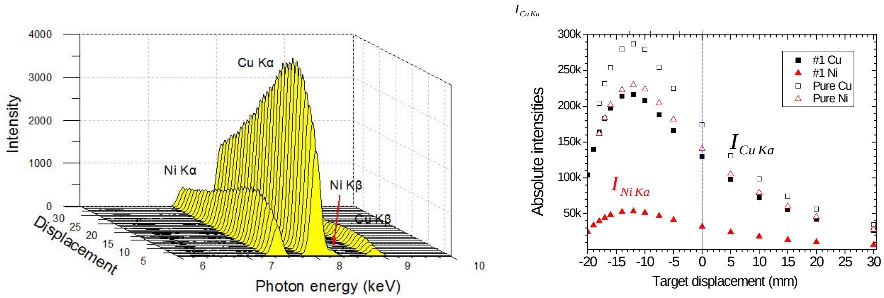
Energy dispersive X-ray fluorescence spectroscopy allows quantitative analysis, based on the intensity of measured X-ray fluorescence transitions. Intensities are associated with the target's structure and elemental concentration in a complex way, involving the spectrometer's geometrical set-up. Angle-resolved X-ray fluorescence spectroscopy is applied for material structure characterization concerning in depth homogeneity. The fluorescence spectra are recorded moving the target along the X-ray ionization radiation beam path. The incident angle of the excitation beam on the target remains constant, while the fluorescence beam take-off angle, as seen by the detector, changes as function of the target position. Comparison of the measured fluorescence spectra, at various target positions, reveals information related to the target's in-depth structure. Experimental extracted intensities are compared with theoretical predictions based on Monte Carlo simulations [1].



Left) Measured X-ray fluorescence spectra of CuNi target as function of the displacement of the target. The displacement step is 1 mm. Right) Integrated intensities of the Cu and Ni Kα transitions as function of the target displacement, from the CuNi sample, and reference Cu and Ni targets. The intensity variation as function of the displacement contains information about the sample's in depth structure.

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EDX calibration using polynomial fitting over the X-Ray production factors of thin elemental standards

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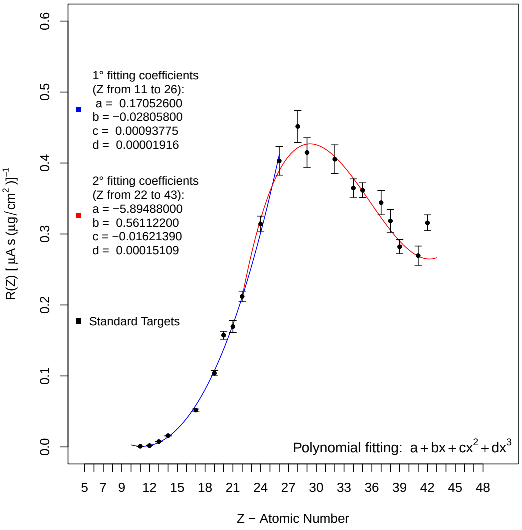
The uncertainty of the quantitative elemental composition determined by energy-dispersive X-ray spectroscopy (EDX) is connected to the uncertainty of the available standard targets. They define the starting level of the uncertainty for calibrations when they are individually performed for each element. Fixing general parameters of an EDX, and in the absence of enhancement effects [1], we may consider that

$$N(Z)=R(Z)\cdot I\cdot \Delta t\cdot \frac{m(Z)}{A} \quad ,$$

where N is the number of X-ray photons integrated in a characteristic peak of an element with atomic number Z, I is the current fixed in the X-ray tube, Δt is the live time of the spectrum, and m/A is the ratio of mass to the area in the sample. The production factor R may be reversely calculated using standards with known m/A ratios.

At the IFUSP PIXE system they fit, to experimental points, the theoretical equation expected for factor R versus Z [2]. In this work we adopted this idea for EDX, but making a polynomial fit to $R \times Z$, using matrix last square methodology (LS-M) [3]. Since LS-M uses all values in the fit to define the final uncertainties, we obtain R with a uncertainty better than individualized calibration do for each element. Else, the continuity of the functional fit, provides R values for elements we do not have standard targets, as show in the figure for X-ray K lines of thin Micromatter standards (excited with X-ray bean from a Rh tube at 50 kV, after an Al filter). Calibration drift with time was evaluated, and blind inter comparison with real aerosol samples analyzed by US-EPA showed good agreement.



[1] Tajani, A., Markowicz A.. EDXRF Analysis of Thin Samples, in Quantifying uncertainty in nuclear analytical measurements, IAEA-TECDOC-1401, ISBN 92–0–108404–8, p.45, 2004.

[2] Tabacniks, M. H.. Análise de Filmes Finos por PIXE e RBS, Instituto de Física-USP, Available at http://www2.if.usp.br/~lamfi/pixe&rbs.pdf, 2000, accessed on 30/03/2018.

[3] Helene, O.. Métodos dos Mínimos Quadrados, Editora Livraria da Física, 2006.

FRX, electronic microscopy and micro-computed tomography characterization of silver-infused gel dosimeters

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Different types of nanoparticles have proved to be suitable for biomedical applications including both diagnose and therapy procedures [1]. Particularly, infusion of high atomic number compounds within tumor target may benefit dosimetry performance due to so-called dose enhancement produced by secondary electrons, mainly. Therefore, incorporation of high atomic number nanoparticles in gel dosimetry technique appears as a potential tool for assessing dose contribution due to the presence of nanoparticles, i.e. estimating the dose enhancement.

The present study focuses on the results obtained from the different X-ray based analytic techniques used to characterize the presence of silver nanoparticles in gel dosimeters. Shape and size were obtained from electronic microscopy, silver nanoparticle concentration within sample was correlated with fluorescence signal and effective mass absorption coefficient was evaluated from high resolution micro-computed tomography. Comparisons with Monte Carlo simulations based on the PENELOPE main code [2] indicated overall good agreement with experimental data.

[1] F. Mattea, J. Vedelago, F. Malano, C. Gómez, M. Strumia, M. Valente, Radiation Physics and Chemistry 130, 2017, 442-450.

[2] F. Salvat, J. Fernández-Varea, J. Sempau, PENELOPE-2008: A Code System for Monte Carlo Simulation of Electron and Photon Transport, NEA France, 2008.

Mapping of SiO_2 nanoparticles in A549 and Macrophages cells

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and L. Pascolo [3]

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The Joint Research Centre of the European Commission (JRC) has developed a research plan on nanoparticles toxicology based on an integrated approach combining cell-based in vitro assays with specific radiochemical and physicochemical facilities. Moreover, recently an activity on the characterization of nanomaterials to be used in nanomedicine has been initiated with the launch of the European Nanocharacterisation Laboratory (EU-NCL, http://www.euncl.eu/). Amongst the different nanoparticles to be tested, Carbon Nanotubes (CNTs) and TiO_2 and SiO_2 nanoparticles (NPs) are also investigated because they model systems selected by the OECD and ISO for both standardization and toxicological studies. Moreover, both TiO_2 and SiO_2 NPs are largely used in commercial products such as food additives and cosmetics.

In previous experiments, we demonstrate the TwinMic [1] capability to map nanoparticle distribution in different cell lines. In particular, the interaction of cobalt ferrite magnetic nanoparticles with Balb/3T3 cells was deeply investigated. The results showed the possibility of observing nanoparticles agglomerates in the cytosol and detect nanoparticle dissolution and Co release at high concentrations [2].

In this work, the behavior of SiO_2 NPs (30nm), synthetized at JRC, in different cell cultures has been investigated. In particular, A549 and U87MG human cell lines were used, because both cell lines are of high interest in toxicology. For the uptake and intracellular distribution of NPs cells were cultured on Si_3N_4 membranes and on polymeric substrates (Mylar). The SiO_2 NPs have been characterized by DLS, CPS, TEM, XPS and ToF-SIMS, whilst their interaction of with the cells was investigated with TEM and LEXRF. For this, we have used TwinMic in STXM mode operated in low-energy XRF setup to map the distribution of different elements, namely Fe, N, O, C, Si, P, Mg and Ti. As expected, results indicate an increase of the Si signal with the NPs concentration. Moreover, as already observed in the case of similar concentration of cobalt ferrites, the SiO_2 NPs are distributed inside cell compartments such as endosomes and lysosomes, and on cell membrane as confirmed by TEM image analysis. Interestingly, when the nanoparticles are covered with an epoxy coating, the Si signal is more than one order of magnitude higher at the same concentration. This indicates a different affinity of the NPs to the cells as a function of the surface functionality.

[1] A. Gianoncelli et al, Journal of Synchrotron Radiation, Vol. 23, pp. 1526-1537 (2016).

[2] P. Marmorato et al., Toxicol. Letters 207, (2011), 128– 136

Influence of bimodal and metallocene linear low-density polyethylenes on crystallinity of compositions

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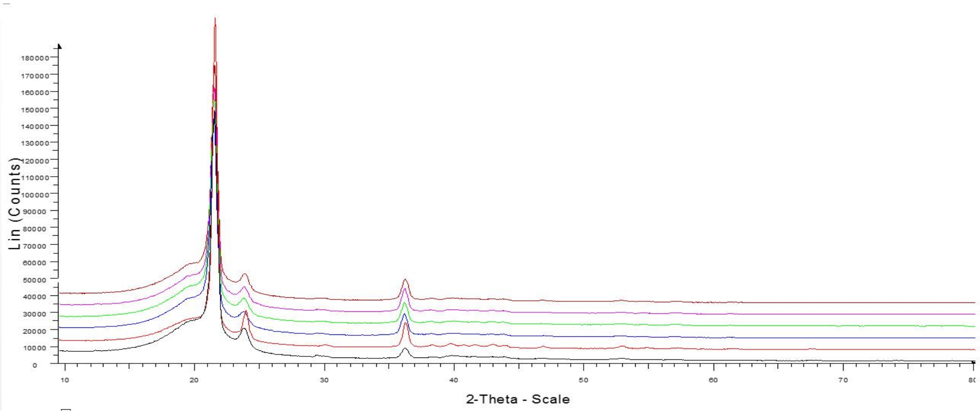
This article provides data on the influence of addition of metallocene linear low density polyethylene (mLLDPE) and bimodal polyethylene on the properties of low density polyethylene (LDPE)-based composition polymer films.

The aim of this research was to study influence of changes of crystallinity of three-composittion films. Polymer mixtures with 10%, 15, 20% of mLLDPE and bimodal polyethylene were investigated. Degree of crystallinity of three-component films and two original films was measured on multifunctional X-ray diffractometer DRON-7 with regular Bragg-Brentato geometry (θ-2θ). Radiation CuKα (with β-filter Ni (28)). X-ray tube regimen 40 kV/20 mA). Goniometer channels 2-1-1mm. Diffractogram was taken at the angles ranging from 5º to 100º, with 0,05º steps (2θ) and 5 seconds exposition, all were scanned three times and then summed up. The processing of data was carried out with EVA v.11.0.0.3. Quantitative estimation of the degree of crystallinity of polymer systems was carried out with TOPAS V3.



Dark red - LDPE(70%)/bimodal PE(30%);
Violet - LDPE(70%)/bimodal PE(20%)/mLLDPE(10%)
Green - LDPE(70%)/bimodal PE(15%)/mLLDPE(15%)
Blue - LDPE(70%)/bimodal PE(10%)/mLLDPE(20%)
Red - bimodal PE(100%)
Black - mLLDPE(100%)
Image 1 – X-ray diffraction pattern

We determined the crystallinity of bimodal and mLLDPE polymers and they are 53,8% and 44,7% respectively. Our results prove that crystallinity of bimodal PE higher than crystallinity of mLLDPE by 9.4% and the influence on the crystallinity of the compositions is more significant.

9 Tuesday program

	Marmorna Hall 1	Marmorna Hall 2
	Chair: B. Beckhoff	
9:00	Invited: **In-vacuum tender X-ray emission spectrometer with eleven cylindrically bent Johansson crystal analyzers** *P. Glatzel* (p. 119)	
9:30	Invited: **High-efficiency X-ray-emission spectroscopy with arrays of transition-edge-sensor microcalorimeters** *W. B. Doriese* (p. 120)	
	Session III (cont.): QUANTIFICATION METHODOLOGY AND METROLOGY Chair: B. Beckhoff	Session V: XRS INSTRUMENTATION I. (X-RAY SOURCES, OPTICS AND DETECTORS) Chair: B. Kanngießer
10:00	**Quantitative determination of the surface of silicon spheres for the redefinition and realisation of the SI unit kilogram** *M. Müller* (p. 122)	**Optical pump soft X-ray probe NEXAFS spectroscopy using a laser-produced plasma source** *A. Jonas* (p. 133)
10:15	**A modified fundamental parameter method dedicated to EDXRF setups** *J. Heckel* (p. 123)	**A Diced von Hamos Spectrometer for Time Resolved X-ray Emission Spectroscopy** *S. Jensen* (p. 134)
10:30	Coffee Break & Conference Photo	
11:00	**Parametrization of a tabletop micro-XRF system** *Ž. Šmit* (p. 124)	**A compact and efficient von Hamos spectrometer based on two full-cylindrical HAPG mosaic crystals for high-resolution XES** *M. Wansleben* (p. 135)
11:15	**Polarization Measurement of Compton Scattered X-rays by 3D-Printed Polarimeter** *R. Tanaka* (p. 125)	**Laboratory von Hámos X-ray Spectroscopy for Routine Sample Characterization in Solution Phase** *Z. Németh* (p. 136)
11:30	**Full Recovering of an X-ray Spectrum from Detector Influence** *J. Fernández* (p. 126)	**Imaging and spectroscopy with X-rays from Carbon to Uranium K lines** *L. Strüder* (p. 137)

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11:45	**A Methodology to Obtain Traceability and Validation of Calibration Samples for Thin Metal Alloy Layers for X-Ray Fluorescence Tools** *A. Nutsch* (p. 127)	**Laboratory-based Cu L X-ray fluorescence spectroscopy** *S. Staeck* (p. 138)
12:00	**In-line characterization of ultrathin MoS 2 and WS 2 materials using XRF-XPS strategies** *E. Nolot* (p. 128)	**Low-E extension of a hand-held Compton spectrometer** *I. Gerardy* (p. 139)
12:15	**Comparison of different quantification approaches in X-ray fluorescence imaging of freeze-dried tissue samples** *P. Wróbel* (p. 129)	**Catalysis research with a laboratory based XAFS spectrometer** *W. Malzer* (p. 140)
12:30	Lunch Break	
	Chair: R. Padilla-Alvarez	Chair: S. Fazinić
14:00	Invited: **Benchtop Analytical XAFS and XES: Applications from Sulfur to Uranium** *G. Seidler* (p. 121)	
14:30	**Absolute high-precision measurements of x-ray transitions with a double crystal spectrometer** *J. Machado* (p. 130)	**Pulse Processing for Practical X-ray Microcalorimetry** *T. Jach* (p. 141)
14:45	**Validation of secondary fluorescence algorithms for thin layered samples using synchrotron radiation based experiments** *A. Wählisch* (p. 131)	**Enhancing CCD Capabilities by Single Photon Counting: A Comparison of Photon Event Evaluation Algorithms** *J. Baumann* (p. 142)
15:00	**Online measurement of deposited energy by ion beams using bremsstrahlung X-rays** *F. Ralite* (p. 132)	**Advanced Pulse Processing Techniques for Photon Science and Other High Rate Applications** *P. Scoullar* (p. 143)
15:15	Coffee Break	

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	Industrial session I. Chair: J. Boman
15:45	**Company and Product Profile – PNDetector GmbH** *J. M. Davis, PNDetector GmbH* (p. 145)
16:00	**An Improved Performance of the Vortex Silicon Drift Detector** *S. Barkan, Hitachi High-Technologies* (p. 146)
16:15	**Improving Detectors for X-Ray Spectroscopy** *R. Redus, Amptek inc.* (p. 147)
16:30	**Bruker XRF, complete and innovative portfolio of portable, benchtop, and floorstanding instruments** *C. Vailati, Bruker Nano GmbH* (p. 148)
16:45 ⋮ 18:00	Poster Session II.
20:00	Public Lecture

In-vacuum tender X-ray emission spectrometer with eleven cylindrically bent Johansson crystal analyzers

Mauro Rovezzi[1], Blanka Detlefs[2], Alistair Harris[3], Pierre Van Vaerenbergh[2], Roberto Verbeni[2], Menhard Kocsis[2], Alain Manceau[4] and Pieter Glatzel[2]

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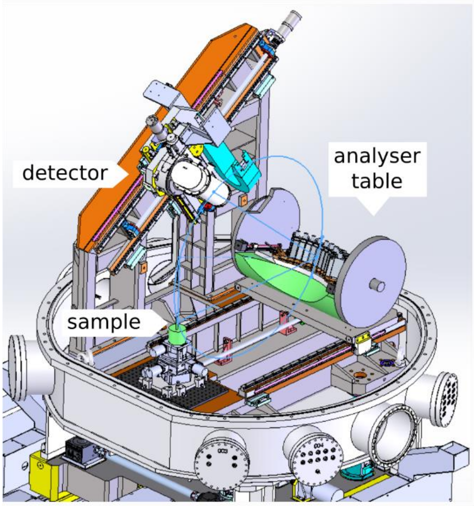
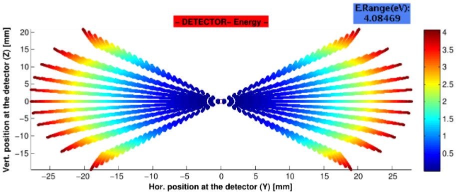
The energy range between 1.5 and 5 keV (tender X-rays) covers absorption edges of important elements whose electronic and magnetic structure is challenging to study in the hard or soft X-ray range. X-ray emission spectrosocpy (XES) in combination with X-ray absorption spectroscopy (XAS) can provide sharper spectral features and allows studying the occupied and unoccupied density of electronic states thus providing a wealth of information. There is a rapidly growing interest in the X-ray spectroscopy community in XAS-XES.

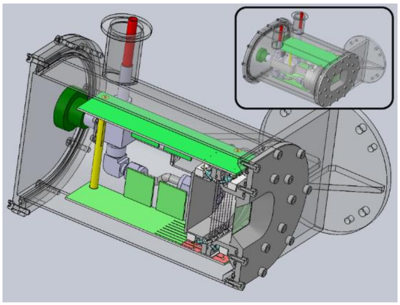
Tender X-ray emission spectrometers have been realized in different geometries. We recently commissioned at the ESRF an instrument in non-dispersive, scanning geometry that employs eleven Johansson crystals in combination with a gas proportional counter. The 80 mm long Si crystal wafers, cut along the (111) direction, are cylindrically bent to 0.5m radius in the meridional plane. The sagittal dimension is 25mm requiring a large detector surface of 50 x 25 mm^2. The angular range of the instrument is 35 to 85 degrees.

The presentation will describe concept and design of the instrument and discuss first results.



Detector area at 35°/500 mm bending radius ≅ 50 x 40 mm^2





High-efficiency X-ray-emission spectroscopy with arrays of transition-edge-sensor microcalorimeters

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Transition-edge-sensor (TES) X-ray microcalorimeters are energy-dispersive detectors with energy resolution of a few eV. Over the last eight years, the NIST Quantum Sensors Group has developed a number of X-ray spectrometers based on multi-hundred-pixel arrays of TESs for a variety of measurement applications. These applications include tabletop time-resolved absorption and emission spectroscopy, synchrotron-based absorption and emission spectroscopy and energy-resolved scattering, metrology of X-ray-emission lines, spectroscopy of hadronic atoms, and particle-induced emission spectroscopy.

TES arrays occupy an interesting region of the spectroscopy parameter space. They have good enough energy resolution to perform many types of X-ray emission spectroscopy (XES), or measurement of the positions, shapes, and relative intensities of emission features. XES has traditionally been accessible only to wavelength-dispersive spectrometers (e.g., gratings, crystals, and multilayers). TES arrays also have many of the best features of traditional energy-dispersive detectors (e.g., silicon-drift detectors): high collecting efficiency (large area, high quantum efficiency, and the possibility of a close sample distance), flexible observing geometries, and simultaneous sensitivity to all X-ray energies. Pixelated TES arrays also allow imaging. This combination of features is most useful in high-resolution applications that are traditionally photon-starved and/or involve radiation-sensitive samples. TES arrays are also enabling expansion to the lab bench of techniques that have been previously available only at synchrotrons or XFELs.

In this talk I will discuss a few evolving measurement techniques. The first is tabletop, time-resolved XES (TR-XES) of emission lines within the ~3–10 keV band (including L lines of the lanthanides and K lines of the 3d transition metals) to determine the valence state, spin, and coordination environment of elements within a photoexcited sample. To test our ability to detect subtle differences in spectra across a range of energies, we have performed static XES on several Ti-containing compounds. The detectors have energy resolution of 3–4 eV (FWHM). We see clear XES shifts among samples in the Ti $K\alpha_{1,2}$ complex, the Ti $K\beta_{1,3}$ line, and the Ti $K\beta_{2,5}$ line. I will discuss various features of the experiment, including the novel energy-calibration procedure.

The second application I will discuss is metrology of the energies and widths of the L-series lines of the lanthanides Sm, Nd, Ho, and Tb as well as Pt and Ta. The NIST Standard Reference Database 128 (X-ray line energies) entries for some of these lines are based on decades-old measurements taken before X-ray wavelength standards were traceable to the meter. Our TES-based measurements improve uncertainties on many of these reference energies and show significant discrepancies with a few others.

Finally, we are developing TES-detected resonant soft-X-ray scattering (RSXS) spectroscopy to search for glassy order in charge stripes in cuprate high-T_c superconductors. Each TES in the array probes a different scattering angle and thus a different momentum transfer. In a proof-of-principle measurement, we detected charge-stripe order at the Cu L_3 edge in LBCO. I will discuss the performance of the spectrometer and show our latest scattering measurements.

Benchtop Analytical XAFS and XES: Applications from Sulfur to Uranium

Gerald T. Seidler[1], Devon R. Mortensen[2], Evan P. Jahrman[1], William M. Holden[1], Alexander S. Ditter[1,3], and Stosh A. Kozimor[3]

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X-ray absorption fine structure (XAFS) and very high resolution wavelength-dispersive x-ray fluorescence (WD-XRF), often called x-ray emission spectroscopy (XES), each have a rich history in technical development and scientific application. They are particularly appropriate for strictly local, element-specific inquiries about electronic, atomic, and magnetic structure. However, XAFS and XES suffer from the reputation of being specialist methods with very low access confined to synchrotron x-ray light sources. The absence of routine, analytical capability for XAFS and XES must represent a considerable lost opportunity for spectroscopy education, scientific and industrial research, and even industrial process control.

Over the past several years, groups at the University of Washington, the Technical University of Berlin, Jan Kochanowski University, and elsewhere have made strong progress toward a modernization of benchtop XAFS and XES using only conventional x-ray tubes. In this seminar, I will survey the technology and application of recent benchtop XAFS and XES with an emphasis on examples from the several instruments developed at the University of Washington.[1-4] Sample applications include: S speciation in biochars for soil remediation, P speciation for core-shell InP electroluminescent quantum dots, detection of nanocrystallization in Fe-oxide based glasses intended for long-term storage of nuclear waste, Cr(VI) speciation for Reduction of Hazardous Substances (RoHS) compliance, charge-cycle fatigue studies in lithium ion battery electrode materials, and the acceleration of research into f-block chemistry by bringing XAFS and XES capability directly into radiochemistry laboratories.

[1] G. T. Seidler, et al., Rev. Sci. Instrum. **85**, 2014, 113906.
[2] G.T. Seidler, et al., J. Phys.: Conf. Series **712**, 2016, 012015.
[3] W.M. Holden, et al., Rev. Sci. Instrum. **88**, 2017, 073904.
[4] D.R. Mortensen, G.T. Seidler, J. Elect. Spectr. and Related Phenom. **215**, 2017, 8.

Quantitative determination of the surface of silicon spheres for the redefinition and realisation of the SI unit kilogram

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In recent years the research for the revised SI needed special efforts of National Metrology Institutes, like PTB, in development and improvement of measurement techniques to determine the value of fundamental constants very precisely. The mass unit kilogram will be based in the revised SI on the Planck constant h. To determine its value PTB was in favor of the XRCD method to determine the number of silicon atoms in a one-kilogram weighing silicon single crystal sphere and hence, Avogadro's number N_A[1].

Beside other values, the composition and mass of the surface layer of these spheres must be measured. For that purpose, Germany's National Metrology Institute, the Physikalisch-Technische Bundesanstalt (PTB), has designed, constructed and taken into operation an experimental setup [2], which allows for the investigation by X-ray photoelectron spectroscopy (XPS) and X-ray fluorescence spectroscopy (XRF) in one instrument.

We will present a short overview of this instrumentation and exhibit XPS and XRF measurements of Si reference samples to demonstrate the increased information content obtained by the combination of both methodologies. Here, the quantification of the surface layer based on synchrotron radiation based reference-free quantification of reference samples will be explained [2,3]

[1] G. Bartl et al.; Metrologia 54, 693 (2017); DOI:10.1088/1681-7575/aa7820

[2] M. Müller, B. Beckhoff, E. Beyer, E. Darlatt, R. Fliegauf, G. Ulm, M. Kolbe; Metrologia 54, 653-662 (2017); DOI:10.1088/1681-7575/aa73c5

[3] P. Hönicke, I. Holfelder, M. Kolbe, J. Lubeck, B. Pollakowski, R. Unterumsberger, J. Weser, B. Beckhoff; Metrologia 54, 481-486 (2017); DOI:10.1088/1681-7575/aa765f

A modified fundamental parameter method dedicated to EDXRF setups

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Sherman [1] at al. have developed mathematical models based on fundamental parameters for the computation of X-ray fluorescent intensities as a function of the elemental composition and the mass area of a specimen, the spectral distribution of the exciting X-ray tube radiation, and geometrical parameters, the so-called fundamental parameter method. Simplifying assumptions were made, for example that incident as well as fluorescent beam are parallel and that the solid angles under which the X-rays from an atom are measured by a detector are identically for all excited atoms in a specimen.

It will be shown, that the Sherman approach cannot be used, if the existing distances between different atoms acting as fluorescent or scattering source within a thick organic or oxidic specimen are comparable with the distance between detector and specimen as it is the case for a lot of XRF applications applying ED setups. A modification of the FP model was developed to overcome some of the assumption made my Sherman and to describe geometrical conditions of typical EDXRF setups. Because of this modification the calculated fluorescent intensities are depending on sample density and sample thickness independently from each other. The density effect caused by different pressures used for pelletizing or between loose powders and pellets or between powders/pellets with different particles sizes can be considered with this new FP method. In case of thin layers or specimens having high densities (most alloys) the new model aligns Sherman’s model.

[1] Sherman J., Spectrochim Acta 7, 283-306 (1955)

Parametrization of a tabletop micro-XRF system

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Tabletop XRF systems with a mini X-ray tube provide simple analytical facilities, which, however, require accurate calibration. Here we propose a series of fundamental-parameter procedures that lead to quantitative analysis of thin layers or bulk concentrations. The test system was the one used at the Czech Technical University in Prague, which consists of an X-ray tube equipped with a policapillary lens and a SDD detector. For calibration, a set of metal foils with known thicknesses was used, and in addition, we relied on the argon signal induced in the air gap between the lens exit and target. The effective air-path was calculated with numerical modelling, which was simplified taking into account the symmetries of the experimental geometry. The bremsstrahlung X-ray spectrum was calculated according to the Bethe-Heitler model, yet we took into account the energy distribution of impact electrons in the target. Here we developed a simple model for radiation of the secondary electrons that carry about one half on the available electron energy. For transmission of the lens, it was sufficient to adopt the $1/E^2$ approximation, but we estimated a correction due to capillary bending. The only variation parameter in the optimization procedure was the thickness of anode material that causes self-absorption of generated X-rays. As a result, the thicknesses of calibrating foils were reproduced with a maximum error of 3.3%. The method was further optimized for the analysis of thin paint layers on organic material.

Polarization Measurement of Compton Scattered X-rays by 3D-Printed Polarimeter

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The polarization of scattered X-rays was measured when an acrylic and a lead plate were used as a polarizer, whose ratio of an elastic and Compton scattering cross section is different. An X-ray tube, a polarizer, a scattering analyzer, and a detector were arranged as shown in Fig.1. With the use of a 3D printer, a holder of devices was made, which could change the detection angle by every 30 degrees in *y-z* plane. The intensity of scattered X-rays was measured changing the detection angle. A low-power X-ray tube (Moxtek, 4 watts, tungsten target) was operated at 25 kV and 20 μA. An SDD (RES-Lab) was used as the detector. An acrylic plate was employed as the scattering analyzer. The degree of polarization of scattered X-rays was evaluated as the ratio of an amplitude of a modulation curve to the average of scattered X-ray intensity.

When using the acrylic plate as polarizer, the degree of polarization was higher compared with the case of using the lead plate (Fig.2). This result, therefore, leads that a polarizer composed of light elements of which Compton scattering cross section is large should generate linearly polarized X-rays with high degree of polarization. Besides, with the simple 3D-printed equipment, polarization properties of scattered X-rays could be evaluated without using high-power facilities.

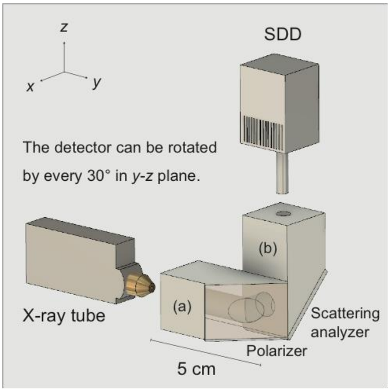

Fig.1. Drawing of 3D-printed polarimeter. (a) is the polarizer holder and (b) is the analyzer holder. The X-rays are made incident on the polarizer at the angle of 45º and they are again scattered from the analyzer at the angle of 45º. The detection angle can be changed by rotating the analyzer holder every 30 degrees in *y-z* plane.

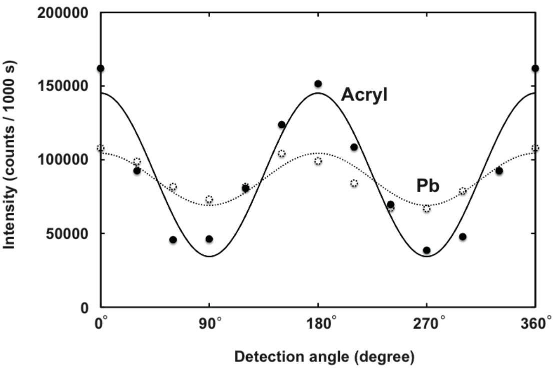

Fig.2. Angular dependence of the scattered X-ray intensity in the energy range of 0 to 25 keV. Solid dots (measured) and line (fitted) are for acryl, and broken ones are for Pb. When using the acrylic plate as polarizer, the amplitude of the modulation curve is larger than when using the Pb plate.

Full Recovering of an X-ray Spectrum from Detector Influence.

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It is well known that a measured energy dispersive X-ray spectrum differs from the original spectrum arriving to the detector. This is due to changes introduced by the detection device and by the pulse electronics during the measurement. The detection device contributes with a deformation attributed to the detector response function (DRF) which is well described in terms of physical processes of radiation diffusion inside the detector. The pulse electronics contributes in two different ways: (a) with a convoluted broadening due to an asymmetrical distribution at each recorded energy (resolution effect) which produces an uneven smoothing of the spectrum, and (b) with the pulse pile-up which introduces a distortion which changes the total counts and the shape of the spectrum. Once characterized the DRF comprising the resolution broadening effects, it is possible to recur to an unfolding algorithm to recover the original spectrum.

In this paper it is introduced a detailed description of the four steps which are necessary to recover the source spectrum from a measurement by using a set of computer codes developed in Bologna. In first place, it is applied a PPU correction algorithm on the measured spectrum which renders a corrected measure having the proper number of counts in the proper energies. Then it is computed the combined effect of the DRF and the asymmetrical resolution for each energy of the source spectrum. By discretizing these single energy distributions it is possible to obtain the response matrix feeding the next step. The last step consists in the application of a robust unfolding procedure like UMESTRAT, the maximum entropy technique which takes advantage of the known a priori information and preserves the positive-defined character of the X-ray spectrum.

The results obtained are very good and are illustrated with some paradigmatic examples involving popular SSDs like Si, Ge and CdTe.

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A Methodology to Obtain Traceability and Validation of Calibration Samples for Thin Metal Alloy Layers for X-Ray Fluorescence Tools

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Statistic process control as well as process capability demand for calibrated determination of layer thicknesses in various industries, e.g. automotive, aerospace, microelectronics manufacturing. Calibration requires well known and well characterized samples. A calibration laboratory accredited according to DIN EN ISO 17025 has the objective to distribute standards traceable to SI units to industrial laboratories for quality control of manufacturing of various products. Especially, the thickness determination of thin metallic coatings e.g. from galvanic processes or layer deposition using X-Ray Fluorescence can be significantly improved by customized calibration samples. This is essential as the measurement uncertainty directly correlates to the capability of reliable process control. For calibration laboratories, the validation of results using round robins and the direct comparison to national metrology institutes is a prerequisite to demonstrate the competence to perform calibration services.

In this paper a strategy to obtain traceability and validation for thin alloy layers as well as first results are presented. The combined use of the accredited method for determination of mass per area from measurement of mass and area combined with standard free X-Ray Fluorescence [1] as well as chemical analysis of dissolved samples with thin layers is deployed for material systems as Ni_xZn_{1-x} as well as Ni_xP_{1-x}. The obtained results are compared to reference free X-Ray Fluorescence at the BESSY II laboratories of Physikalisch-Technische Bundesanstalt [2]. An excellent agreement of the obtained measured values as mass per unit area and alloy concentrations from the different applied methods within the measurement uncertainty was observed for Ni_xP_{1-x}. These results demonstrate the successful performed traceability of the calibration samples to SI units in combination with a validation of results by national metrology institutes and the round robin approach.

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In-line characterization of ultrathin MoS$_2$ and WS$_2$ materials using XRF-XPS strategies

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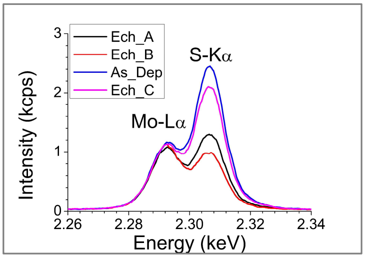
Transition metal dichalcogenides (TMD) are emerging as a class of exceptional materials with many potential applications (supercapacitors, batteries, electronics, optoelectronics, etc). For instance, mono- and few-layer sulfur-based TMD such as MoS$_2$ and WS$_2$ exhibit bandgaps that can be tuned by thickness, strain, and composition, making them promising 2D semiconductors complementary to graphene and hexagonal boron nitride in various optoelectronic applications [1]. Sulfur-based TMD appear explicitly in the roadmaps of biggest industrial players [2], and new deposition processes are being developed that should soon address the need for industry-scalable fabrication methods for TMD on large-scale substrates with atomic scale precision.

Whereas the stoichiometry of sulfur-based TMD can be obtained by X-ray photoemission spectroscopy (XPS) [3, 4] or Transmission Electron Microscopy in EDX-mode [4], strategies based on X-ray fluorescence (XRF) are highly desirable, not only to support material process development but also to perform reliable and fast in-line analysis on large-scale substrates. In this paper, we will assess the performance of in-line wavelength-dispersive XRF (WDXRF) for the characterization of ultrathin MoS$_2$ and WS$_2$ layers grown by highly scalable chemical vapor deposition process [5, 6] on silicon oxide or sapphire substrate.

First, we will discuss the compositional analysis of MoS$_x$ samples with significantly different S/Mo ratios (Figure) using RBS (Rutherford Backscattering Spectrometry), grazing-incidence XRF in the tender X-ray range, inline XPS and WDXRF. Then, we will illustrate the interest of WDXRF-based monitoring of composition and deposited mass for the optimization of WS$_2$ deposition process on sapphire.



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Comparison of different quantification approaches in X-ray fluorescence imaging of freeze-dried tissue samples

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The X-ray fluorescence imaging (micro-X-ray fluorescence analysis) is a common technique for analysis of spatial distribution of elements in various tissue samples. A proper quantification scheme is a key step towards comparison of results achieved with X-ray fluorescence imaging with results obtained with other methodologies. There are two major problems that makes the quantification problematic: the presence of dark matrix (composed mainly with H, C, O and N) and the natural heterogeneity of sample density and thickness.

In this study six samples of human ovarian tissue were examined with micro-XRF technique. For each sample a 20 μm thick tissue slice was cut with the cryo-microtome onto the Ultralene® foil stretched on a plastic ring and then freeze-dried at the temperature of - 80°C without using any fixation protocol. The measurements were carried out at IAEAXspe endstation of X-ray fluorescence beamline of Elettra Sincrotrone Trieste [1]. A RuB_4C multilayer monochromator was used to achieve a bi-chromatic beam with energies of 1.65 keV and 10 keV, respectively. The beam size was defined by exit slits – the final footprint of the beam on the sample was 120 x 250 μm^2. The experiment was performed in vacuum ($2 \cdot 10^{-7}$ mbar) in a standard 45°/45° geometry using a silicon drift detector with an ultra-thin polymer window [1]. The time of the measurements was 5 s per pixel and the average scan area was 30 mm^2.

Due to the capability of detection of low energy X-rays the quantification was done by use of two approaches: the full-fundamental method and the simplified method for which a constant composition of the dark-matrix is assumed for the correction of the absorption effects [2]. The calculation of the tissue mass per unit area was done with use of Compton scattering intensities after calibration based on a set of standards of variable thickness. The validation of both methods was done with use of the in-house developed multi-elemental tissue-like standard samples. The results achieved with both methods are compared and discussed.

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Absolute high-precision measurements of x-ray transitions with a double crystal spectrometer

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Abstract

We present our measurements of x-ray transitions from *n=2* to *n=1* in highly charged ions of argon using a double flat-crystal spectrometer [1]. The ions were produced in a plasma of an ECRIS (Electron-Cyclotron Resonance Ion Source). We have measured four different transition energies in three different charge states of argon, the $1s2p\ ^1P_1 \rightarrow 1s^2\ ^1S_0$ in He-like argon, the $1s2s^22p\ ^1P_1 \rightarrow 1s^22s^2\ ^1S_0$ in Be-like argon and the $1s2s2p\ ^2P_J \rightarrow 1s^22s\ ^2S_{1/2}$, J = 1/2, 3/2 Li-like argon doublet, with a relative accuracy better than 3 ppm. The $1s2p\ ^1P_1 \rightarrow 1s^2\ ^1S_0$ transition measurement [3] confirms the recent reference-free measurement of the Heidelberg EBIT (Electron-Beam Ion Trap) [2] while the $1s2s^22p\ ^1P_1 \rightarrow 1s^22s^2\ ^1S_0$ [3] and the $1s2s2p\ ^2P_J \rightarrow 1s^22s\ ^2S_{1/2}$ Li-like argon doublet transition energies are the first reference-free measurements for transitions in an ion with more than two electrons. The natural widths have been also experimentally obtained by applying a fitting procedure to the experimental spectra that uses full Monte-Carlo simulated spectra and an experimental value for the Doppler broadening of the lines obtained in Ref. [4]. Both energies and widths are in agreement with the most advanced calculations. The accuracy in the ppm level provides tests of QED (Quantum Electrodynamics) and relativistic effects. It also provides accurate x-ray standards in narrow transitions of highly charged ions that can be used to calibrate instruments in this energy range.

The experiment setup, the most recent results and the current status of the experiment will be presented focused in the DCS working principle and in the planned measurements and setup updates.

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Validation of secondary fluorescence algorithms for thin layered samples using synchrotron radiation based experiments

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In multi-elemental samples the radiation of one element can enhance the fluorescence intensity of another. This is referred to as secondary fluorescence (cf. figure 1). Taking this effect into account appropriately is crucial for producing correct results in quantitative X-Ray fluorescence analysis. This is especially relevant for thin layered samples, for which the individual mass depositions of each element in each layer are to be determined. If the respective densities are known, this knowledge then can be converted into corresponding layer thicknesses. Many new materials, e.g. in the semiconductor industry, are essentially thin layered samples at the nanoscale. Since appropriate reference materials are often not available, a reference-free approach based upon SI traceability might be the method of choice.

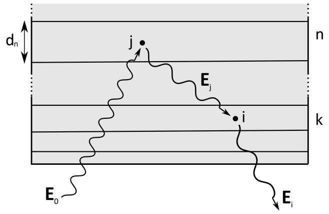

Figure 1: Inter-layer secondary fluorescence in a layered sample

The theoretical tools to calculate the required fluorescence intensities for the quantification algorithms are well-known and can be found in the literature [1, 2]. The present work aims to study the validity of these higher-order algorithms for selected thin layered samples, consisting of multiple transition metals with thicknesses in the low µm range. For these samples the contribution of secondary excitation fluorescence can easily exceed 20%, depending on the elements involved, the spatial composition and dimensions of the layered system, the excitation energy and the angle of incidence. This study has been carried out by using monochromatized synchrotron radiation on a fully characterized beamline in the PTB laboratory at the electron storage ring BESSY II. The radiometrically calibrated instrumentation and the reference-free fundamental parameter approach [3, 4] allow for a direct validation of the computed theoretical intensities with measured intensities.

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Online measurement of deposited energy by ion beams using bremsstrahlung X-rays

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The detection of bremsstrahlung X-rays emitted directly by low-Z medium is a promising noninvasive technique to obtain all or part of the information of the deposited energy online [1], in hadrontherapy framework. The aim of this study is to understand the relation between the bremsstrahlung and the deposited energy in the medium. The experimental set-up allows the irradiations of targets (PMMA,C,Al) by alpha particles or protons delivered by the cyclotron ARRONAX (energy < 70MeV). The detection of bremsstrahlung X-rays is performed using a silicon detector. A theoretical model that takes into account the different contributions of bremsstrahlung (QFEB, SEB and AB) was used to simulate the emitted bremsstrahlung spectrum [2].

A first experiment, with 68MeV alpha particles, shows a good agreement between measured and simulated spectrums (c.f. figure). The overall number of bremsstrahlung X-rays detected for one gray received by the medium is 1060±140 as compare to 970 X-rays/Gy determined by simulation. Thus, the number of X-rays per gray demonstrates a good sensibility. In order to investigate the evolution of this bremsstrahlung X-rays signal as a function of the deposited energy in the medium, experiments using different beams have been performed. The analyses are in progress and the results will be presented. These experiments are also helpful to study the predominance of bremsstrahlung components and understand the small discrepancies observed between our measured and simulated data.

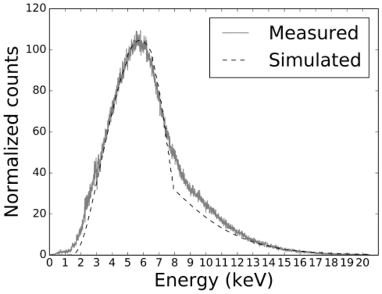

Figure: Bremsstrahlung spectrum measured (full line) and simulated (dashed line) from PMMA target.

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Optical pump soft X-ray probe NEXAFS spectroscopy using a laser-produced plasma source

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Near edge X-ray absorption fine structure (NEXAFS) spectroscopy is a powerful characterization tool for molecules and their bonding environment. With soft X-ray excitation biological samples can be studied directly at the K-edges of carbon, nitrogen and oxygen. Transient absorption changes of excited molecules can be measured with the pump-probe technique, where an optical pump excites the molecule and an X-ray pulse probes the dynamics.

Laser produced plasma sources (LPP) are well established laboratory X-ray sources. They generate highly brilliant, pulsed, polychromatic radiation. For NEXAFS measurements a highly resolving X-ray optic is needed to disperse the polychromatic radiation. Jitter free pump probe measurements are possible because the same laser pulse can be used to generate the pump and the probe pulse.

With our LPP source [1,2] and a newly developed twin beam reflection zone plate spectrometer, we have the ability to carry out high resolution NEXAFS measurements in the energy range between 100 eV and 1200 eV with a resolving power of $E/\Delta E > 1000$. The spectrometer is capable to simultaneously acquire the sample and the reference spectrum. Due to the high efficiency of the zone plates and the brilliant LPP source, the measuring time of one NEXAFS spectrum could be reduced to the length of one single nanosecond pulse. This greatly reduces sample dose and enables to monitor changes after each pulse.

We applied this spectrometer for first proof-of-principle pump-probe experiments at the carbon K-edge. The twin beam reflection zone plate spectrometer will be presented. NEXAFS measurements of thin organic dye films with and without optical pumping will be shown accompanied with UV/VIS spectroscopic investigations.

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A Diced von Hamos Spectrometer for Time Resolved X-ray Emission Spectroscopy

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Time resolved x-ray emission spectroscopy (XES) is a growing technique for studying redox reactions. While this technique can be used to measure spin densities in situ, the inherently weak signals can often be limiting. To address the issue of low signal we designed and built a cost efficient, custom x-ray spectrometer. The casing was made using 3d printed materials. The large diced analyzer was made following our versatile fabrication protocol that allows us to create diced analyzers with almost any radius and material [1]. The dispersive geometry (von Hamos) allows detection of both Mn $K\beta_{1,3}$ and Kβ' peaks on a shot by shot basis. The spectral changes between two biomimetic compounds, $[Mn_{IV}(OH)2(Me2EBC)]^{2+}$ and $[Mn_{IV}(O)(OH)(Me2EBC)]^{+}$, were determined after 10 seconds of data collection. More recently, a new three analyzer spectrometer has also been commissioned which uses the same 3d printed design and creates three parallel vertical stripes. Preliminary results for RIXS and time resolved XES of dilute samples will also be shown.

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A compact and efficient von Hamos spectrometer based on two full-cylindrical HAPG mosaic crystals for high-resolution XES

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X-ray emission spectroscopy (XES) presents the potential to substantially contribute to the further development of complex nano-materials with distinct chemical properties. Also in the field of catalysis, the identification and quantification of active sites is important for a more thorough understanding of catalytic systems. Using a physically traceable x-ray analytical approach based on radiometrically calibrated instrumentation and the knowledge of atomic fundamental parameters, absolute elemental and species mass depositions or concentrations can be determined without the need for any reference material or calibration standards.

For this purpose we will present a calibratable and compact high-resolution wavelength-dispersive spectrometer for XES in the photon energy range of 2.4 keV to 19.0 keV. Using two full-cylindrical Highly Annealed Pyrolytic Graphite (HAPG) crystals as dispersive elements in modified von-Hamos geometry [1], a large solid angle of detection resulting in high detection efficiency is realized while achieving a moderate to high resolving power. HAPG is a synthetic type of carbon which forms mosaic crystals and can be mounted to substrates with small radii of curvature down to 50 mm. Although the peak reflectivity is smaller than for perfect crystals, the crystal mosaicity results in a rather high integrated reflectivity [2].

In this work we will show the instrumental characterization of the spectrometer including achievable energy resolution and efficiency as well as the spectral response as a function of experimental parameters. Furthermore, the chemical speciation capability of the device is demonstrated on the basis of different transition metal compounds. The calibration of the instrumental response of the presented wavelength-dispersive spectrometer enables an accurate determination of binding state related structures in X-ray spectra, thus enabling reliable identification and discrimination capabilities contributing to a thorough uncertainty budget.

Thus, a calibration procedure for fully quantitative experiments at synchrotron radiation facilities is being developed in order to progress towards traceable, quantitative XES measurements. This procedure will be demonstrated on the basis of the determination of L-shell atomic fundamental parameters of gadolinium and requires dedicated experiments for the determination of partial scattering cross sections.

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Laboratory von Hámos X-ray Spectroscopy for Routine Sample Characterization in Solution Phase

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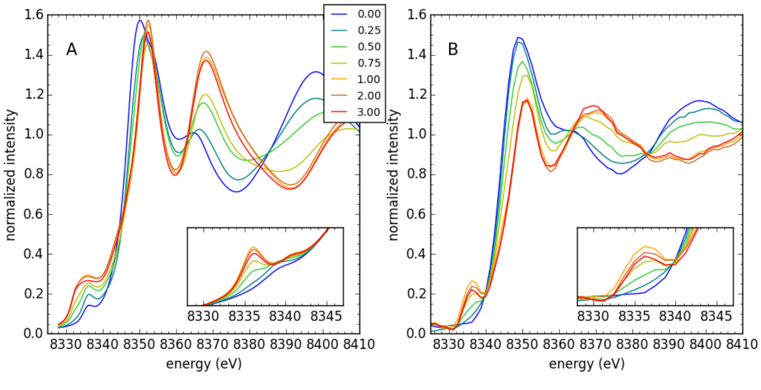
We demonstrate how our recently developed laboratory von Hámos X-ray spectrometer can be used on a daily basis as a versatile and efficient tool for the detailed investigation of solutions containing transition metal complexes. It is shown on the Ni^{2+} – EDTA – CN^{-} ternary system investigated that a complete speciation study can be performed from laboratory XANES as well as EXAFS measurement series, including the determination of the formation constants of the corresponding complexes. Moreover, the technique permits us to determine the local atomic structure around the Ni ion, with particular sensitivity to variations in symmetry. *To best of our knowledge this is the first time that laboratory X-ray absorption spectroscopy was used for such a comprehensive study in solution.*

X-ray absorption spectroscopy has long been considered as a local structural probe that can only be used at synchrotrons. However, in this article we prove it to be also a laboratory method with capabilities far beyond the determination of the oxidation state and local structure of the absorbing atom especially if it is supplemented with theoretical calculations. The number of the suitable beamlines at synchrotrons is limited, they are usually highly overbooked, and a long lag is experienced between the date of the demand and that of the actual measurement. We argue that a considerable fraction of the emerging questions could be solved by laboratory X-ray absorption spectroscopy as well.



(A) Laboratory XANES spectra of solutions containing constant 0.25 M NiCl2 and 0.30 M EDTA, while the concentration of the added KCN was varied between 0 and 3 M. (B) Calculated XANES spectral series for the measured samples based on the determined nickel distribution. The insets show the preedge region with a peak around 8336 eV, representing the formation of four- and/or five-coordinated nickel(II) complexes.

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Imaging and spectroscopy with X-rays from Carbon to Uranium K lines

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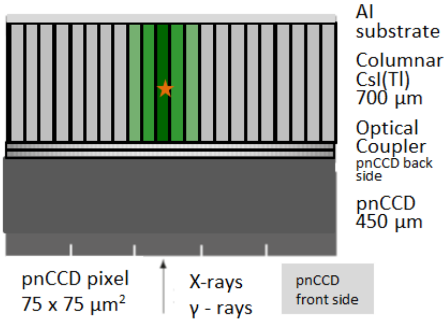
The spatially and spectroscopically resolved detection of X-rays in the range of 0.2 keV up to 25 keV is usually performed with fully depleted Silicon detectors (segmented SDDs, CCDs and active pixel sensors) with sensitive thicknesses up to 700 µm. The photoelectric cross section in silicon drops rapidly with increasing X-ray energy ($\sigma \sim Z^4 \cdot E^{-3.5}$, Z is the atomic number of the detector material, E the energy of the incident X-rays). To improve the detection efficiency towards the higher energies a detector material with a higher Z can be selected. We have coupled a columnar CsI scintillator [Z(I) = 53, Z(Cs) = 55, compared to Z(Si) = 14] to the radiation entrance window side of the pnCCD as shown in the Figure. The X-rays enter the system through the pnCCD such that all X-rays which are stopped in the Silicon can be spectroscopically resolved at the Fano limit. In this case we can apply our signal charge cloud algorithms and achieve simultaneously deep spatial subpixel resolution. Most of the X-rays between 250 eV and 15 keV will be directly detected in the pnCCD. X-rays between 15 keV and 100 keV are mainly converted into visible light in the CsI(Tl) scintillator and this light is simultaneously detected in the CCD. The 10 µm wide CsI columns act as a light guide and concentrate the light in a few pixels only. We used 700 µm thick CsI scintillator yielding a quantum efficiency of 50 % at 100 keV. The columnar CsI scintillator is available up to 3 mm for X-ray energies up to 200 keV. The signals from the optical light from the scintillator and the directly detected X-rays converted in the Silicon can be unambiguously distinguished. This way an imaging spectrometer from 250 eV up to 100 keV has been realized with a high quantum efficiency over the entire energy range. We will show laboratory experiments with a ^{57}Co source (prominent lines at 122 keV and 136 keV) and Laue diffraction experiments at the hard white EDDI X-ray beamline BESSY. Fast readout (500 frames per second) and high spatial resolution ($3\ \mu m \leq \Delta x,y = 30\ \mu m$, depending on the X-ray energy) have been achieved. The new instrument improves XRD, XRF and PIXE experiments in the above described energy range. We will report about the latest achievements of such a detector system operated at synchrotrons and in laboratories with radioactive sources up to an energy of 136 keV.



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Laboratory-based Cu L X-ray fluorescence spectroscopy

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Wavelength-dispersive X-ray fluorescence spectroscopy (WDS) is a well-established technqiue for analysing the elemental composition and chemical states of a sample [1]. While in the hard X-ray range crystals are used as the dispersive element of the spectrometer, in the soft X-ray range reflection gratings can be applied instead. Most commonly, WDS in this wavelength regime is performed at synchrotron radiation facilities, where the high photon flux mitigates the poor reflectivity of the grating [2]. However, synchrotron access is limited and expensive, so a laboratory-based application is desirable.

An efficient dispersive element for a spectrometer in the soft X-ray range is a variable line-space (VLS) grating. A conventional grating focuses the divergent fluorescence radiation of different wavelengths along the Rowland circle and a detector is used to record the intensities by scanning along this circle. A VLS grating focuses fluorescence radiation over a broad range of wavelengths on a plane, in this case a charge-coupled device (CCD) detector [3]. This way, the wavelength range does not have to be scanned but can be measured at once without reducing resolving power.

In this work, a highly brilliant laser-produced plasma source is used to generate soft X-ray radiation around 1078 eV [4]. Two large area toroidal multilayer optics focus and monochromatizethe radiation onto a copper sample. This efficient combination enables the wavelength-dispersive measurement of L line emission in the soft X-ray range. The Cu L radiation is recorded by an in-house designed spectrometer with a VLS grating on a CCD. Furthermore, the CCD can be operated energy-dispersively by detecting single-photon events [5]. By applying this technique, fluorescence photons can be distinguished from stray light, cosmic particles or CCD noise, improving the signal-to-noise ratio.

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Low-E extension of a hand-held Compton spectrometer

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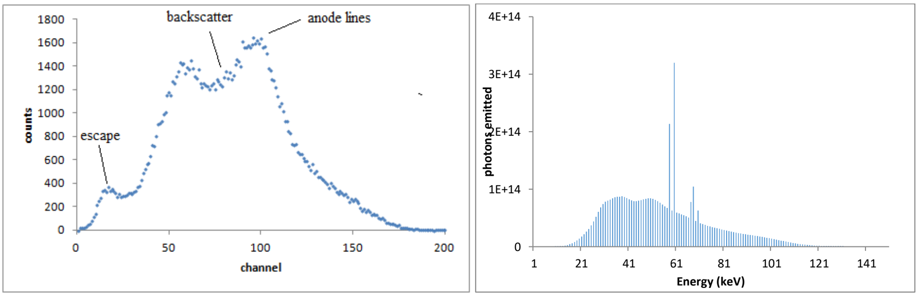
The Compton spectrometer is a device in which radiation coming from a X-ray generator is scattered at known angle in order to reduce the flux and to allow spectrometric measurements without saturating the detector. A small-size prototype Compton spectrometer usable in the range 20-150 keV was presented earlier, using a pen-type NaI detector [1]. The source spectrum was reconstructed by unfolding the measured spectrum, using the response matrix calculated by the Monte-Carlo method and a deconvolution algorithm derived from GRAVEL [2]. The Pb shield was later replaced by a W alloy.

An extension of the energy range down to ~5 keV was realized using a pen-type NaI detector with Be window. The goal is to measure the low-E tail in the spectrum of common medical X-ray generators, in order to better evaluate the impact of filtration.

Specific problems had to be solved for the deconvolution in this energy range. Under ~12 keV, the measured spectrum is dominated by the escape of iodine fluorescence X-rays arising from the detection of incoming photons of ~35-40 keV. GRAVEL was not able to correctly evaluate the balance between the contributions of low-E photons and the escape contribution. A step-by-step strategy was used to solve the problem: (a) evaluate separately the intensity of anode K-lines, (b) unfold the spectrum above the iodine K-edge, (c) evaluate the escape spectrum under the K-edge and subtract it from the measured spectrum, (d) unfold the remaining spectrum under the K-edge.

An integrated software was developed for the acquisition and deconvolution, using the pocket-size MCA “TOPAZ” developed by Brightspec® (www.brightspec.be). Results of measurements with various settings for high voltage and filtration will be presented.



Left: raw spectrum before energy calibration and smoothing; right: unfolded spectrum

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Catalysis research with a laboratory based XAFS spectrometer

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While the origins of X-ray absorption spectroscopy 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 is based on the use of a special, very efficient type of crystal which is used as dispersive element. This graphite mosaic crystal is called Highly Annealed Pyrolytic Graphite (HAPG) developed by Optigraph GmbH [1]. Its first use in X-ray spectrometers was demonstrated by Legall et al. [2] in 2009. By now, the spectral resolving power can be as high as $E/\Delta E \approx 4000$, good enough to resolve major XANES features. Due to its high efficiency, the spectrometer also is capable of taking EXAFS spectra within reasonable time.

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 two successful applications of laboratory XANES in catalysis research. One is a contribution to research with (Mn,Fe)Ox-promoted Rh nanoparticles for the hydrogenation of CO to higher alcohols [3]. The second is related to the use of Cu/mordenite for the selective oxidation of methane to methanol [4]. The emphasis will be on the specific experimental strategies and particularities for laboratory XAFS. By means of the two examples possibilities and perspectives as well as restrictions and constraints will be illustrated. A discussion of future developments to address the later ones will complete the contribution.

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Pulse Processing for Practical X-ray Microcalorimetry

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X-ray microcalorimeters using transition edge sensors offer high energy resolution over a considerable energy range. However, the calibration and reduction of pulse heights to spectra present special problems due to the long time constants of the thermal detectors and the high resolution required of pulse heights. We present a system that converts pulses into energy spectra in real time, taking account of pulse pileup, flux jumps in the SQUID electronics, and nonlinearities in the spectrum calibration. We have demonstrated a system aggregating the outputs of 8 independent detectors operating simultaneously, and anticipate that it could be expanded to at least 64 simultaneously operating detectors. We have demonstrated resolution of about 5 eV for detectors covering a range of 7500 eV.

Enhancing CCD Capabilities by Single Photon Counting: A Comparison of Photon Event Evaluation Algorithms

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X-ray photons, which hit the absorber layer of a charge-coupled device (CCD), create an amount of charge carriers proportional to their energy, which are stored in the CCD's pixel structure. Often, CCDs applied in X-ray spectroscopy or imaging are used in an integral mode. This means, that the pixels in a CCD accumulate the charge of many detected photons, thus loosing information about the energy and exact position of each detected photon. If the photon density per recorded frame is low enough to distinguish single X-ray photon events, computer algorithms can be applied to retrieve the energy of each detected photon and sometimes allow the determination of the primary interaction position of the X-ray photons with sub-pixel accuracy.

Photon event evaluation algorithms for CCDs have successfully been applied in space missions [1,2], X-ray fluorescence (XRF) analysis [3], micro-XRF imaging [4], wavelength-dispersive spectrometers [5] and diffractometers [6]. In the latter, the energy-dispersive and sub-pixel-resolution properties lead to enhanced signal-to-noise ratios and better spatial resolution.

However, there are various possibilities how to discriminate and analyze photon events in a CCD frame and sometimes the applied algorithms are only roughly explained and rarely validated. We simulated the event pattern distribution of photons from a discrete X-ray spectrum (O K_α, Al K_α, Sc $K_{\alpha,\beta}$, Cu $K_{\alpha,\beta}$) for various CCD noise settings and charge cloud sizes. Then, we used several photon event evaluation techniques to analyze the event patterns and compared the retrieved energy-dispersive spectra with respect to e.g. resolving power, peak position and efficiency. Finally, a few examples for the useful application of photon event evaluation with a CCD are presented.

To exploit the described energy-dispersive and sub-pixel-resolution properties of a CCD, the CCD must be operated in a single photon counting mode (i.e. photon flux on the CCD must be sufficiently low) and a further data analysis step must be performed. Both can be easily applied to conventional CCDs in any kind of spectrometers, allowing in principle a wide user community to benefit from photon event evaluation algorithms.

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Advanced Pulse Processing Techniques for Photon Science and Other High Rate Applications

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Techniques such as X-ray fluorescence and multi-energy X-ray transmission are powerful tools for the non-destructive analysis and characterisation of material. However, across a range of application, in both industry and photon science, these techniques are severely limited by detector throughput. Consequently there is significant interest in developing higher throughput detector processing systems to reduce dead-time and improve measurement.

This presentation details a model-based approach to digital pulse processing which, by using *a priori* information about the detector characteristics, dramatically improves the count-rate and throughput performance of detectors. By estimating the pulse shape, number, time of arrival and energy of all photons in the digitised detector data stream, output count rates of greater than 3 million c/s per channel can readily be achieved.

This approach to digital pulse processing has been implemented across a range of application (see Fig. 1) including: soft X-ray florescence analysis at Synchrotron beamlines; high rate prompt gamma neutron activation analysis; and energy resolved, photon counting X-ray transmission analysis for real-time process control in the mining sector.

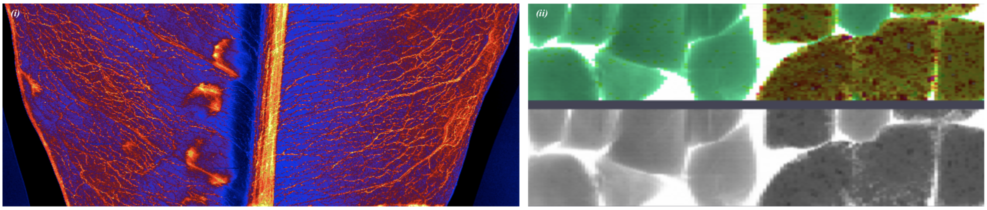

Figure 1: Shown in *(i)* an application using the X-ray micro probe at the Australian Synchrotron, mapping the Mn, Zn and Ca content of a freeze-dried leaf section with a resolution of 25 um pixels over an area 36.5 × 36.0 mm, the image size is 2.1 million pixels and required 2.5 hour collection time. A multi-energy X-ray transmission scan is show in *(ii)* scanning coal on a conveyor. The attenuation or structural image is shown in the lower sub-figure, while the upper figure shows the Effective-Z image depicting the rapid and accurate separation of good quality coal (in green) from bad quality coal (red). These images are produced in real-time, have a pixel size of 3 × 3 mm and an individual pixel dwell time of 50 milliseconds.

Company and Product Profile – PNDetector GmbH

Adrian Niculae, Jeff Davis, Andreas Liebel, Melanie Schöning and Heike Soltau

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PNDetector is developing and manufacturing innovative and efficient radiation detectors for material analysis in a wide range of applications, such as microanalysis, quality assurance and materials science. The focus is on marketing sensors and detector systems with best resolution and high speed, optimized to the needs of the customers.

The silicon sensors are fabricated in PNDetector's own cleanroom facilities, situated on the Siemens technology campus in Munich. The cleanroom is dedicated to the ultra-pure fabrication of modern silicon radiation detectors, with a high level of contamination control, insuring very low dark-current levels. The emphasis in production and development is on Silicon Drift Detectors (SDDs), Backscattered Electron Detectors (BSD) and Charged Coupled Devices (pnCCDs).

Silicon Drift Detector Chips and Modules

PNDetector's SDDs are at the forefront of radiation detector technology, as they provide both excellent energy resolution and high count rate capabilities at short processing times. With energy resolution values down to the theoretical limit, the SDDs are available in various sizes and shapes, with detector active areas from 5 mm^2 up to 200 mm^2. For applications where very large detection areas or highest possible throughput are required, such as in synchrotron experiments, monolithic, multi-element SDDs have been developed, among them the well-known so-called Rococo 2 detector. With all the individual cells integrated onto a single chip, the dead area between the cells is kept to minimum, leading to the most compact combination of SDD cells on the market. SDD arrays are available with total active areas of up to 300 mm^2 and up to 7 monolithic cells, capable of input count rates of more than 7 Mcps.

The Complete XRF Detector System and Preamplifier Modules

PNDetector's XRF Detector System and Preamplifier Modules combine the excellent detector performances with specific electronics in a compact housing. With the Complete Series, the SDDs are mounted in a controllable, hermetically sealed vacuum package. Integrated pressure and temperature sensors offer the possibility to monitor the vacuum conditions inside the detector housing, which can be refreshed by reactivating the getter. This allows the operation of the SDD under optimum vacuum conditions over a long lifetime, even in applications with rough ambient air conditions.

pnCCD Color X-ray Camera

With the pnCCD Color X-ray Camera (CXC), PNDetector has developed a unique X-ray imaging spectrometer providing simultaneous high-resolution X-ray imaging and spectroscopic capabilities in any pixel at ultra-fast frame rates of up to 1000 fps and total count rates of over 500,000 counts per second. The CXC can be used in Full-Field µXRF imaging applications, as well as spectroscopy applications such as simultaneous X-ray fluorescence and X-ray diffraction imaging, energy dispersive small angle X-ray scattering (SAXS), energy dispersive computed tomography and X-ray transmission imaging in both the laboratory and at synchrotron sources.

An Improved Performance of the Vortex Silicon Drift Detector

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We have improved the resolution, high count-rate performance and quantum efficiency (QE) of the Vortex® silicon drift detector (SDD) by integrating it with new front-end electronics and by increasing the thickness from 0.5 mm to 1.0 mm. A series of tests indicates excellent results: a QE that matches theoretical values and enhancement of the throughput at practical dead time (DT) operation. An output count rate of 1.6 Mcps at 2.0 Mcps input count rate (20% DT) using the “Quantum Detectors” Xpress3 processor is achieved with an energy resolution of 200 eV.

The different designs of the Vortex® SDD models, have been successfully applied to XRF (x-ray fluorescence), TXRF (total XRF), synchrotron, and x-ray mapping applications. These advanced SDD models all provide three characteristics simultaneously: large solid angle, excellent energy resolution, and high count rate performance.

To increase the x-ray detection efficiency of the SDD in the 30 – 40 keV range, we have developed new devices which are 1 mm thick. At the standard 0.5 mm thickness, silicon efficiency rapidly falls off above 12 keV and decreases to ~12% at 30 keV, whereas 1 mm silicon is still 23% efficient at 30 keV. Several custom-made SDDs, including multi-element devices, for synchrotron applications were designed and built and are currently in use in many synchrotron facilities all over the world.

A significant improvement in the high count-rate capability is clearly presented with the 4-element SDD, the Vortex ME4®, combined with either the advanced DPP “Xspress 3”, developed by Quantum Detectors (Harwell Oxford, UK), or with another advanced DPP, the “FalconX” developed by XIA LLC (Heyward, CA. USA).

The new Vortex® SDD models combine the above performance characteristics of higher quantum efficiency, improved low energy performance and very high count rate capability, which benefit users with state of the art SDD performance.

Improving Detectors for X-Ray Spectroscopy

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What does it mean to "improve" detectors for X-ray spectroscopy? The energy resolution at ^{55}Fe is the "flagship" specification but is only indirectly related to the precision, accuracy, and detection limits of EDXRF and EDS instruments. Many recent improvements in X-ray detectors and electronics do not show up in simple specifications but have critical impacts on instrument performance in various applications. This paper will discuss improvements in several areas and the applications which most benefit from these.

Statham [1] posed the question: "Would a device that offered an excellent energy resolution of only 7 eV but could only acquire at 60 cps be more useful than a device that could acquire at 10,000 cps but gave much poorer resolution of 150 eV?" This was also explored in [2], which proposed a "figure of merit" based on the time required to achieve a statistical uncertainty. This "figure of merit" is still useful and will be applied to the range of detectors available today.

In many applications today, the detection limit is central. This often depends less on resolution and more on factors such as peak to background and peak to tail ratios, photopeak shape (and its stability), and the spectral purity of the detector. Although less dramatic in the spectrum than 55Fe FWHM or high count rates, improving these parameters can significantly improve analytical results. We will discuss recent efforts at Amptek which have resulted in significant improvements, particularly at low energies (e.g. the C K_α line) and at energies near the Ag and Sn K_α lines.

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Bruker XRF, complete and innovative portfolio of portable, benchtop, and floorstanding instruments.

C. Vailati

Bruker Nano GmbH
cristian.vailati@bruker.com

XRF spectrometry is one of the best techniques to perform elemental analysis in different kind of samples, liquids, solids or powders.

XRF combines highest accuracy and precision, with or without sample preparation, for the analysis of elements from Beryllium (Be) to Uranium (U) in the concentration range from 100% to sub-ppm.

Energy dispersive X-ray fluorescence spectrometry (EDXRF) is the best choice for applications in quality and process control with demands for ease of use and compact size. It delivers analytical flexibility for research and monitoring tasks.

Portable XRF spectrometers (P-XRF) allow you to take the analyzer to the sample rather than bringing the sample into the lab. This is especially useful when the test specimen is large, heavy, or needs to be analyzed in-situ.

Micro X-ray fluorescence spectrometry (Micro-XRF) is the method of choice for the elemental analysis of large non-homogeneous or irregularly shaped samples as well as small samples or even inclusions.

Total reflection X-ray fluorescence spectrometry (TXRF) is a well-established method for trace element analysis on a variety of samples down to the sub-ppm-level.

Wavelength dispersive X-ray fluorescence spectrometry (WDXRF) is known for its unrivalled accuracy, precision and reliability. This robust analytical technology has made its way into all kinds of industrial applications, such as cement, polymers, refineries, mining, and industrial minerals.

S2 PUMA – EDXRF spectrometer

M4 TORNADO – Micro-XRF spectrometer

S4 T-STAR – TXRF spectrometer

9.2 Poster session II

9.2.1 XRS instrumentation

1 **Advanced SDD to Address Different Applications Simultaneously**
Shaul Barkan, Yen-Nai Wang, Mengyao Zhang, Eugene Tikhomorov, Elena Damron and Valeri Saveliev (p. 155)

2 **Development of a primary X-ray filter for XRF analysis of uranium and plutonium**
Kota Ishii, Tsugufumi Matsuyama, Yukie Izumoto, Yasuhiro Sakai, Yoshiyuki Oguri and Hiroshi Yoshii (p. 156)

3 **Spatial resolution properties of krypton-based mixtures using a 100 μm thick Gas Electron Multiplier**
Rita Roque, Hugo Natal Da Luz, Lara Carramate, Carlos Azevedo, Jamil Mir and Fernando Amaro (p. 157)

4 **Low power, low noise, JFETs for room temperature x-ray detectors**
Leonhard Sturm, Lars Nebrich, Ignaz Eisele and Christoph Kutter (p. 158)

5 **Improved XRF Detector System for High Resolution Spectroscopy in Ambient Conditions**
Hartmut Schmidt, Heike Soltau, Adrian Niculae, Andreas Liebel, Robert Lackner, Daniel Steigenhöfer, Moritz Kopetzki and Bechir Talbi (p. 159)

6 **In-house X-ray absorption and X-ray emission spectroscopy with double von Hamos spectrometer**
Wojciech Błachucki, Joanna Czapla-Masztafiak, Jakub Szlachetko and Jacinto Sa (p. 160)

7 **Enhanced cooling technologies for Silicon Drift Detectors at very high count rate**
Mathieu Morelle, Jonas Douwen, Simon Benichou, Cédric Cohen and Menyhert Kocsis (p. 161)

8 **Proportional counter filled with fine powder aerosol**
Nuno Duarte (p. 162)

9 **Towards on-the-fly X-ray Fluorescence mapping in the soft X-ray regime**
Luca Bombelli, Michele Manotti, Matteo Altissimo, George Kourousias, Roberto Alberti and Alessandra Gianoncelli (p. 163)

10 **How many Fano factors should characterize an X-rays scintillation spectrometer?**
Victor Samedov (p. 164)

11 **Performance Evaluation of a 50 mm^2 Silicon Drift Detector for TXRF Trace Metal Analysis**
Cheri Anne Dingle, Neil Raymund Guillermo and Pablo Saligan (p. 165)

12 **Frontiers in Attosecond X-ray Science: Imaging and Spectroscopy**
Victoria Mazalova, Petra Fromme and Franz Kärtner (p. 166)

13 **Digital Pulse Processing for X-Ray Spectrometry with a single board computer/laboratory measuring instrument**
Riccardo Campana, Evgeny Demenev and Giancarlo Pepponi (p. 167)

14 **Development and performance test of X-ray Source for industrial Benchtop & Handheld XRF**
Jeongdong Kim, Sanghyo Kim, DonghoonLee (p. 168)

15 **Characterization of a triple-GEM position sensitive detector for X-ray fluorescence imaging**
Geovane Souza and Hugo Da Luz (p. 169)

9.2.2 Synchrotron XRS, XAFS, high resolution XES, and RIXS

16 **The U-induced changes in crystal-field and covalency effects of Th^{4+} in $Th_{1-x}U_xO_2$ mixed oxides probed by HERFD-XANES**
Yuying Huang (p. 170)

17 **Cu Nanoparticles: Structural Effects Determined By Supports**
Antonella Balerna and Claudio Evangelisti (p. 171)

18 **Potential Environmental Applications by Medium Energy Micro-probe Beamline Proposed in SSRF Phase-II Project**
Lina Li (p. 172)

19 **XAS studies of Sn modified TiO_2 coatings**
Ksenija Maver, Iztok Arčon and Urška Lavrenčič Štangar (p. 173)

20 **SR XRF in identification of elements in milligrams amounts of humic acids**
Valentina Trunova, Maria Dergacheva and Dmitrii Sorokoletov (p. 174)

21 **Chemical speciation of sulfur in lithium polysulfides via Core-to-Core and Valence-to-Core XES**
Marko Petric, Matjaž Kavčič and Alen Vizintin (p. 175)

22 **Nickel coordination in hyperaccumulator plants studied by XANES and EXAFS**
Jana Padežnik Gomilšek, Katarina Vogel-Mikuš, Alojz Kodre and Iztok Arcon (p. 176)

23 **Sample Topography from Synchrotron XRF and STXM for the examination of Diatom Microalgae**
George Kourousias, Fulvio Billè, Maya Kiskinova and Alessandra Gianoncelli (p. 177)

24 **Uptake and translocation of silver nanoparticles in Lactuca sativa: accumulation and ligand environment studies**
Laura Torrent, Mònica Iglesias, Eva Marguí, Katarina Vogel-Mikuš, Alojz Kodre, Anja Kavčič and Manuela Hidalgo (p. 178)

25 **2D-Maps of Cu Paintings by Resonant Inelastic X-ray Scattering (RIXS) with Multivariate Methods**
Héctor Sánchez, Jose I. Robledo and Juan José Leani (p. 179)

26 **Experimental Methodology for Retrieving Chemical State Information from L lines by Resonant Inelastic X-Ray Scattering**
Jose I. Robledo, Juan José Leani and Héctor Sánchez (p. 180)

27 **Preliminary characterization of organic dyes towards NEXAFS experiments using a laser-produced plasma source**
Lisa Glöggler, Adrian Jonas, Birgit Kanngießer, Ioanna Mantouvalou and Holger Stiel (p. 181)

28 **Synchrotron radiation total reflection X-ray fluorescence (SR-TXRF) and X-ray absorption near edge structure (XANES) of ovarian cyst fluid.**
Maria M. Grzelak, Paweł M. Wróbel, Marek Lankosz, Beata Ostachowicz, Łukasz Chmura, Dariusz Adamek and Robert Jach (p. 182)

29 **X-ray Raman scattering as a novel probe to discriminate carbon-based compounds in ancient art and fossil materials**
Rafaella Georgiou, Pierre Gueriau, Jean-Pascal Rueff, Uwe Bergmann, Nathan Daly and Loic Bertrand (p. 183)

30 **RXES experiments using stochastic data from non-monochromatized XFEL SASE radiation**
Yves Kayser, Chris Milne, Pavle Juranic, Leonardo Sala, Joanna Czapla-Masztafiak, Rolf Follath, Matjaž Kavčič, Gregor Knopp, Jens Rehanek, Diling Zhu, Roberto Alonso-Mori, Rafael Abela, Jacinto Sá and Jakub Szlachetko (p. 184)

31 **Iron accumulation in the aging retina: a synchrotron μ-XRF study**
Kalotina Geraki, Glen Jeffery and Marta Ugarte (p. 185)

32 **ESUO: The European Synchrotron and FEL User Organisation: Aims & Activities**
Iztok Arčon, Pervin Arikan, Carla Bittencourt, Federico Boscherini, Francisco M. Braz Fernandes, Nick Brooks, Maja Buljan, Benedetta Casu, Marie D'Angelo, Matteo D'Astuto, Martin Feiters, Annick Froideval, Silvia Gross, Christian Gutt, Thomas Hase, Simo Huotari, Krystyna Jablonska, Matej Jergel, Tommi Kajander, Amir Khan, Marco Kirm, Mike Kokkinidis, László Kövér, Doriano Lamba, Helge Larsen, Rainer Lechner, Derek Logan, Olga López, Kirsi Lorentz, Jan Luning, Carlo Mariani, Bratislav Marinkovic, Cormac McGuinness, Martin Meedom Nielsen, Sigitas Mickevicius, Petr Mikulík, Andrei Petukhov, Ullrich Pietsch, Boaz Pokroy, Juris Purans, Louis Renault, Gonzalo Santoro, Boris Shivachev, Moniek Tromp, György A. Vankó, Cecilia Blasetti, Alicja Górkiewicz, Mandy Grobosch, Manfred Helm, Barbara Schramm, Beatrix Kamelia Seidlhofer, Mirjam van Daalen and Antje Vollmer (p. 186)

33 **Magnesium-sulfur batteries studied by in-operando S K-edge RIXS and XAS spectroscopy**
Ana Robba, Alen Vizintin, Jan Bitenc, Iztok Arčon, Matjaž Kavčič, Matjaž Žitnik, Klemen Bučar and Robert Dominko (p. 188)

9.2.3 XRS applications in Art and Cultural Heritage

34 **GILDED COPPER AND TUMBAGA BY THE MOCHE: A TEST OF THE INTERNAL RATIO METHOD**
Roberto Cesareo (p. 189)

35 **STUDIES ON THE FAMOUS MOCHE "CABEZA DE MONO DORADA"**
Roberto Cesareo and Angel Bustamante (p. 190)

36 **PORTABLE EDXRF-SCANNER FOR MAPPING ANCIENT GOLD AND SILVER ALLOYS**
Roberto Cesareo, Giovanni Gigante, Stefano Ridolfi and Ricardo Lopes (p. 191)

37 **Spectroscopic analysis of polychromatic sculptures belong to the cultural heritage of Extremadura (Spain).**
Maria J. Nuevo, Alejandro Martín Sánchez and Miguel Angel Ojeda (p. 192)

38 **SEM/EDAX and optical microscopy study of an ancient cloth**
Stefania Bruni, Carmela Maria Cellamare, Alessandro Gessi, Giuseppe Marghella and Loredana Stante (p. 193)

39 **Use of Spectral Angle Mapper to extent macro-XRF results: first application on a Giotto's masterpiece**
Anna Galli, Letizia Bonizzoni, Michele Caccia, Roberto Alberti, N. Aresi and Marco Martini (p. 194)

40 **The vignetting effects in full-field X-ray fluorescence imaging system based on pinhole optics and gaseous detector**
Pawel Wrobel, Tomasz Fiutowski, Piotr Fraczek, Stefan Koperny, Marek Lankosz, Bartlomiej Lach, Agata Mendys, Bartosz Mindur, Krzysztof Swientek, Piotr Wiacek and Wladyslaw Dabrowski (p. 195)

41 **Technological examination of Renaissance ceiling in The Great Council Room of Gdańsk City Hall using various X-ray techniques**
Anna Klimek, Agata Mendys, Anna Klisińska-Kopacz, Piotr Frączek and Michał Obarzanowski (p. 196)

42 **Analysis of metallic objects from tomb of the 'Lady of Cao' by X-ray microtomagraphy and digital radiography**
Soraia Azeredo, Roberto Cesareo, Franco Jordan, Giovanni Gigante, Arabel Fernandez, Angel Bustamante, Artur Vilar and Ricardo Lopes (p. 197)

43 **The full-field X-ray fluorescence imaging combined with the multivariate data analysis for the painting layers investigations**
Agata Mendys, Tomasz Fiutowski, Piotr Frączek, Stefan Koperny, Marek Lankosz, Bartłomiej Łach, Bartosz Mindur, Krzysztof Świentek, Piotr Wiącek, Paweł M. Wróbel and Władysław Dąbrowski (p. 198)

44 **Textile metal analysis of the first Brazilian emperors' vestments**
Marcia De Almeida Rizzutto, Pedro H. O. Viviani de Campos, Jessica F. Curado, Elizabeth A. M. Kajiya and Valdirene C. Ambiel (p. 199)

9.2.4 Mobile and portable XRF

Advanced SDD to Address Different Applications Simultaneously

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Different designs of silicon drift detector (SDD), the Vortex® models, have been successfully applied to XRF (x-ray fluorescence), TXRF (total XRF), synchrotron, and x-ray mapping applications. These advanced SDD models all provide three characteristics simultaneously: large solid angle, excellent energy resolution, and high count rate performance. Several recent detector design developments have resulted in improved performance for many x-ray applications as follows:

Improved Quantum Efficiency - A thicker device enables the detector to be more efficient at higher energy. The today's typical device thickness of 0.5 mm has a quantum efficiency of 0.37 and 0.12 for 20 keV and 30 keV, respectively. A new SDD with a 1 mm thick SDD showed an efficiency which matches the theoretical values of 0.6 and 0.37 for 20 keV and 30 keV, respectively.

Improved Low Energy Performance - A significantly improved peak-to-background ratio, as well as the detection of C, B and Be is achieved with the advanced SDD with a new shallower entrance window [1]. Spectra of B and Be samples can be collected and analyzed.

High Count Rate Performance - With the availability of high brightness from synchrotron beam lines and new imaging techniques, scientists have a need for x-ray spectrometers capable of analyzing high x-ray flux for chemical analysis applications as well as for high quality x-ray mapping. To address that requirement, a multi-element SDD was developed, which, combined with an advanced Digital Pulse Processor (DPP), resulted is a spectroscopic system capable of collecting quality x-ray images with short exposures.

A significant improvement in the high count-rate capability is clearly presented with the 4-element SDD, the "Vortex ME4®", combined with either the advanced DPP "Xspress 3", developed by Quantum Detectors (Harwell Oxford, UK), or with another advanced DPP, the "FalconX" developed by XIA LLC (Heyward, CA. USA).

The combined system of the Vortex ME4 and either of the new advanced DPPs exhibits a dramatic increase in count rate capability which enhances the efficiency of measuring methods whenever high count rate and good energy resolution play important roles. The new spectrometer was evaluated at the Advance Photon Source (APS), located at the Argonne National Laboratories, by collecting a wide range of data using mapping and tomography techniques.

The new Vortex SDD models combine the above three performance characteristics of higher quantum efficiency, improved low energy performance and very high count rate capability, which benefit users with state of the art SDD performance.

[1] S. Barkan, V. Saveliev, J. Iwanczyk, L. Feng, C. Tull, B. Patt, D. Newbury, J. Small, N. Zaluzec, "A New Improved Silicon Multi-Cathode Detector (SMCD) for Microanalysis and X-Ray Mapping Applications", Microscopy Today, 12 (2004) 36-37.

Development of a primary X-ray filter for XRF analysis of uranium and plutonium

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Workers at nuclear fuel handling facilities are faced with a risk of suffering uranium and plutonium contamination due to injuries during their operation. In such a situation, on-site and rapid detection of uranium and plutonium is required to determine the appropriate course of treatment. Generally, during surface contamination due to uranium and plutonium exposure to a healthy skin, α-particle counting is performed. However, in case of wound contamination, it is difficult to detect the α-particle emitted from uranium and plutonium from blood oozing out of the wound. Therefore, we focused on X-ray fluorescence (XRF) analysis because X-rays can easily pass through several millimetres of blood [1]. Because this examination involves X-ray exposure to the affected area, the detection efficiency of uranium and plutonium should be maximized.

In XRF analysis, a primary X-ray filter made of metal foils is, generally, inserted between the X-ray tube and the sample to reduce the scattered X-ray. In the case of XRF analysis of uranium and plutonium, the incident X-rays at 13.61 keV (U Lα peak) and 14.28 keV (Pu Lα peak) should be reduced, while X-rays with energy exceeding 17.17 keV (L-III threshold of U) should be maintained to excite uranium and plutonium. However, conventional portable type XRF devices are not equipped with primary X-ray filters that satisfy above requirements. Therefore, we employed Bruker Tracer III-SD. Since, in this device, we can install a self-build primary X-ray filter, we are able to efficiently detect these elements in the wound by using a filter optimized for uranium and plutonium analysis.

The purpose of this study is to develop a new primary X-ray filter that facilitates high-sensitivity simultaneous analysis of uranium and plutonium in wound. Ni, Cu, and Zn were selected as materials for the filter, and the relationship between the thickness of these materials and the detection limit of uranium and plutonium were investigated using the contaminated wound model.

[1] Yoshii et.al., PLOS ONE, 9, (2014), e101966.

Spatial resolution properties of krypton-based mixtures using a 100 µm thick Gas Electron Multiplier

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A cascade of two non-standard GEM plates manufactured from a 100 µm thick kapton foil was coupled to a 2D strip readout and immersed in krypton-CO_2 mixtures. This micro patterned gaseous detector (MPGD) with an active area of $10 \times 10\,\text{cm}^2$ was irradiated with x-ray sources, recording the energy and interaction position of incoming x-rays, with a detector less prone to sparking-caused damage.

A sharp edge was imaged by irradiating the MPGD with an x-ray generator operating in five krypton-based mixtures and in Ar-CO_2 (70:30) (for comparison purposes). The electric field setup, charge gain and energy resolution in these mixtures was previously studied in [1, 2] using mono-energetic x-ray sources. In this work we have irradiated the MPGD with x-rays with a continuous energy distribution, up to 30 keV. For each acquisition, a set of sub-images was reconstructed from the original one by sectioning the total energy histogram into sequential energy regions 2 keV wide, starting at 2 keV.

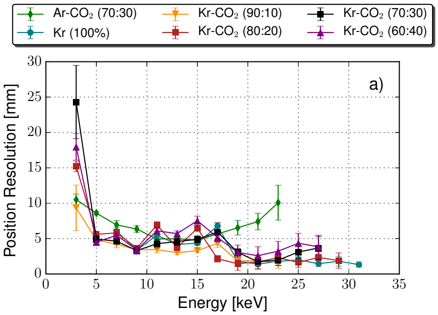

Figure 1: **Spatial resolution as a function of radiation energy:** the error bars quantify the ESF goodness of fit to the Gauss error function.

For each sub-image, the position resolution was determined by the edge-gradient method. Figure 1 illustrates the results obtained. For krypton-based mixtures, the spatial resolution value remains at low values for energies above 18 keV. This behavior is much different than the one reported for argon mixtures, where the position resolution is known to degrade above the 15 keV threshold [3].

Taking the obtained results into account, we conclude that krypton usage in MPGDs for imaging purposes brings substantial improvements in terms of spatial resolution for energies above 18 keV.

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[2] R.C. Roque, H. Natal da Luz, L.F.N.D. Carramate, C.D.R. Azevedo, J.A. Mir and F.D. Amaro, 2017, *Gain characteristics of a* 100 µm *thick GEM in Krypton-*CO_2 *mixtures*, Journal of Instrumentation, JINST 12, C12061.

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Low power, low noise, JFETs for room temperature x-ray detectors

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Abstract

We developed improved short channel JFETs for room temperature x-ray spectroscopy preamplifiers. They have a transition frequency above 2 GHz, low 1/f noise, low power consumption and are ready for integration into CMOS. Performance in an x-ray fluorescence spectroscopy application is shown.

Figures of merit for JFETs in charge amplifiers for x- and γ-ray fluorescence spectroscopy

The figures of merit transition frequency $f_T[:= gm/(C_{gs} \cdot 2\pi)]$, where gm is the transconductance and C_{gs} is the gate-source capacitance, gate leakage current I_{LT} and flicker-corner frequency f_C determine the resolution limits for a given detector. There are three major noise contributions in x- and γ-ray spectrometers employing semiconductor detectors that are affected by parameters of the input transistor[1]: white series noise depending on $1/f_T$, white parallel noise depending on I_{LT}, 1/f-type series noise depending on f_C/f_T. To minimize noise contributions from the transistor the fabrication process was optimized to allow shorter gate length for higher f_T while keeping low f_C and I_{LT} below 1pA at operating point. This allows JFETs with lower power consumption and higher transition frequency than comparable JFET devices [2] [3]. To compare power consumption, the gm to saturation drain-current Ids_0 ratio gm/Ids_0 is calculated.

Device: W / L [µm]	f_T [GHz]	f_C [Hz]	I_{LT} ^{1} [pA]	gm ^{1} [mS]	C_{gs} ^{1} [pF]	Ids_0 ^{1} [mA]	gm/Ids_0 [1/V]
100 / 1.2	2.2	250	0.2	2.8	0.24	1.5	1.9
400 / 1.2	2.4	100	0.7	10	0.85	5	2
800 / 1.2	2.4	100	1	20	1.75	10	2
2N4416[3]	0.43	100-10000	<1	6	2.2	10	0.6
MX10[2]	1.3	100-1000	-	6.5	0.8	-	-

^{1} Measurement conditions for EMFT JFETs: Vds=3V, Vgs=0V, temperature: 23°C

Application Results

At room temperature without cooling the Si-PIN detector a resolution of 180eV FWHM from Mn(Kα) (5,9keV) at 3µs shaping time and 1pF detector capacitance has been measured.

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[3] Vishay, “Datasheet 2N4416,”

Improved XRF Detector System for High Resolution Spectroscopy in Ambient Air Conditions

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Silicon Drift Detectors from PNDetector are used in analytical systems in microanalysis as well as in XRF-analytic devices for more than 10 years. The well-known spectroscopic performance, characterized by excellent energy resolution down to 123eV @ Mn Kα as well as the light element performance down to 38eV @ carbon is the result of the optimized SDD chip design and the ultraclean processes in our production. With the newest chip development, the Genius Line, the energy resolution at short shaping times could be further improved and the operation of this silicon drift detector with minimum chip cooling up to real room temperature becomes realistic.

In our Complete Series the Silicon Drift Detectors are mounted in a completely controllable, hermetically sealed vacuum package. Integrated pressure and temperature sensors offers the possibility to monitor the vacuum conditions inside the detector housing, which can be refreshed by reactivating the getter. This allows operating the SDD under optimum vacuum conditions over a long lifetime even in applications with rough ambient air conditions.

Fig. 1: The Complete - XRF Detector System

The XRF Detector System combines the excellent detector performance with the specific electronics in a compact housing.

In this contribution, we will discuss new developments as well as long time experience with our Complete Series. We will report about the excellent performance of our second generation XRF Detector System and we will present our newest development, the Complete Preamplifier Modules dedicated for Industrial Application.

In-house X-ray absorption and X-ray emission spectroscopy with double von Hamos spectrometer

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Until now a few laboratory experimental setups for X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES) were developed. It was shown that they allow to obtain synchrotron-quality spectra during a few hour-measurement [1]. Unlike large scale facilities where the access is infrequent and not guaranteed, laboratory X-ray setups can be fully adapted to dedicated scientific projects and used every day over entire year delivering the experimental data and approaches that can further support experiments at synchrotrons and X-ray free-electron lasers (XFELs). New experimental setup for in-house simultaneous XAS and XES studies has been developed.

The setup is at the Institute of Physical Chemistry of the Polish Academy of Sciences in Warsaw. It consists of one X-ray source, sample and two X-ray spectrometers in the von Hamos geometry [2]: one for measurement of the radiation transmitted through the sample and another for fluorescence detection. The X-ray source is XOS X-Beam Superflux PF X-ray tube. It can operate at the maximum voltage and the maximum current of 50 kV and 1 mA, respectively. It has an integrated optics which focuses the exit beam to an angle of about 3º. Two cylindrically bent Si(110) crystals of 25 cm-radius of curvature are used. The diffracted radiation is registered by two Andor Newton DO920P cameras with front-illuminated CCD matrices of 1024×256 26 μm-sized pixels shielded by 250 μm-thick Be windows. The pressure in the sensors' proximity is decreased to 10^{-7} mbar by means of a vacuum pumping system connected to the cameras. The high vacuum allows to safely cool down the sensors down to -70 ºC with the thermoelectric coolers built in the cameras. The X-ray setup is operated in air.

The XAS unit has been recently tested. Ni *K* edge X-ray absorption spectrum was measured for 5 μm-thick Ni foil at X-ray tube voltage and current of 40 kV and 0.9 mA, respectively. The 4th order of diffraction was used and the beam was diffracted at the Bragg angle of 65.2º. The detection was done with cameras cooled down to -40 ºC. The setup registered spectral intensity of about 1 photon/(s×eV) and the entire measurement lasted about 19 hours. The acquired spectrum is in excellent agreement with the data measured with synchrotron radiation.

The XES unit is currently under commissioning. The developed X-ray setup is intended for probe of the lowest unoccupied and the highest occupied electronic orbitals of Ni atoms in different compounds. It can, however, be easily adjusted to detect any X-ray radiation in the energy range 5 – 10 keV which includes, e.g., *K*-edge binding energies of elements for atomic numbers 23 – 30.

Acknowledgments: This work is financed from the budget allocations for science for years 2016-2019 within the IDEAS PLUS II project of number IdPII2015000164.

[1] G. T. Seidler *et al.*, Review of Scientific Instruments 85, 2014, 113906.
[2] L. von Hamos, Naturwissenschaften, 20, 1932, 705.

Enhanced cooling technologies for Silicon Drift Detectors at very high count rate

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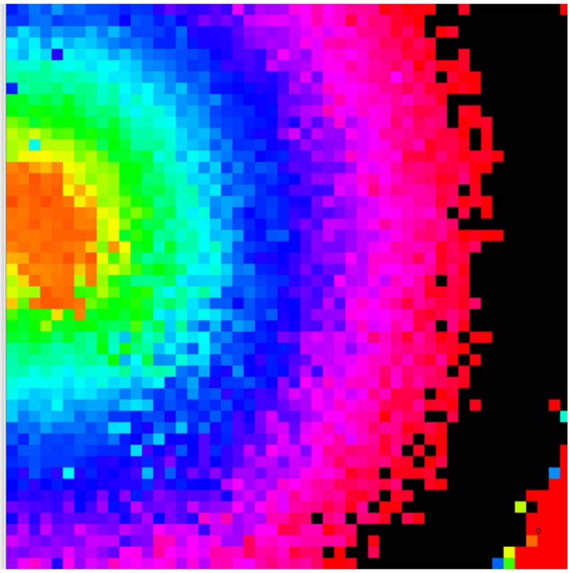
X-ray spectroscopy at high brilliance requires faster measurements systems. New generation CMOS preamp and digital pulse processor algorithms have drastically improved the throughput. A key parameter determining the throughput of SDDs is the signal rise time. An extensive study of the signal rise time as a function of different key parameters is presented in this article. The most important parameters determining the signal rise time are the temperature, the bias voltage and the distance from the interaction to the collecting anode. The temperature has a strong influence on the charge collection speed and collection. This study presents results of the characterization of SDD of different sizes cooled using multi-stage Thermo-electric coolers and compact cryogenic coolers in a temperature range down to -100°C. At these temperatures signal rise times below 20ns have been obtained.



Scan of the signal rise time on an area of 3.2x3.2mm of a SDD with a beam spot with a size smaller than 100µm.

Proportional counter filled with fine powder aerosol

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A novel radiation detection concept is being developed, which consists on the dispersion of fine powders in a gaseous proportional counter, forming an aerosol. The sensitivity of this aerosol to a specific type of radiation can be adjusted by the appropriate selection of the composition of the fine powder.

The initial motivation for the development of this technique was to find a viable alternative to the ^{3}He proportional counters used in neutron detectors [1]. The novel detection concept was tested in a prototype filled with boron-carbide (B_4C) micro-powder dispersed in a P10 (90% Ar + 10% CH_4) gaseous proportional counter. Exposure to a 5 Å neutron beam line yield an efficiency of 4% using a rudimentary prototype, with large room for improvements and optimization. A full energy deposition peak was also observed, which is extremely relevant for gamma ray discrimination in neutron detectors.

In this work we present the results of further investigations, obtained by irradiation with x-rays from a ^{55}Fe source, concerning the effects of the presence of micro particles in the proportional counter to gain and energy resolution. We discuss the implications for the detection of hard x-rays and gamma rays, using high micro/nano particles made of high-Z materials.

[1] F.D. Amaro, C.M.B. Monteiro, J.M.F. dos Santos, A. Antognini, Novel concept for neutron detection: proportional counter filled with 10B nanoparticle aerosol, Sci. Rep. 7 (2017) 41699. doi:10.1038/srep41699.

Towards on-the-fly X-ray Fluorescence mapping in the soft X-ray regime

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The possibility of fast X-ray Fluorescence (XRF) imaging using on-the-fly acquisition is very attractive since it allows fast collection, assuming to have enough XRF emitted photons collected by the detectors. On-the-fly XRF has been already demonstrated at mid and high X-ray energy energies, common range for both for laboratory instruments and synchrotron-based instruments.

Here we report on the capability of DANTE digital pulse processing unit in the soft X-ray regime. DANTE is a novel Compact and Low-Power Digital Pulse Processor with High Energy Resolution and High-Count Rate. This work presents preliminary measurements performed at the TwinMic beamline [1] at Elettra synchrotron (Trieste, Italy) addressing the feasibility of on-the-fly low energy X-ray Fluorescence imaging.

[1] A. Gianoncelli, G. Kourousias, L. Merolle, M. Altissimo and A. Bianco, J. Synchrotron Radiat. 23, 2016, 1526.

How many Fano factors should characterize an X-rays scintillation spectrometer?

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Bousselham A., et al. in their article “Photoelectron anticorrelations and sub-Poisson statistics in scintillation detectors” [1], introduced two Fano factors – the Fano factor for scintillation photons and the Fano factor for photoelectrons. Their experimental results published in [2] for scintillation photons’ and photoelectrons’ Fano factors are in doubt.

The exact mathematical description of processes at registration of X-rays by a scintillation detector allows receiving correct formulas for the mean value and the variance of the amplitude at the output of a scintillation detector. From the analysis of these formulae, it follows that a scintillation detector should be characterized only by the one Fano factor determining fluctuations in the process of electron-hole pairs’ generation. Only this Fano factor is determined by the electronic structure of a scintillation crystal, and does not depend on the transparence and the coating of the scintillation crystal, the characteristics of photodetector, and the crystal-photodetector interface.

[1] Bousselham A., et al. Nucl. Instr. Meth. in Phys. Res. A, 2010, V. 620, p. 359.
[2] Bora V., et al. Nucl. Instr. Meth. in Phys. Res. A, 2016, V. 805, p. 72.

Performance Evaluation of a 50mm^2 Silicon Drift Detector for TXRF Trace Metal Analysis

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Total-Reflection X-Ray Fluorescence (TXRF) is an established multi-elemental analysis technique used for the determination of ultra-trace elements. It overcomes some of the drawbacks of conventional ED-XRF such as the need to correct for absorption-enhance effects [1]. Over the past decades, innovations of the TXRF technique yielded better and better detection limits, where parts per trillion (ppt) or femto gram has been successfully achieved [2]. Detector systems also have been improved to compliment TXRF's demands for lower detection limit.

In this study, the performance of a 50mm^2 Silicon Drift Detector for TXRF spectrometry for ultra-trace metal analysis in liquid matrix have been evaluated. In addition, fabricated collimators of varying diameters were tested to determine the most suitable collimator size for ultra-trace metal analysis. Sample preparation, calibration, sensitivity determination and detection limits are likewise presented. A layer on layer internal standardization procedure using two sets of multi-element standards was implemented to determine the calibration line, sensitivity curve and detection limits of the technique. Spectrum analysis was done with the aide of Python-based program. The results indicated that the values of detection limits are within 1–5 μgl^{-1} for some metals of interest. The smallest collimator diameter produced the highest signal-to-noise ratio but the difficulty of centering the deposit is a disadvantage.

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Frontiers in Attosecond X-ray Science: Imaging and Spectroscopy

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In the AXSIS project, funded by the European Research Council, we will use the new method of attosecond serial X-ray crystallography and spectroscopy, to give a full description of ultrafast processes atomically resolved in real space and on the electronic energy landscape, from co-measurement of X-ray and optical spectra, and X-ray diffraction. This technique will revolutionize our understanding of structure and function at the atomic and molecular level and thereby unravel fundamental processes in chemistry and biology like energy conversion processes. Ultimately, attosecond serial X-ray crystallography and spectroscopy will be applied to one of the most important problems in structural biology, which is to elucidate the dynamics of light reactions, electron transfer and protein structure in photosynthesis.

The AXSIS project demonstrates two ground breaking technologies that may change how we accelerate particles and we can use X-rays broadly. First, the AXSIS machine is based on a new high gradient accelerator technology, THz acceleration, where the THz radiation is generated via high energy high power lasers. The technology has the potential to move from today acceleration gradients on the 10 MV/m level for the European X-FEL to 1 GV/m, which would reduce the length of such advanced X-ray sources to the 10 m scale. Second, the output of the AXSIS source with respect to flux and brilliance rivals modern synchrotrons, bringing the most advanced scientific and medical x-ray probe into the university, industrial, and medical laboratory.

Digital Pulse Processing for X-Ray Spectrometry with a single board computer/laboratory measuring instrument

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A commercial single board computer equipped with an analog to digital converter (ADC) and a Field-programmable gate array (FPGA) designed as a general purpose measuring and control laboratory instrument is evaluated as a possible low-cost solution for the acquisition and digital pulse processing [1] of semiconductor spectroscopic x-ray detectors and in particular for silicon drift detectors (SDD). The instrument is fully programmable and can be tailored to the specific needs, in particular for didactic purposes. It is provided with open source applications to use it as an oscilloscope, a waveform generator, a spectrum analyzer. In order to use the instrument for detector signal acquisition and digital pulse processing, the pre-amplified signal is filtered to remove the ramp of the charge sensitive preamplifier and to convert the steps due to the photon detections into pulses with maximum height adapted to the input range of the ADC. For the digital filter and the multichannel analyzer algorithms, three options are considered:

1. real-time DPP directly executed by the FPGA
2. executed onboard the embedded CPU: probably slower but more flexible
3. transferring the digitized signal to a client PC with off-line processing: slower but more flexible solution giving full insight in the signals and the conversion process.

Preliminary results will be presented and application scenarios for the system, from compact portable instrumentation to education will be discussed.

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Development and performance test of X-ray Source for industrial Benchtop & Handheld XRF

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X-ray fluorescence (XRF) spectrometry is a non-destructive method used to analyze elements within materials quantitative and qualitative [1]. The XRF is widely used in industries such as steel and mining industry, material research, and nondestructive inspection. Presently, the foreign companies' X-ray source of XRF and XRD equipment are mostly used.

The research for the X-ray source development has actively conducted to develop source technology and strengthen technology competitiveness. The XRF spectrometry consists of four parts: X-ray tube, high voltage, detector and analysis software. In this study, the high output X-ray tube for Bench-top & Handheld is developed based on ø8 ceramic X-ray tube which is used for soft X-ray ionizer.

First, the anode and cathode structures were newly designed to incerease tube voltage to 50kV and reduce focal size. Second, the optimum thicknesses of W and Ag target materials were determined by using the mcnpx code [2]. Third, the energy spectrum and radiation amount of X-ray tube was measured using the CdTe detector [3]. Finally, the component analysis of five materials was conducted using the SDD detector. The performance of a X-ray tube was verified through the comparison between the analyzed results and the actual composition ratio.

Characterization of a triple-GEM position sensitive detector for X-ray fluorescence imaging

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X-ray fluorescence imaging is a powerful technique for analysis of samples where the spacial distribution of elements is important. Applications of this technique can be found in archaeology, industry or studies of cultural and historic heritage.

Detectors able to reach large detection areas and a good position resolution are key components of such systems. The Gas Electron Multiplier (GEM) [1] is a Micropattern Gaseous Detector introduced in 1997 that has undergone a fast development, mainly due to the demands of high energy physics experiments for very large sensitive area, fair energy and position resolution, and high counting rates. Thanks to these developments, it is possible nowadays to use such detectors in X-ray applications. Although it is known that gaseous detectors have limited resolution when compared to solid state detectors, taking into account their large sensitive area and ability to determine simultaneously the position of interaction of the radiation and the deposited energy, they are becoming a very interesting solution when large areas must be analyzed.

GEM-based systems for X-ray fluorescence imaging have been successfully tested before, allowing to determine the elements present in hidden paintings [2], using a large number of electronic channels.

In this work, the performance of a triple-GEM detector that will be part of a X-Ray fluorescence imaging system is described, where a total of five electronic channels are used, one for global trigger and energy measurement and four for position determination by resistive charge division. The first GEM of the detector has a smaller pitch to allow higher drift fields, minimizing the effects of electron diffusion, without compromise the energy resolution. Simulation results with the `Garfield++` libraries [3, 4] supporting this geometry will be shown. The readout is composed of strips interconnected by a resistive chain for charge division. The resistive chain is totally independent of the detector and can be easily replaced. The number of electronic channels can also be increased to improve the position resolution at lower energies. To create the primary ionization the detector uses a mixture of Ar/CO_2 (90/10). The detector operates stably at gains of the order of 10^4, working with 7.5 % (σ) energy resolution and 1.5 mm (FWHM) spatial resolution, both at 5.9 keV.

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The U-induced changes in crystal-field and covalency effects of Th^{4+} in $Th_{1-x}U_xO_2$ mixed oxides probed by HERFD-XANES

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Owing to recent advances in spectroscopy, high-energy-resolution fluorescence-detected X-ray absorption near edge spectroscopy (HERFD-XANES) with reduced spectral broadening can be measured by employing an X-ray emission spectrometer. The HERFD-XANES spectra at the Th or U L_3 edge are generally recorded by monitoring the maximum of the $L_{\alpha1}$ ($3d_{5/2}$–$2p_{3/2}$) emission line, which has the highest transition probability compared with other emission lines. The spectral broadening can be further reduced if the L_3-edge XANES spectrum is collected at the $L_{\beta5}$($5d_{5/}2$–$2p_{3/2}$) emission line. The U L_3-edge HERFD-XANES spectrum recorded using the $L_{\beta5}$ emission line was first used to detect the crystal-field splitting of the U 6*d* states in UO_2. This approach makes it possible to detect the crystal-field effects on the Th 6*d* states in Thorium-based mixed oxides, which cannot be obtained by conventional X-ray absorption methods.

In this work, by adjusting the amount of the metal precursors of $Th(NO_3)_4{\cdot}6H_2O$ and $UO_2(NO_3)_2{\cdot}6H_2O$, we synthesized thorium-uranium mixed oxides with nominal Th/U atomic ratios of 3:1, 1:1 and 1:3, which are denoted as $Th_{0.75}U_{0.25}O_2$, $Th_{0.5}U_{0.5}O_2$ and $Th_{0.25}U_{0.75}O_2$, respectively. The local structures of Th in the $Th_{1-x}U_xO_2$ (x=0.25, 0.5, 0.75) mixed oxides, including the crystal-field splitting and distribution of the Th 6*d* states, are investigated by using the Th L_3-edge HERFD-XANES spectra collected at the $L_{\beta5}$ emission line combined with the first-principles calculations based on the local-density approximation (LDA) taking into account Coulomb interaction U (LDA + U).

Knowledge of the local Th structure is a prerequisite for a better understanding of the physicochemical properties of the thorium-based mixed oxides involved in the Th-based nuclear fuel cycle. The detected crystalline electric field split between the 6*d* e_g and t_{2g} orbitals in ThO_2 consisting of ordered Th-O_8 cubes with cubic symmetry is ~3.5eV for the Th^{4+} ion. Because the split peaks of the white line corresponding to the crystal-field splitting of the unoccupied 6*d* states were resolved in the HERFD-XANES spectra, the analysis of these split peaks combined with first-principles calculations revealed that an increase of the U content involves the distortion of the Th-O_8 cubes in the $Th_{1-x}U_xO_2$ mixed oxides. The lower symmetry of the Th-O_8 cube induced by the incorporated U trends to reduce the local crystal field around Th^{4+} as well as the hybridization of Th $6t_{2g}$-O 2*p*, which is mainly responsible for the covalent property of the Th-O bond. The phenomenon is noticeable in $Th_{0.25}U_{0.75}O_2$, whose splitting is decreased by approximately 10%, and covalent mixing between Th 6*d* t_{2g} and O 2*p* orbitals is substantially reduced compared to pure ThO_2.

Cu Nanoparticles: Structural Effects Determined By Supports

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Copper nanoparticles (NPs) were prepared by metal vapour synthesis (MVS) technique and deposited onto three different supports (*i.e.* Al_2O_3, PVPy and Carbon). MVS approach ensured to get size-controlled Cu NPs in the zero valent state stabilized by weak interaction with the solvent (acetone) before being immobilized on the support. The role of the support on the structural features of the Cu NPs was investigated using high resolution transmission electron microscopy (HRTEM) and X-ray absorption fine structure (XAFS) spectroscopy.
While as already shown [1] Cu NPs, supported on PVPy, resulted in a Cu(I) oxidized phase and the ones on carbon were in a Cu(II) phase, here we will show that only in the NPs on Al_2O_3 a Cu(I) and Cu(0) phase were found.
The catalytic activity and stability of the three Cu-based catalysts were evaluated in Huisgen azide-alkyne cycloaddition reaction (CuAAC) of benzyl azide with phenylacetylene, taken as model reaction. The role of the morphological and structural effects induced by the different supports played a crucial role in determining their catalytic properties.

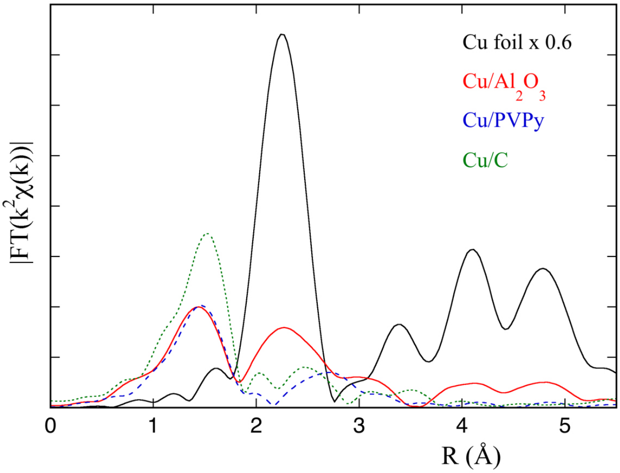

Figure.1 - Fourier transforms of the experimental EXAFS spectra of the Cu foil reference sample and of the Cu NPs supported on Al_2O_3, PVPy and Carbon.

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Potential Environmental Applications by Medium Energy Micro-probe Beamline Proposed in SSRF Phase-II Project

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There are low levels of pollutants in the environment with a certain potential harmfulness. A medium-energy x-ray spectroscopy beamline is proposed in SSRF Phase-Ⅱ Project and μ-XRF method will be realized. For the design indicators, the energy resolution (ΔE/E) is 2×10^{-4}@2.5keV and the photon flux is 1.5×10^{12}phs/s@2.5keV (after K-B mirror focusing). The focused spot size will be $6\times2\mu m^2$@2.5keV (K-Bmirror) and $0.3\times0.2\mu m^2$ @2.5keV (small K-B mirror) respectively. The combination of high-brightness, sub-micron X-ray beams, nondestructive method and high sensitivity detectors are able to analyze environmental pollutants on the micro-scale, especially on sulfur and phosphorus compound. The beamline energy range is from 2 to 16 keV, covering most pollutant elements of K or L absorption edge in the field of the environmental science, such as copper, zinc, lead, cadmium, chromium, mercury and arsenic, etc. The detection capability of ppb level can be provided for accurate detection of the metals. XAS and XRF analysis can be carried on the end station, such as XANES, TEY, TXRF, and so on. At the end-station there are equipped the liquid cell, the device for high temperature and pressure (600K，4MPa), and different gas supplies and safe exhaust, eg. for H_2S. For the experiments to study chemical catalyzer, a low temperature sample holder and the helium chamber will be equipped. Similar beamline on Medium Energy XAFS research are Diamond-I18, APS-2-ID-B and ESRFID-21 beamline.

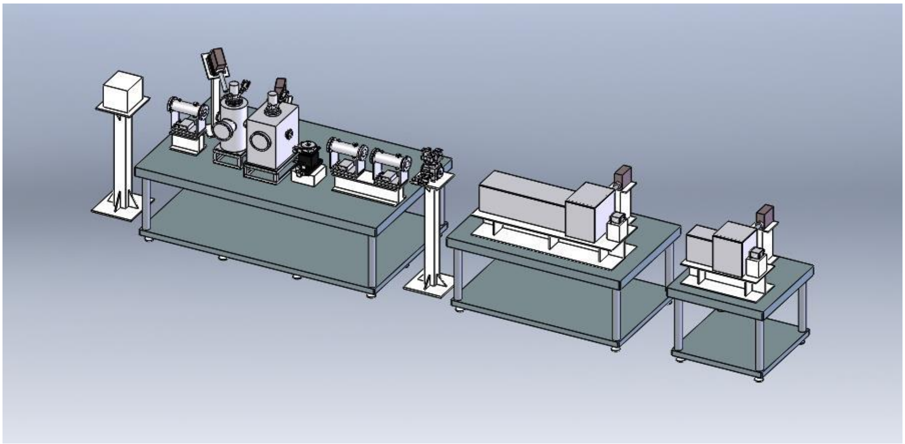

Figure1: Schematic diagram of the end-station at the medium energy beamline

XAS studies of Sn modified TiO_2 coatings

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Coatings based on TiO_2 are extensively investigated material for the preparation of surfaces which are referred as self-cleaning. Under solar illumination these coatings catalyze pollutants degradation and enhance their removal from the surface due to photoinduced superhydrophilicity [1]. There are two main drawbacks of using pure TiO_2 (anatase) as a photocatalyst; i) its band gap lies in the UVA region so it can exploit only a part of the sunlight spectrum, and ii) it has a high degree of recombination between photo generated electrons and holes on the surface. There are various strategies to improve the photocatalytic efficiency of TiO_2, one of them is the modification with transition metals.

Based on our previous experiences with sol-gel synthesis of low-temperature TiO_2 thin films [2], we prepared a series of Sn modified TiO_2 photocatalysts. As a starting material only organic (Ti and Sn alkoxide) precursors were used. The loadings of Sn cations were varied in the range of 0.05 to 20 mol.%. The coatings, deposited on glass substrates by dip-coating technique, were dried at 150 ^oC. In addition, another set of photocatalyst coatings was prepared by further calcination at 500 °C in air. The comparison of photocatalytic activities of Sn modified TiO_2 to unmodified TiO_2 showed that Sn loadings in the range of 1-10 mol.% improved photocatalytic activity up to 8 times. At lower loadings of Sn, the photocatalytic activity was improved only by 30 %. After the coatings are calcined, their photocatalytic activity was significantly reduced.

The objective of the research was to examine the mechanism responsible for photocatalytic properties of Sn modified TiO_2 and to to clarify the role of Sn cations in the TiO_2 photocatalytic process. For this purpose, Sn and Ti K-edge XANES and EXAFS analysis was used to precisely determine the local structure and the site of incorporation of Sn cations on titania nanoparticles in the coatings. We examined the hypothesis that the solid-solid interface was a crucial structural feature that facilitates charge separation and enhances photocatalytic efficiency of titania.

Acknowledgements

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SR XRF in identification of elements in milligrams amounts of humic acids

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Humic acids are natural substances that perform in the biosphere aimed at maintaining its stability functions. Humic acids are capable of binding and preserving carbon and a wide range of elements for long geologically- comparable periods. The content of humic acids in soils and paleosols can be tenths of a percent. The processing of large masses of studied soil samples makes it possible to extract from them only milligrams of humic acids and this poses the problem of selecting non-destructive methods for humic acid investigation and creating a base of humic acid preparations for their further sequential study.

The testing of different analytical methods (NAA, TJP-AES, etc.) allowed us to conclude that the X-ray fluorescence analysis using synchrotron radiation (XRF-SR), being non-destructive and multielement analysis is most suitable for solving a wide range of issues on the ecological state of the environment and its variability in time.

The XRF method was developed for the determination of the elements (S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Kr, Rb, Sr, Mo, I, Pb, Th, U) on the basis of K-lines and L-lines in samples of milligram mass.

Analyzes of paleosols formed in the cold conditions of the Sartan glaciations period (approximately 28.5–12.5 ka BP) on the Priobskoe plateau was performed by the XRF-SR method. It was established that humic acids contain a wide specific set of elements. Despite the very low share of humic acids (no more than 5–7% of the total mass of humic substances), difficult to fix elements in this component of humus were determined: Th and U, Rb and Sr, Br, Y, Zr, Nb, etc.

The use of the XRF-SR method at the installation of the Siberian Center for Synchrotron and Terahertz Radiation of the Institute of Nuclear Physics of the SB RAS reveals a wide range of elements in humic acid samples of milligram mass. It allows us comparison of soils and paleosols of any age and formation conditions, regardless of their content in the soil mass, and using them for reconstruction of paleoenvironment and substantiation of predictions of soil behavior in the near and distant future.

Chemical speciation of sulfur in lithium polysulfides via Core-to-Core and Valence-to-Core XES

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The x-ray inner shell spectroscopic methods are commonly used for study chemical environment of the central atom. The x-ray absorption spectroscopy (XAS), commonly used at the synchrotron probes the unoccupied states above the Fermi level. In contrast to XAS, in the x-ray emission spectroscopy (XES) the occupied state are studied by recording x-ray emission following inner shell ionization. The XES technique can be performed also with laboratory excitation sources, e.g. x-ray tube or proton beam. The necessary condition for performing XES is the high-energy resolution in the detection channel. The XES technique can be applied to characterize the electronic structure of the elements in different system in different field of science. One interesting system are Li-S batteries, which are considered as one of the most promising candidates for future batteries in high energy density applications [1]. In general, the reaction in the Li-S batteries is known, the elemental sulfur (α-S_8) is reduced to lithium sulfide (Li_2S). In reality, the process goes through a series of stepwise redox reaction forming various long-chain lithium polysulfides.

In this work, the high energy resolution x-ray emission spectroscopy is used to examine the local electronic structure of the sulfur atom in the three phases which appear in the Li-S battery; elemental sulfur (α-S_8), lithium polysulfides Li_2S_x ($x = 2, \ldots, 8$) and lithium sulfide (Li_2S). The high-resolution $K\alpha$ and $K\beta$ emission spectra of the sulfur were recorded by in-vaccum crystal spectrometer[2] combined with the particle induced x-ray emission (PIXE) in our laboratory, at the Jozef Stefan Institute. In order to interpret measured spectra, the quantum chemical calculations based on the density functional theory (DFT) were performed. The energy shifts of the Kα line which originate from the Core-to-Core (CtC) electron transition were correlated with calculated effective charge of sulfur atom. The measured Kβ spectra, which correspond to the Valence-to-Core (VtC) transition were compared to the ab-initio calculations based on density functional theory (DFT).

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Nickel coordination in hyperaccumulator plants studied by XANES and EXAFS

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Soils derived from ultramafic or serpentine rocks are characterized by elevated concentrations of Ni, Cr and Co. About 2% of plants on ultramafic soils accumulate metals in their shoots: a phenomenon known as hyperaccumulation. Ni coordination in plant organs of a Ni hyperaccumulators (HA), *Berkheya codii* Roessler, *Berkheya zeyheri* subsp. *rehmannii* var. *rogersiana*, and its non-hyperaccumulating (NHA) counterpart *Berkheya zeyheri* subsp. *rehmannii* var. *rehmannii* was studied by EXAFS and XANES. All varieties originate from the vicinity of Barberton Mpumalanga, South Africa.

Ni *K*-edge spectra of HA and NHA leaves, veins, stems and roots were measured at BM23 beamline of ESRF synchrotron facility, Grenoble, France and at P64 beamline of PETRA III, Hamburg, Germany. Samples were rapidly frozen against a metal plate cooled with liquid nitrogen, put into a windowless cryostat and evacuated. The spectra were collected in fluorescence mode. For comparison, spectra of soil and Ni standards *i.e.* nickel bound in citrate, malate, methionine, proline, catecholate and histidine complexes were measured in transmission mode. IFEFFIT program package [1] was used for data evaluation.

The shape and position of the Ni K edge strongly indicate that nickel is in the form of Ni^{2+} ion in all samples. Spectra of HA leaves, veins and stem are almost identical and consistent with spectra of Ni bound to organic acid complexes, while Principal Component Analysis of the roots spectra exhibits a mixture of Ni coordinated as in the soil structure, to the organic acids and to histidine. NHA plants accumulate much lower amount of Ni, from which only the roots spectra give enough signal for analysis: there, Ni is predominantly bound as in the soil, and in a lesser amount to histidine. Results show that - in comparison with the NHA plant - HA roots not only uptake more Ni but they transform its chemical environment to a higher degree, enabling transport of the metal ions to higher parts of the plant.

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Sample Topography from Synchrotron XRF and STXM for the examination of Diatom Microalgae

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X-ray Fluorescence spectroscopy (XRF) is one of the most widely used nearly non-destructive techniques for elemental analysis of a wide variety of samples. XRF emission is an isotropic phenomenon, still, despite the known angular dependence of XRF *detection*, artefacts remain an issue especially when using micro- or nano-X-ray beams and detectors located at small angles with respect to the sample's surface. When analyzing inhomogeneous samples with non-flat surface such as biological specimens, the sample topography and surface roughness play an important role and may cause misleading interpretation if not carefully evaluated. However this angular dependence may be an advantage in some cases: if correctly exploited it can allow retrieving topographical information on the analysed samples. This work is based on an ongoing research project on this topic [1]. The poster will present the results of a synchrotron experiment where diatom microalgae [2] were studied through STXM and XRF (Figure 1) using 8 silicon drift detectors (SDD) in the TwinMic beamline [3] in Elettra Sincrotrone Trieste for the purpose of advancing the research on XRF topography.

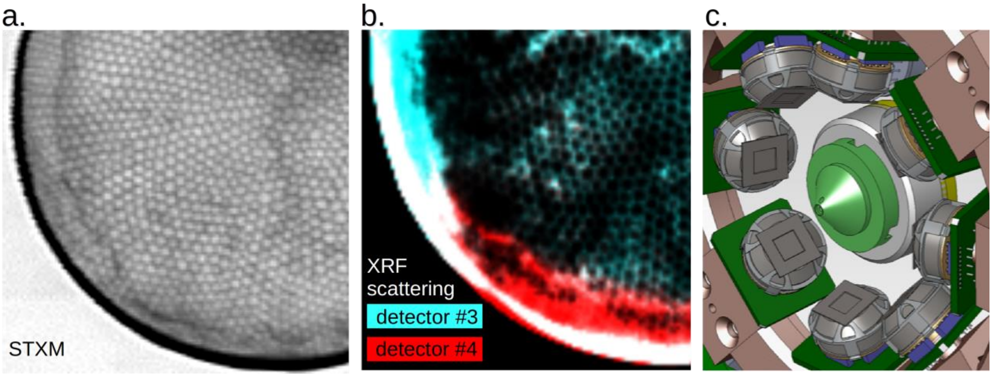

Fig.1 (a) STXM map of a portion of a diatom: 60 μm x 60 μm with 500 nm step size, 1450 eV incident photon energy. (b) XRF map of Scattering highlighting the detection difference from 2 of the 8 SDDs (c).

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Uptake and translocation of silver nanoparticles in *Lactuca sativa*: accumulation and ligand environment studies

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Silver nanoparticles (AgNPs) are among the most commercialized NPs due to their antibacterial properties. The wide use of AgNPs in industry and everyday life highly increases the possibility of AgNPs to enter environment and exert toxic effects on organisms in water and terrestrial ecosystems. Understanding of the uptake, accumulation, translocation and biotransformation of these emerging pollutants in plants is of great importance in assessing their toxicological impacts on food chain and consequentially animal and human health [1,2].

In this study, *Lactuca sativa* (lettuce) plants were cultivated, during 9 days under lab-controlled conditions, in Hoagland nutrient medium containing AgNPs with different (a) coatings: citrate, polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) or ionic silver (Ag(I)); (b) sizes: 75 nm, 100 nm (PVP-AgNPs) and (c) concentrations: 3, 5, 10 $mg \cdot L^{-1}$ (75 nm PVP-AgNPs or Ag(I)). After harvesting, root uptake and translocation of silver to the leaves was confirmed through total silver measurements by inductively coupled plasma optical emission spectroscopy after an acidic microwave digestion of plant samples. Results indicated that different AgNPs coatings do not affect their uptake by lettuce roots and further translocation to the leaves. Large-sized AgNPs (100 nm) are better absorbed by lettuce roots than small-sized AgNPs (75 nm), but they are less well transported to plant aerial parts. Additionally, it has been demonstrated that Ag(I) is better accumulated in lettuce tissues than AgNPs. The accumulation in roots increased progressively with the concentration of either silver chemical forms, but the translocation of silver to the leaves decreased at concentrations higher than 7 $mg \cdot L^{-1}$.

The possible biotransformation of AgNPs in *Lactuca sativa* root tissues, including speciation and ligand environment, was investigated by Ag K-edge X-ray absorption spectroscopy (XAS). The measurements were performed at BL22 (Claess) beamline of ALBA synchrotron in Spain on frozen hydrated plant samples. The signal of the 12 Ag neighbors in a NP is strongly prevailing in the spectra, with small contributions of organic ligands S and O (or N). Up to 20 % of Ag atoms are eluted from the NP, forming a thio-bond with root cell walls. The contribution of O is less well defined. Conversely, some NP signal is found also in the spectra of plants grown on Ag(I), indicating the reformation of NP in the root system.

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2D-Maps of Cu Paintings by Resonant Inelastic X-ray Scattering (RIXS) with Multivariate Methods

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Recent works have shown that the species of an element can be determined by inspecting the fine structure of the RIXS emission peaks [1,2]. One of the most important characteristics of RIXS, using SDD systems with low-resolution in energy, is the possibility of combining this tool with all of the experimental techniques and geometries associated to XRF spectroscopy. Combinations of this RIXS tool with total reflection, depth-profiling analysis using grazing incidence geometries and confocal setups have been already reported [3-6].

In this work, we present results of RIXS-2D maps in different samples containing Cu paints. The measurements were carried out at the XRF beamline @ Brazilian Synchrotron Light Laboratory (LNLS, Campinas). The samples were irradiated with photons having a fixed monochromatic energy just below the K absorption edge of copper. After a simple data processing, involving multivariate methods, the fine structure of the RIXS spectra show oscillation patterns that depend on the different Cu chemical states.

The studied samples are interesting since they present a rich contrast of compounds of the same element, being difficult to analyze using conventional/time-consuming spectroscopic techniques, as the absorption ones. Using this novel RIXS tool, we produced fast and reliable maps/images showing the different species of the element of interest, providing atomic environment information at micrometer level in a 2D regime.

Examples of applications of this RIXS tool for chemical state determinations in Cu paintings are presented and discussed.

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Experimental Methodology for Retrieving Chemical State Information from L lines by Resonant Inelastic X-Ray Scattering

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By way of Resonant Inelastic X-Ray Scattering (RIXS), also named X-ray Resonant Raman Scattering (RRS), the speciation of samples can be attained in a variety of experimental conditions, as total reflection, grazing incidence and even confocal setups [1-4]. Until now, this discrimination methodology had been applied only to K lines, i.e. for transitions from the L to the K internal shells. Because of this, there is a lack in knowledge about the sensitivity of the method for the discrimination of compounds by the analysis of L lines, i.e. for transitions from the M to the L atomic shells.

In this work, the first results of speciation of several element compounds using this novel RIXS tool are presented.

The measurements were performed at the Brazilian Synchrotron Light Source (LNLS, Campinas) in the D09B-XRF beamline using the typical 45°-45° geometry and an energy dispersive system. The incident beam energies were selected just beneath the different L absorption edges of the studied elements. Spectra were analyzed by two independent mathematical methods: fine structure deconvolution and Principal Component Analysis (PCA).

After the data processing using multivariate methods, the results show a clear discrimination of the different element compounds. The outcome is significant since this novel RIXS tool allowed observing different species of the studied elements by means of the inspection of the L lines. Basis and comparisons with the characterization power by the analysis of K lines by RIXS are discussed.

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Preliminary characterization of organic dyes towards NEXAFS experiments using a laser-produced plasma source

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NEXAFS measurements can be used to obtain information about the local geometry around the probed atom, such as oxidation state or inter-atomic distances. Thus, the correlation between the structure of a biological sample and its function can be investigated [1].

The absorption edges of the main constituents of biological samples (C, N, O) are located in the soft X-ray range. Soft X-ray radiation can be produced e.g. at large scale facilities like synchrotron radiation facilities and free electron lasers, where beamtime is limited. Laser-produced plasma (LPP) sources [2], as available at the Berlin Laboratory for innovative X-ray Technologies (BLiX), render NEXAFS measurements in the laboratory possible.

For NEXAFS measurements in transmission mode, sample preparation is crucial to obtain spectra that can be analyzed. The sample needs to be thin enough to obtain a sufficiently high signal after transmission, and thick enough for absorption features to manifest in the spectrum. Due to larger beam sizes and smaller brilliances at LPP sources, the sample being homogeneous is very important. Thin film fabrication through thermal evaporation was found to be a suitable method to prepare samples with the above-mentioned properties.

Before performing NEXAFS measurements at the BLiX LPP source, the samples must be characterized in order to determine if they meet the required specifications in terms of thickness and homogeneity. Therefore, preliminary measurements including nonlinear transmission (NLT) and absorption spectroscopy with ultraviolet and visible light (UV-VIS) have been performed. The results of these measurements are presented.

The sample systems investigated are thin films of eosin Y and pseudoisocyanine (PIC), respectively. PIC is a polymethine dye, which shows non-linear optical properties promising for future application e.g. in optical telecommunication [3]. Eosin Y is a derivative of the xanthene dye fluorescein, with numerous applications e.g. in histology. It is suitable to probe biological molecules due to its sensitivity to the physical environment [4].

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Synchrotron radiation total reflection X-ray fluorescence (SR-TXRF) and X-ray absorption near edge structure (XANES) of ovarian cyst fluid.

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Cancer is a worldwide public health problem. One of the most common gynecological malignancy, among the women, is the ovarian cancer. In the pathogenesis process, lots of factors play a role, including the metal content, the molecules content and the gene mutation. The elemental abnormalities in a various form of tumours were reported over the past decade [1]. The aim of this study was to investigate the elemental content and iron speciation of human cyst fluids.

In our investigation 5 samples, from different patients were analysed. The experiment were conducted at the IAEA XSpe end-station at X-ray Fluorescence beamline of Elettra Sincrotrone Trieste facility. The primary photon energy was set with use of Si(111) monochromator to 13 keV and the fluorescence radiation was detected with a SDD detector in total reflection geometry. The measurements were performed in vacuum ($2 \cdot 10^{-7}$ mbar).

The SR- TXRF technique revealed that elements such as Na, Mg, P, S, Cl, K, Ca, Mn, Fe, Cu, Zn and Se were present in all fluids analyzed. Using the collected spectra the values of the Method Detection Limit (MDL) were determined. As the standard for XANES $FeSO_4 \cdot 7H_2O$, $Fe_2(SO_4)_3 \cdot nH_2O$, hemoglobin and transferrin were used. The position of Fe K-edge suggests that cystic fluids and cancer tissue contain both chemical forms of iron (Fe^{2+} and Fe^{3+}). However a substantial is fraction of iron on the third oxidation state.

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X-ray Raman scattering as a novel probe to discriminate carbon-based compounds in ancient art and fossil materials

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Deciphering the chemical nature of carbon-based compounds in ancient materials although challenging is an essential source of information in many archaeological and paleontological studies [1,2]. Carbon is ubiquitous and occurs in a diversity of chemical forms. However, difficulties in the characterization and identification of organic carbon compounds are common both due to specificities of the material (e.g., alteration during time, fine scale association with inorganic phases, turbostraticity) and to experimental constraints (high absorbance across the electromagnetic spectrum). X-ray Raman scattering (XRS) recently proved very promising to probe carbon speciation in complex heterogeneous solid ancient samples [3]. In this hard X-ray inelastic scattering technique, a small fraction of the X-ray energy is transferred to the electrons by inelastic scattering, allowing to collect speciation signal for light elements in a nondestructive manner, in air, with bulk sensitivity, to provide information not compromised by surface contamination, thus overcoming important constraints in the characterization of ancient materials [3].

The potential of XRS will be demonstrated through the analysis of carbon-based artists' pigments, which are until today poorly understood due to their complex chemistry [4]. We determined the carbon speciation of a consistent set of modern and historical samples used in the arts. As an example, the sensitivity of XRS is high enough to distinguish carbon black pigments obtained by the burning or pyrolysis of gas or oil from fine charcoal. We also collected XRS-based carbon K-edge XANES on fossil samples that allow discussing their fossilization. By providing information on the degree of aromaticity, the signatures of oxidized COO groups, the presence of carbon bound with heteroatoms and turbostraticity, XRS appears as a novel powerful and convenient probe to discriminate carbon-based compounds in complex, heterogeneous samples, and could be further applied to a wide range of ancient and historic materials.

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RXES experiments using stochastic data from non-monochromatized XFEL SASE radiation

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At synchrotron radiation facilities resonant X-ray emission spectroscopy (RXES) is a widely used tool to probe the electronic structure of a sample using monochromatic X-rays and a high-energy resolution X-ray emission spectrometer. Indeed, RXES represents a combination of the X-ray absorption process, which reflects the unoccupied density of states (DOS), and the X-ray emission process, which allows characterizing the occupied DOS by monitoring specific X-ray emission lines. Thanks to the penetrating properties of hard X-rays, RXES allows performing in situ studies, without practical environmental restrictions on the sample, providing for example information about the occupied and unoccupied DOS of catalyst materials under working conditions [1,2].

In a pioneering experiment we demonstrated for the first time that RXES experiments can be performed at hard X-ray free electron laser (XFEL) facilities using non-monochromatized self-amplified spontaneous emission (SASE) pulses with photon energies in the vicinity of an absorption edge. The RXES maps, i.e., the dependence of the X-ray emission spectra on the energy of the incident X-ray photons, can be reconstructed using the spectra of the incident SASE pulses and of the emitted X-ray photons for only about 1200 XFEL pulses (10 seconds acquisition time at 120 Hz repetition rate). Both spectral distributions were recorded on a single-shot basis and with high-energy resolution. The stochastic incident photon energy and intensity distribution inherent to XFEL experiments is the key for a successful reconstruction of the RXES maps.

Our reconstruction methodology allows using the full pulse power while avoiding temporal broadening related to the monochromatization of the X-ray pulses [3] and finally to expand the range of spectroscopy techniques available at hard XFELs operated in the SASE mode. This aspect is not only of importance for the applications RXES has found at synchrotron facilities, but also to investigate the unique physics accessible only at XFELs like intensity-induced X-ray transparency, non-linear absorption mechanisms, electron relaxation and rearrangement processes.

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Iron accumulation in the aging retina: a synchrotron μ-XRF study

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One of the most prevalent and debilitating eye diseases is age-related macular degeneration (AMD), a condition that affects the central retina and choroid and can lead to loss of central vision. Metals essential to human biology include iron, copper and zinc and their homeostasis is crucial for the functioning of the retina. In particular, the role of iron metabolism in age related conditions of the retina has been the focus of a number of studies. In the work reported here, the levels and distribution of these elements have been studied in retinas from mice and non-human primates.

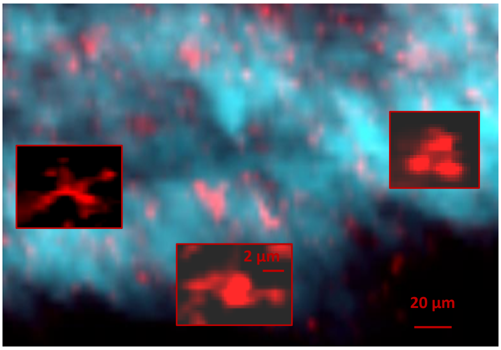

Fig.1: Iron (red) agglomerations against zinc (blue) in the choroid of an aged primate. Inserts are high resolution details of various Fe structures.

Synchrotron X-Ray Fluorescence micro and nano probe analysis has been employed to map the distribution of iron and other elements in the retina of young and aged animals of the two species. Initially the whole length of each retina was scanned at μm-level resolution (I18, Diamond Light Source) to get an overview of all elemental distributions. The elemental maps acquired revealed that the choroid is burdened with iron accumulations that do not follow the broadly homogenous distribution of the other elements (see Fig.1). The choroid iron levels range between the tens and low hundreds of ppms for the mice and in the several hundreds for the primates, while the content of the agglomerations is between three-fold and ten-fold that of the surrounding tissue iron content. The iron levels of these structures as well as their prevalence increase in the aged animals. Following these findings two higher resolution studies (B16, DLS and ID16B, ESRF) were performed to further investigate the iron agglomerations. These revealed that the structures start as particles of hundreds of nanometers diameter that tend to aggregate into larger structures of several microns.

In an effort to determine the nature of the iron deposits, size, structure and association with the other essential metals will be discussed. These results are a step forward in the understanding of the role of iron in the mechanism of AMD.

ESUO: The European Synchrotron and FEL User Organisation: Aims & Activities

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The European Synchrotron and free-electron laser (FEL) User Organisation (ESUO) established in 2010 [1] today represents about 30.000 users. We aim at representing the users from all European countries. Each country is represented within ESUO by one up to four national delegate(s), depending on the size of the user community in the respective country. ESUO's main objectives are (i) to promote an integrated approach throughout Europe for the use of European synchrotron and FEL facilities, (ii) to enable all European scientists to make use of the existing European synchrotron and FEL research infrastructures, solely based on scientific merit of their submitted proposals for beamtime requests, and this independently from the financial situation of the user (country), (iii) to facilitate open transnational access to European light sources through programmes of the European Union, (iv) to disseminate information about scientific opportunities and funding mechanisms for access to synchrotron and FEL facilities, and (v) to be a discussion and acting partner regarding the coordination of the synchrotron and FEL user activities within Europe.

In the past few years, ESUO has contributed to several joint activities in the frame of successfully completed European FP7 projects such as ELISA (March 2009 - August 2011) and CALIPSO (June 2012 - May 2015). Some past ESUO activities concern, amongst others:

- the user representation in e.g. the CALIPSO and BioStruct-X European projects by ESUO delegates;
- the contribution to the CALIPSOplus project application;
- the dissemination of ESUO activities by means of e.g. poster presentations and talks delivered at international conferences, specialized user meetings/workshops, and;
- several initiatives which have been attended to promote transnational access activities [3] and to favor the continuation of transnational user access to national facilities in Europe within the new European Framework Program Horizon 2020 [4].

Today, chance is given to ESUO to keep constructively acting for the users in the frame of joint networking activities being part of the HORIZON 2020 project CALIPSOplus [5] (May 2017 – April 2021, Grant Agreement No 730872) coordinated by Helmholtz-Zentrum Dresden-Rossendorf (HZDR). In the framework of CALIPSOplus, ESUO is contributing to project networking activities which are, amongst others, shown in the present contribution. With the aim to further prepare the future science at European synchrotron and FEL user facilities, ESUO is contributing to the League of European Accelerator-based Photon Sources (LEAPS) initiative [6].

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Magnesium-sulfur batteries studied by in-operando S K-edge RIXS and XAS spectroscopy

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Sulfur based batteries are considered as very attractive energy storage devices. In combination with alkali metals, sulfur forms electrochemical couples with much higher theoretical energy density compared to Li-ion batteries commonly available today. At the moment, the electrochemical couple with Li is most extensively studied. Even more promising is the electrochemical couple with Mg providing almost twofold higher volumetric energy density due to its ability to provide two electrons during oxidation. However, Mg-S batteries are still in the very early stage of research and development and the complex mechanism of sulfur conversion has been less extensively studied.

In this work, resonant inelastic X-ray scattering (RIXS) and XAS measurements at the sulfur K-edge performed in operando mode were used to study the mechanism of a Mg−S battery operation. Measurements were performed at ID26 beamline of the ESRF synchrotron using tender X-ray emission spectrometer [1]. Our measurements revealed very similar mechanism to the Li-S battery system. The electrochemical conversion of sulfur with magnesium proceeds through two well-defined plateaus, which correspond to the equilibrium between sulfur and Mg polysulfides (high-voltage plateau) and polysulfides and MgS (low-voltage plateau) [2].

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GILDED COPPER AND TUMBAGA BY THE MOCHE : A TEST OF THE INTERNAL RATIO METHOD

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A multilayered metal structure can be correctly interpreted, and the thickness of the various layers determined, by using energy-dispersive X-ray fluorescence (EDXRF)-analysis, and by dedicating a sophisticated quantitative study to the X-ray peaks [1].

An ideal test of this method was recently offered by the study of 15 spear throwers on gilded copper (Figure 1), and a necklace composed of 12 small heads, on tumbaga (poor gold subject to depletion gilding). These artifacts , from the Moche culture, north of Peru, about 300 A.D. were found in the filling of the pyramid's top platform, and in the tomb of the lady of Cao.

The gilding composition (or equivalent gilding in the case of tumbaga), was determined in the usual manner, while the thickness was determined from the ratios Cu(Kα/Kß) , Au(Lα/Lß) and Au-Lα/Cu-Kα. These ratios are altered with respect to thick sheet of same metals, and the difference depends on the gilding (or equivalent gilding) composition and thickness.

Results confirm the effectiveness of the method, but also highlights the related difficulties and uncertainties.

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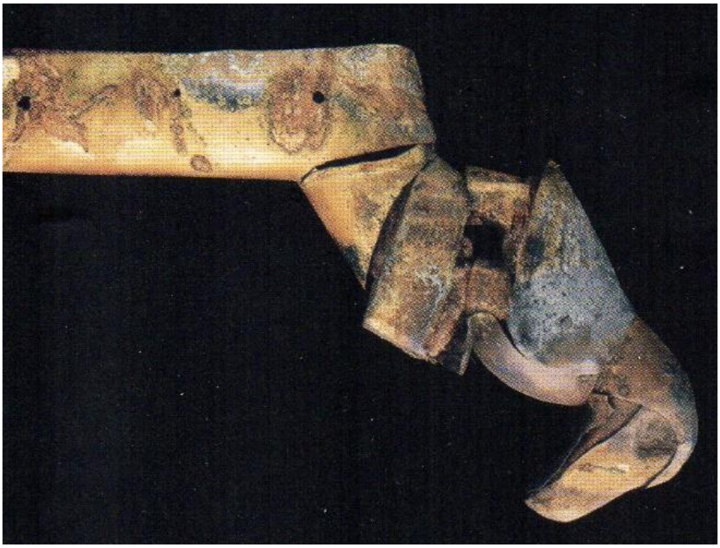

Figure 1 – Bird decoration at one end of a spear thrower on gilded copper.

STUDIES ON THE FAMOUS MOCHE “CABEZA DE MONO DORADA”

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A famous gold monkey head from the Moche culture (north of Peru, about 300 A.D.) was returned from U.S.A. to the government of Peru on December 8th, 2011. The head had been exhibited for years at the Museum of New Mexico in Santa Fe. It had been donated by private collector John Bourne, and was identified in 1998 as a Moche artifact by Peruvian archaeologist Walter Alva. Since 2012 , the monkey head is kept at the Peruvian Ministry of culture, located in the same building at the “museo de la nación“ in Lima, waiting for final destination. There it was analyzed by EDXRF-analysis and transmission measurements.

The beautiful monkey head measures 4.5 cm tall by about 7 cm wide and has a weight of 49 g. This indicates that the head is not on bulk gold, but made using a gold sheet. The nose and the eyes are composed of blue crystals, which could be turquoise or crysocolla the eyes, because of the presence of copper, and lapis lazuli the nose, because of the presence of calcium and iron. There is no evidence of welding except for the two ears, but no welding material was found.

On 9th and 16th of February 2018, the monkey head was studied with a portable equipment for energy-dispersive X-ray fluorescence analysis (Figure 1). Also transmission measurements were carried out, with the same equipment, to determine the gold sheet thickness.

Figure 1 – The monkey head during EDXRF-analysis

PORTABLE EDXRF-SCANNER FOR MAPPING ANCIENT GOLD AND SILVER ALLOYS

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In the last years, energy-dispersive X-ray fluorescence (EDXRF)-analysis of single areas often evolved into EDXRF-scanning, i.e. complete analysis of a sample . That happened in the field of medicine and biology [1,2], and in archaeometry, particularly for elemental mapping of paintings [3,4]. In these last cases, chemical elements are mapped, adding more complete information to the knowledge of the sample. In the case of biomedical samples, the X-ray source is generally a synchrotron, because of the low level of concentration of elements to be studied, while in the second case the source can be a X-ray tube, because of the high elemental concentration in the pigments. In this last case, the EDXRF-scanner can be easily transportable, or even portable.

A portable EDXRF-scanner is extremely useful in the field of archaeometry, not only to map paintings, but also to study metals and alloys, particularly when inhomogeneities, oxidations or soldering are present.

With this vision, several gold-silver nose ornaments were examined, from the tomb of the "lady of Cao", a prominent governor from the Moche culture, dated around 300 A.D.

A dedicated portable EDXRF-scanning spectrometer was therefore assembled, based on the following components :

-small-size X-ray tube, working at 50 kV and 100 µA maximum voltage and current; it must be properly filtered and collimated ;

-a Si-drift, collimated X-ray detector ;

-a x-y movable table with related software ;

-a dedicated software for analysis of data and imaging.

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Spectroscopic analysis of polychromatic sculptures belong to the cultural heritage of Extremadura (Spain).

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Several devices have been applied in order to characterize the polychromatic pigments used in diverse religious sculptures belonging to the cultural heritage of Extremadura (west of Spain). Firstly, two EDXRF portable devices were used. On one hand, a homemade assembled equipment [1-3] composed by an Ag-X-ray tube (ECLIPSE III, Amptek, 30kV and 100μA, maximum), and a Si-detector (XR-100CR, Amptek). On the other hand, a handheld spectrometer (S1 TITAN LE, Bruker) composed by an Rh tube up to 50kV and 100μA, and a Fast SDD detector. The measurements performed with these devices were carried out *in situ,* were the artworks were being restored. Apart from these non-destructive analyses, various samples with millimeter size were taken from some of the sculptures, embedded in polyester resins, and analyzed in an S-3600N (Hitachi) scanning electron microscope in the low vacuum mode with two different (SE and BSED) detectors in the central laboratories of the University of Extremadura.

Five artworks have been considered in this study: *Virgen del Valle* (ca. 13th cent.), *Peana of Virgen del Valle* (ca. second half 17th cent.), *Angel* (belonging to the *Peana*, and probably from the 17th or 18th cent.), *San Juanito* (18th cent.) and *Cristo del Perdón* (16th). Except the last two artworks whose realization are attribuited to the prestigious masters of wood carving Juan Martínez Montañés and Jorge Fernández Alemán, respectively, the rest of pieces are anonimous. The obtained results allowed the characterization of the different pigments used in their ellaboration, as well as the identification of several re-paints observed. Moreover, the SEM tecnhique applied to the millisamples allowed the determination of the deep of layers, and the distribution of the elements inside them.

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SEM/EDAX and optical microscopy study of an ancient cloth

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The analyses presented in this work were carried out on a piece of wool fabric in grey/brown colour, dating back to the XIII century and probably related to a particularly important garment coming from central Italy. The aim of this work was the study of the fibres' conservation, in order to identify both the chemical and physical deterioration phenomena that may have affected the fabric itself over the centuries.

The study was performed by means of optical and electron (SEM) microscopy, in order to get more information on the fibre structure, comparing the results obtained by the two techniques. Three different types of wool fibres were isolated from the fabric for the analyses, one in light colour, one in brown and one in dark.

SEM observation was coupled with an electronic microanalysis (EDAX) for elemental analysis, which highlighted a different chemical composition for the three types of fibres: in detail, the dark coloured fibre showed a percentage concentration of S, Al and Si slightly lower than the others, balanced by higher values of Mg, K and Ca. This result can be related to the greater degradation suffered by these fibres, as detected also in the morphological observations.

The deterioration processes of the fibres are linked to a series of factors such as their origin (vegetal/cellulosic or animal/protein), their chemical composition and their physical state, and clearly the environmental conditions in which they were stored. More specifically, wool fibres are more vulnerable to the attack of fungi and bacteria, enhancing the physical and chemical damage of the fibre due to non-optimal storage conditions, such as high temperature and humidity, which cause the loss of substance and the weakening of the structure.

In fact, very often artefacts of high historical-artistic value such as fabrics, clothes, garments, costumes, tapestries are stored in environments which are not suitable for preventing microbial biodegradation and the attack by Prokaryotes and Eukaryotic organisms. Therefore, providing useful information for a correct process of restoration and conservation can be fundamental in order to avoid the deterioration of precious objects and the loss of their historical and artistic testimony.

Use of Spectral Angle Mapper to extent macro-XRF results: first application on a Giotto's masterpiece

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The stratigraphic distribution of chemical elements, i.e. structure and composition, in art paintings reveals details about the technique and the creative process of the artist, as a great deal of information lies below the surface. MA-XRF (macro X-Ray Fluorescence) scanning provides fast, sensitive and reliable results, making the study of element distribution inside the different painting layers feasible without any sampling and in situ [1].

In the present work, we exploit ELIO MA-XRF spectrometer (XGLAB s.r.l.) to go deeper into Giotto's masterpiece God the Father with Angels (ca 1330, San Diego Museum of Art). Thanks to the extreme portability of this spectrometer, we performed the scanning during one closing day of the exhibition "Giotto, l'Italia" (Milan, 2015/2016) without moving the panel from the exhibition collocation. Since the scan of the whole panel was not compliant with the closure time, a selected area has been chosen for the XRF mapping; a set of 22 local XRF spots spread overall the painting was considered, too. The large number of acquired spectra was first analysed by applying the image processing algorithms typical of hyperspectral images [2].

We propose now a statistical supported classification of the local XRF spectra that become more meaningful if used as reference for map gathered data in the context of a Spectral Angle Mapper (SAM) analysis. SAM algorithm determines the spectral similarity by calculating the angle between the spectra treating them as vectors in a space with dimensionality equal to the number of bands [3]. Our data handling foresees a hybrid strategy that combines the mapping of a significant but limited area with various isolated XRF spectra spread all over the painting. The method has been previously tested on mono and multi-layer trials comprehending various combination of selected pigments. This approach allowed to extend mapping information and to argue the stratigraphy behind the isolated spectra. Even if SAM alone cannot exhaust the description of complex works of art, different short mapping sessions tailored on the SAM suggestions could constitute a good and feasible experimental strategy to gain a better scientific description of cultural valuable works in the full respect of their integrity.

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The vignetting effects in full-field X-ray fluorescence imaging system based on pinhole optics and gaseous detector

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The full field X-ray fluorescence (FF-XRF) imaging is a technique capable of analyzing the spatial distribution of elements in a sample. An alternative technique is the scanning macro-XRF method. Both techniques are powerful tools for non-destructive analysis of artworks including historical paintings. Technically, FF-XRF imaging is usually realized by coupling of a pinhole camera and a position sensitive and energy dispersive X-ray detector. The main advantages of the pinhole camera compared to a collimator are its simplicity and infinite depth of field, however it introduces vignetting. For a visible light pinhole camera one distinguishes natural vignetting following the cos^4 law) and mechanical vignetting due to finite thickness of the camera material. For an X-ray pinhole camera one has to take into account an additional component of vignetting due to absorption of X-rays in the air or other gas unless the setup is kept in vacuum. Moreover the matrix effects in the sample and dependence of detector efficiency on the X-ray incident angle have to be taken into account. The goal of this study is to work out an analytical model of vignetting effects for a FF-XRF apparatus using an X-ray pinhole camera. Complete quantitative characterization of the vignetting effects is a key step towards proper correction of the vignetting artefacts in recorded images. It also enables optimization of the excitation geometry for the given projection geometry and vice-versa. The elaborated analytical model has been confirmed by measurements of test samples and an example of vignetting correction is presented.

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Technological examination of Renaissance ceiling in The Great Council Room of Gdańsk City Hall using various X-ray techniques

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Scientific research can help in planning and implementing a conservation treatment or dating of works of art based on specific information such as pigment composition and their availability or chronology. When it comes to unique and valuable cultural heritage objects a special care has to be taken. X-ray analytical methods seem to be the best option since they are non-destructive and non-invasive.

The aim of this poster is to present the results of research conducted in Gdańsk City Hall – the former headquarters of the authorities of the city. With it's architecture and interior decorations in the style of Netherlandic Mannerism, it is one of the top heritage sites in Northern Europe.

Scientific imaging was conducted using digital X-ray radiography as well as different electromagnetic radiation ranges (VIS, UV, IR) to determine the overall state of preservation and to obtain information on the overpaintings and paint loss. These images provide accurate information about the surface and subsurface of the objects allowing the selection of measurement areas to be studied by physico-chemical methods. The next step was to determine the elemental composition of paint layers by X-ray fluorescence (XRF) analysis in order to obtain information about the pigments used by the artists. Additionally, the morphology and composition were examined by means of cross-sections, using scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDS). The complementary information obtained through the use of the SEM-EDS has permitted to acquire a comprehensive knowledge about the composition and structure of this important monument.

Using stationary and handheld X-ray fluorescence spectrometers is challenging when it comes to examination of three-dimensional objects, such as woodcarvings incorporated into ceiling construction. Therefore, capabilities of newly developed full-field XRF (FF-XRF) system [1] in analyzing this type of objects have been tested, using a wood carved phantom. New system is designed to simultaneously investigate 10×10 cm area. Application of pinhole camera, with the infinite depth of field allows one to investigate spatial objects. Presented studies show a potential of the FF-XRF in elemental analysis of three-dimensional heritage objects.

The research has been carried out within the project *National Centre for Cultural Heritage Science* co-funded by the Polish Ministry of Culture and National Heritage. The objects under examination belong to collection of the Historical Museum of the City of Gdańsk.

Part of this work was carried out thanks to the financial support of The National Centre for Research and Development within Applied Research Programme (project no. PBS3/A9/29/2015).

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Analysis of metallic objects from tomb of the 'Lady of Cao' by X-ray microtomagraphy and digital radiography

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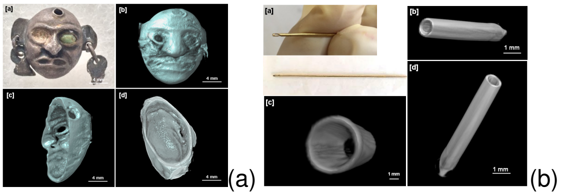
Investigative analyzes of metallic objects from the tomb of a queen of the Moche civilization, who lived around 100 to 300 AD in the northern coast of current Peru, known as Lady of Cao, have been carried out by researchers in the last four years using various techniques destructive [1]. Many of these objects found inside the tomb are jewelry produced using silver, copper and gold sheets.

The application of X-ray microtomography (mCT) [2] and X-ray digital radiography (DR) techniques using a portable system had the objective of obtaining more information on the structures of the objects studies, and thus, to obtain evidence of the production method used by Moche artisans. In this way, radiographic and microtomographic images were produced, and qualitative and quantitative analyzes were performed. In the analysis of a silver earring (Fig. 1a), the mCT images allowed to investigate its internal structure. It was identified not to be compact, but produced with a thickness of 300-400 microns.

In a gold needles (Fig. 1b), used in the manufacture of clothes by Moche, which believed to be completely filled in with gold, however it was identified to have a cylindrical form with wall thickness of 100-200 microns. The two applications of non-destructive X-ray techniques were satisfactory and fast to obtain more information about the production of these objects by the Moche civilization.



(a) (b)

Figure 1. Silver earring (a) and Gold needle (b) from the Moche tomb Lady of Cao and in the mCT.

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The full-field X-ray fluorescence imaging combined with the multivariate data analysis for the painting layers investigations

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In this work we present a new full-field XRF (FF-XRF) imaging system designed to safely examine large flat surfaces and spatial objects. Compared to the scanning macro-XRF systems, it offers a shorter measurement time while providing greater safety due to the elimination of fast motion close to the image surface. XRF photons from large area are simultaneously projected on the detector through a pinhole camera. The infinite depth of field of the pinhole camera allows one to investigate non-flat surfaces, which is not possible using any other system. Large data sets obtained in this technique, combined with chemometric and statistical approach constitute a powerful tool for nondestructive investigation of artworks.

Our system is equipped with two X-ray tubes and employs $10 \times 10\mathrm{cm}^2$ Gas Electron Multiplier (GEM) detector, custom developed Application Specific Integrated Circuits, and custom developed readout and data acquisition system [1, 2]. Moderate energy resolution of GEM detectors limits elemental selectivity of the system, however, in many applications, especially for initial fast screening of large area objects, the GEM based systems can be very useful. Research potential of the developed apparatus is greatly enhanced by the use of the multivariate data analysis methods, that allows quick separation of data carrying relevant information from those containing noise or point defects in detector.

The results of XRF mapping obtained with the new system, followed by application of decomposition algorithms used towards fast and automatic identification of pigments as well as distinction of similar areas are presented. The measurements were performed on several phantoms painted with different pigments.

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Textile metal analysis of the first Brazilian emperors' vestments

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Textile products were manufactured due to the development of spinning and weaving that began in ancient Egypt around 3400 B.C. Since this period these textile materials are become essential for everyday life in all societies and are used in clothes to environmental protection and warming. In some case they are adorned with threads from precious metals combined with the fibers to clothes decoration in order to create luxury fabrics for secular and religious elites indicating wealth and social status. During the last centuries (17th to 20th), kings and queens wore usually garments with metal threads to demonstrate power and sovereignty in different regions in the world, including Brazil (19th century).

In this work we report and discuss the results obtained in a multidisciplinary historical archaeological research performed in the remains of the first Emperor of Brazil, D. Pedro I and his first wife D. Leopoldina. Both were buried in the Imperial Chapel of the Independence Monument at São Paulo, Brazil where several physicochemical analytical methods were employed in the study of various materials of the remains. Textile metal materials were found in the both vestments and X-ray techniques such as Energy Dispersive X-Ray Fluorescence (EDXRF), Particle Induced X-Ray Emission (PIXE) and Scanning Electron Microscopy with X-ray fluorescence (SEM-EDX) were performed to better understand this kind of material. The textile material analyses show that gold, silver and copper were used as major elements in textile in concordance with historically textile metal reported by K. Simic et al [1]. The results show that the oldest metal textile found were composed of threads like stripes, cut from a hammered foil and directly incorporated in textile (Fig. 1a) used by the empress D. Leopoldina. The analyses of the vestment of the Emperor D. Pedro I (Fig. 1b) show that the technology evolved to production of combined textile metallic yarns and metal wires. These combined textile metallic yarn was made of metal stripes or just one spiral wrapped around the textile yarn, which represent the core, called ''srma" (metal thread wrapped around textile yarn).

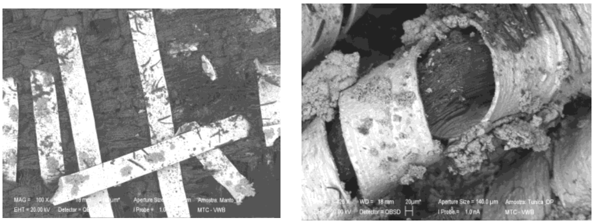

Figure 1: Backscatter images of two different types of the metal threads investigated by SEM-EDX: a) narrow stripes of the Empress clothing; b) combined textile metallic yarn (''srma") of the Emperor clothing.

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The use of handheld XRF supplemented with LA-QICP-MS in the analysis of composite silver artefacts – the case study of the late Roman Seuso Treasure

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The Seuso Treasure is one of the most significant silver hoards of Late Roman Imperial Age, dated to the 4th century AD. It consists of 14 large silver vessels used for dining and washing [1]. The major objectives of the archaeometric research performed on the treasure are the determination of the elemental composition of the objects, the mapping of their chemical homogeneity as well as the comparison and classification of the objects based on their chemical composition. Two platters (Seuso and Geometric Platters) of the treasure were already analysed [2]. In this study we focus on the composite silver objects (ewers, casket, *situlas*, and amphora) of the treasure. X-ray fluorescence, a widely used technique in the analysis of archaeological and historical metal objects, was applied to analyse them non-destructively as in the case of other late Roman silver finds [3, 4, 5]. The hXRF measurements were performed systematically along a pre-designed grid at several points, in contrast to other studies, in which objects were measured only at a few locations. In order to determine the bulk elemental composition of the vessels and to verify the hXRF results, metal samples taken from the different parts of the objects were analysed by using LA-QICP-MS.

The analysed objects consist of rather pure silver (88–98 wt% Ag). Copper was added intentionally as an alloying element. The copper content is not identical in the various parts of the composite objects. Bases, handles, thumb-pieces, and rims, which are more exposed to mechanical impact, have higher copper content in order to increase the strength and hardness of soft silver. Gold and lead contents of the objects indicate that not reused or remelted, but primary, cupelled silver was used for manufacturing the artefacts. The objects are classified into several groups based on their Bi/Pb ratios indicating the use of silver-lead raw materials with different Bi contents. The LA-QICP-MS measurements verified the results of the hXRF analyses. However, the effect of the corrosion can also be well traced, namely enrichment of silver and depletion of copper on the surface.

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Multi-analytical X-ray study of a pop art secco

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One of the most important pop art paintings was analysed. It is a large-sized secco painted in 1971 by the Hungarian artist, György Kemény with vibrant colours depicting the characteristic political and public figures and symbols of the era. This protected work of art covers the walls of the former servant's room of a downtown apartment in Budapest. The total size of this mural painting is 48.5 m^2. Different types of deterioration phenomena appeared on the surface of the painting and in the ground, due to many years of permanent environmental effects. Therefore, to save this valuable and unique work of art, thorough restoration and conservation became inevitable. Although there are some superficial contamination (dust, darkening, etc.), the colours are still in a quite good condition and are almost in their original state.

In order to support the restoration and conservation works, a detailed archaeometric study was performed. Our aims were to determine the typical materials of this period used by the artist, and to find the causes of the deterioration phenomena. The chemical composition of the paints was determined in situ, non-destructively, using a handheld X-ray fluorescence (hXRF) spectrometer. In addition, paint samples were analysed by polarized light microscopy, X-ray diffractometry (XRD), micro-X-ray diffractometry (micro-XRD), electron microprobe analysis (EPMA) and Fourier-transform infrared spectroscopy (FTIR).

The ground of the secco is an emulsion paint layer applied on the carrier lime mortar plaster. Coloured Wallkyd paints were used to make the secco. The inorganic components of the white (uncoloured) Wallkyd paint are calcite, rutile, talcum, and clinochlore, whereas the organic component is alkyd resin. Based on the hXRF and EPMA measurements, the colorants are lead and chromium in the yellow, chromium and copper in the green, copper and cobalt in the blue, and iron and manganese in the red colours. The phase composition of the colorants was also determined using micro-XRD analysis, for example the red is FeO and Mn2O3.

Based on the XRD results deteriorations (detachment, exfoliation) are due to the transformation of carbonates to gypsum in the ground. The growing gypsum crystallites distort the paint layer causing detachment and exfoliation. The gypsum crystallisation is induced by the watering from pipe cracking and sulphur-containing gases from the environment.

pXRF analysis and MA-XRF imaging of Mycenean Wall-Painting pigments from the Nestor's Palace at Pylos

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The excavated painted fragments of wall–paintings from the Mycenaean "Palace of Nestor" at Pylos, are characterized by their high artistic quality, their unusual iconographic variety and the distinct for that period use of tempera and secco techniques [1].

Systematic pXRF analyses revealed an enriched gamut of inorganic pigments with respect to the common Aegean "palette", including calcite, kaolinite and gypsum at white areas, different black pigments (iron-based, pyrolusite, charcoal black and bone black), red ochre or hematite for red areas presenting colors ranging from dark brown to orange, and pink, umbers for dark brown areas, goethite and Egyptian blue as unique pigments for yellow and blue colors, respectively, whereas an unusual diversity of green pigments (chrysocolla, malachite, atacamite or paratacamite) was also identified [2].

The present work aims to enhance the obtained pXRF results by adding quantitative information regarding the compositional profile of black and brown colored pictorial layers, rich in Mn and Fe. The quantification of pigments was based on a new analytical protocol developed on a synergistic application of XMI-MSIM Monte Carlo open source tool [3] and of the PyMca X-ray Fluorescence Toolkit [4]. The accurate simulation of all spectrum features, including analyte peaks and the Compton scattered tube radiation ensures internal consistency of the employed fundamental, set-up geometrical and hardware parameters. PyMca enables next the elemental analysis of the pictorial layer and under realistic assumptions the iterative estimation of its thickness.

In-situ MA-XRF imaging [5] was also applied on selected wall-painting fragments with visible and heavily deteriorated pictorial layers to uncover the lost polychromy and the figurative drawings or the decorative motifs. The improved capabilities of advanced XRF analytical approaches for the quantitative reconstruction and visualization of wall-painting pictorial layers are discussed and selected examples are demonstrated.

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Development of a multiwavelength XRD combined with EDXRF for cultural heritage in-situ analysis

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Energy Dispersive X-ray Diffraction (XRD) and X-ray Fluorescence (XRF) have shown to be powerful tools to analyze all kind of samples, and especially for the analysis of samples of cultural heritage, geological and archaeological interest [1–4]. Due to exclusive setups, XRD and XRF are used independently yielding results not necessarily of the same spot and sometimes difficult to be combined. Ideally XRD and XRF should be performed together at the same spot. In this work we tested a prove of concept using a standard X-ray source (Cu rotate X-ray tube - Rigaku) and a proxy of an imaging X-ray detector employing a single detector (Si-PIN Amptek, 139eV@5.98keV, collimated to 1 mm diameter) and mounted on a computer controlled XY stage.The main advantage of the method is that no sample preparation is required and the XRF-XRD analyses are done simultaneously on the same spot. The time consuming is still large due to multiple single spectra acquisition (40x20). PyMCA [5] software was used to image the XRF signal, generating an homogeneous image, and the XRD signal, represented by bands in the hiperspectrum, similar to a Laue diffractogram. The next step is extracting the d-spacings compatible with the XRF analysis and possible quantitative results.

The XY stage as well the data acquisition software (written in Labview) were designed and executed by the technical staff of the laboratory LAMFI-USP (Laboratory for Ion Beam Analysis of Materials). The measurements were done at LabCr-USP (Crystallography Laboratory).

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Determination of gold leaf thickness using X- Ray Fluorescence and Monte Carlo simulation

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X Ray Fluorescence (XRF) spectrometry is one of the most powerful tools in studies of material characterization of Cultural Heritage, due to user-friendly features, quick qualitative interpretation of the spectra and available portable instrumentation. However, the materials analyzed are seldom homogeneous and are mostly stratigraphic with more or less complexity. This way, Monte Carlo (MC) simulation methods have proven suitable for the evaluation of the spectra and interpretation of the composition of each layer.

In this work, we present the simulation of a portable XRF system using MC methods and its application to the determination of the thickness standard reference gold leaf foils (1, 2 and 2.5 µm thick).

This methodology was compared with the analytical thickness determination using two similar spectral evaluation methodologies. On the one hand, we used an approach based on self-attenuation of gold characteristic lines in the gold layer by comparing the intensity ratios of the Lα and Lβ lines of gold in the XRF spectrum. Another approach is using the selective attenuation that the different lines of a given element of an under-layer undergo in a gilded layer [1]. The obtained results showed that both MC and analytical methodologies are very promising in the analysis evaluation of gilded artworks without requiring the removal of a sample.

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Application of multianalytical technique for the characterisation of materials on the glaze colour layer

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This paper presents an investigation into the wood artworks created by one of the most famous artist Monogrammist IP of the beginning of 16th century. Material investigation of the small relief by *The Visitation of the Virgin* (Passau, after 1521, inv. no. P 5197) and the carving of *Christ Saviour from Death* that is central part of *Zlíchov Altarpiece* (Passau, before 1526, inv. no. P 4673) from the collections of the National Gallery in Prague have led to the understanding of the historical techniques used in the medieval art workshops. On the surface of these carvings there were preserved original surface finishes consisting of a thin glaze layer that was directly applied on the wood. The thin glaze colour layers could be complex mixtures of pigments, dyes and binder medium [1, 2]. The chemical characterisation of these materials from the colour surface layers and the structure of wooden carvings were performed combining a range of analytical techniques. To achieve appropriate results, when examining materials of the artworks, the combination of the non-invasive or non-destructive technique is often necessary. The initial investigation of materials was realised by means of portable X-ray fluorescence analyser (XRF) and for characterisation of the internal structure of wood there was the non-invasive investigation using methods of X-ray imaging and computer tomography (CT) carried out. The samples were taken from the carving *Christ Saviour from Death* and analysed using optical microscopy (OM), scanning electron microscopy coupled with energy dispersive x-ray spectroscopy (SEM-EDX), micro-Raman spectroscopy (μ-RS) and subsequently investigated by gas chromatography-mass spectrometry (GC-MS) to detect particular binding medium. The CT investigation was realized utilizing patented scanner Toratom [3]. Tomographic reconstruction made possible to identify wood types, to observe the internal structure of the artwork in details, to study the technological procedures, to identify earlier reparations, additions and damaging. Combining XRF and GC-MS methods was crucial to identify particular pigments and binder medium in the thin glaze surface layer. The elemental characterisation of the earth pigments was confirmed by XRF. GC-MS analysis proved the presence of proteinaceous binder, which was specified according to the profile of amino acids as animal glue.

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ANALYSIS OF COINS RECOINED FOR “960 RÉIS” BY XRF AND SEM-EDS

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The analysis of archaeological and museological objects provides valuable information on the manufacturing techniques used by the ancient artisans, commercial routes explored by our ancestors and on the state of conservation of objects. Due to the rarity, fragility, and reduced size of some of these objects, the problems associated with their study are accentuated by the need to perform nondestructive analyzes. In this situation the majority of cases, gold and silver objects, coins and other kinds of jewelery are found.

This paper demonstrates the application of a number of analytical techniques on collections of 960 reis silver coins. The history of these coins combines the history of the arrival of the Portuguese crown to Brazil in 1808, when the prince regent, D. João, felt Portugal between the Continental blockade decreed by Napoleon in 1806 and the impossibility of cutting trade relations with England, the Portuguese court moved to Brazil and determine that all hispanic coins of 8 "reales" that circulated in the Brazil were recoined with a value of "960 réis". The silver coins were chosen for analysis because of their large amount and lack of scientific information on their constitution and origin, thus helping the museologists in the creation of a database of analytical results of the coins, containing probable origin and elemental composition.

The XRFand SEM-EDS in associated with Principal Component Analysis (PCA) provided answers to the possible trace element characteristic of coins, responsible for the specific chemical signature of each silver mine. This paper still provides new information on the inside of the "960 réis" coins as well as information on the silver trade as a global during in the 16th, 17th and 18th centuries.

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Application of the X-Ray Fluorescence Analysis to determine the composition of samples and to the detection of metals in cultural assets

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The X-Ray Fluorescence Analysis (XRFA) is a method of analyzing materials widely used for more than fifty years for different studies in archaeology and artistic heritage among other fields [1]. In comparison to other composition analysis methods, XRFA is less time-consuming. A spectrum with well-defined peaks can be obtained after some minutes of irradiation.

The application of XRFA to determine the composition of different samples as well as to the detection of metals in cultural assets is highly interesting and it has been proposed to students of Energy Engineering of the Universitat Politècnica de València (UPV) for their Master Thesis.

A qualitative analysis, which is immediate applying XRFA, permits to detect the presence of metals in samples, as well as to identify them. For a quantitative analysis, it is necessary to have the adequate standards, constituted by certified pieces of metals and alloys.

In this paper, the XRFA has been applied in two fields. First, to analyze roman denarii from different periods of both Roman Republic and Empire. A first idea of the historical period in which a coin was minted can be acquired by comparison of the measured composition to some published studies [2, 3]. Secondly, to determine the presence of various metallic substances and pigments responsible for the coloring of both paints and pyrotechnic powder. Results of the analysis have been compared with the information found in the literature [4, 5].

It was verified the devaluation of the roman denarius since last years of the Roman Republic till the period of Septimius Severus as Rome Emperor. The silver contents decreased while copper replaced it.

On the other hand, the assembly arranged in the laboratory (X-ray tube and Si detector with the associated software) is not able to detect all elements of the periodic table, in particular the organic materials and some heavy metals. However, this limitation did not prevent the detection of the most important pigments such as those containing Ti, Zn, or Fe and fillers (Ca and Ba) of the paint samples analyzed. As well, some metals, such as Ba and Sr, responsible for the coloring of the pyrotechnic powder samples analyzed have been found.

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Analysis of copper corrosion in binary bronze alloys by XANES and complementary spectroscopic methods

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For efficient preservation of cultural heritage objects, a thorough understanding of corrosion of indoor bronze pieces of art, especially clarification of corrosion phenomena occurring on bronze exposed to different corrosive media, is of high importance [1,2].

In this work, two binary bronze alloys prepared by magnetron sputtering deposition were investigated using several analytical methods in order to clarify the growth of corrosion products on bronze. Bronzes were exposed to two corrosive media simulating marine and urban corrosion environment for 15 days. The main goal was then to monitor corrosion phenomena (formation of Cu (I) and Cu (II) species) in the first and the most pronounced period of corrosion layer formation in duration of two weeks. For this purpose the X-ray absorption near edge structure (XANES) measurements were performed at the XAFS beam-line of the Elettra synchrotron.

The position and intensity shift of the XANES spectra components during the corrosion buildup clearly discriminate Cu(0), Cu (I) and Cu (II), thus providing the copper oxidation states in the corrosion layers as a function of the exposure duration of bronze to corrosion media.

Furthermore, ion beam analysis (PIXE and RBS) was used to define the general stoichiometry and thickness of the sample layers, whereas FT-IR and Raman measurements were employed to find out if beside copper I and II, other oxides were present in the corrosion layer as well.

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Comparative study of illuminated Moroccan paper manuscripts from the eighteenth century: non-invasive analysis by X-ray Diffraction (XRD) and Energy Dispersive X-ray Fluorescence (EDXRF)

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Illuminated Moroccan manuscripts are not only objects of fine art but also certificates of human history; they are a valuable work of art, with an inherent artistic value deserving dedicated studies and care [1]. A wide range of analytical methods can be applied to examine illuminated manuscripts for the characterisation and identification of their constituting materials [2].

The characterization of these materials (cellulosic support, filler, inks, and pigments) can help to shed light on different aspects concerning the authenticity, restoration, conservation and dating of historical manuscripts [3]. The EDXRF technique allows elemental analyses (qualitative and quantitative) that are necessary in the process of inorganic phase identification. XRD gives information about compounds present in a crystalline form [2].

Despite the high artistic value of the manuscripts stored in the Royal Moroccan Library of Rabat, no scientific study has been carried out on this universal heritage. Hence, this work is the first investigation of this heritage. Five illuminated manuscripts dating the 18th centuries have been analyzed using the combination of EDXRF and XRD. EDXRF results permit to compare the elemental composition of different inks and pigments used for their calligraphy, while XRD allows to assess their state of conservation by comparing the crystallinity index of the different paper samples.

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Usefulness of a dual macro and micro energy dispersive X-Ray fluorescence spectrometer to develop quantitative methodologies for historic mortars and related materials characterization

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Wavelength Dispersive X-ray fluorescence (WDXRF) spectrometry has been widely used for elemental quantification of mortars and cements. In this kind of instruments, samples are usually prepared as pellets or fused beads and the whole volume of sample is measured at once. In this work, the usefulness of a dual Energy Dispersive X-ray fluorescence spectrometer (EDXRF), working at two lateral resolutions (1 mm and 25 µm) for macro and micro-analysis respectively, to develop quantitative methods for the elemental characterization of mortars and concretes is demonstrated. A crucial step before developing any quantitative method with this kind of spectrometers is to verify the homogeneity of the standards at these two lateral resolutions. This new EDXRF quantitative method also demonstrated the importance of matrix effects in the accuracy of the results being necessary to use Certified Reference Materials (CRM) as standards. The use of standards trying to reproduce the matrix by pure compounds mixing turned out to be not accurate enough, however, this work shows that this calibration could be an alternative to obtain quantitative results for trace elements not usually certificate in the CRMs. The results obtained with the ED-XRF quantitative method were compared with the ones obtained with two WDXRF quantitative methods employing two different sample preparation strategies (pellets and fused beads). The selected EDXRF and both WDXRF quantitative methods were applied to the analysis of real historic mortars. The accuracy of the EDXRF results turn out to be similar to the one achieved by WDXRF, except for the lightest elements (Na and Mg). The results described in this work proved that µ-EDXRF spectrometers can be used not only for acquiring high resolution elemental map distributions, but also to perform accurate quantitative studies avoiding the use of more sophisticated WDXRF systems or the acid extraction/alkaline fusion required as destructive pretreatment in Inductively Coupled Plasma Mass Spectrometry based procedures.

Application of XRF spectroscopy to study differentiation between fragments of potteries found in a same archaeological site in Algeria

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Non-destructive techniques for the analysis of the components of a sample are very useful; indeed, the identification of their constituent materials provides valuable and essential information in many related fields. Historical pieces are unique and have often gone through centuries, even millennia, making them extremely fragile. Their handling must be done with great skill. All analyzes must be non-destructive and ensure that no irreparable damage will be done to these objects. X-ray fluorescence analysis is an appropriate technique for these types of parts and objects. To illustrate the use of this method of analysis, concrete examples of studies of archaeological objects such as fragments of pottery that have been exploited to better introduce this field of study. In this presentation, we will present an analysis of the fragments of pottery dating from the Middle Ages that we analyzed with the portable XRF, we deduced the majority and minority components. Thanks to the multi-varied analysis, we were able to classify the shards of pottery as a family without knowing the initial shape of the latter. These methods can be a crucial tool for archaeologists in the field to differentiate the different periods and the culture present on the site without having the complete pottery (simple small fragments are enough).

Analytical characterization of 3D confocal macro X-ray fluorescence spectrometer

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A new 3D confocal macro XRF (CM-XRF) spectrometer was designed and built for macro (1-0.5 mm) analysis of elementary composition of surface or depth layers of solid objects with non-regular spatial form [1]. The CM-XRF spectrometer was constructed on the mechanical frame of a commercial 3D printer which equipment carries the SD detector and the low-powered air-cooled X-ray tube. Solid samples can be mounted on stage belonging to the 3D printer, allowing to perform linear horizontal scanning on the sample within 20 cm lengths. The best spatial precision of the positioning of the mechanical stages (x-y-z) of the 3D printer is 5 μm with step-size of 100 μm [2]. The minimum value of the achieved diameter of the focal spot of the confocal measuring arrangement was about 480 μm. The collimator systems for both excitation and secondary X-ray beams were planned on the basis of Monte Carlo simulation, performed by MCNP6 software package in order to create a confocal macro measuring set-up. The measuring spot of the excitation and secondary X-ray on the sample surface is positioned by using two laser beam and a digital microscope. Analytical capability and the optimized resolution of the CM-XRF spectrometer were determined in (x-y-z) directions. Some analytical applications of this CM-XRF spectrometer will be presented.

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Rare Earth Analysis by 3D-Printed XRF

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Recently, 3D printing products are investigated for assembling X-ray analytical devices [1-2]. Kyoto University group has assembled X-ray fluorescence (XRF) spectrometers [3] and made some details of optics by a commercial 3D printer. In the present work, we study an applicability of the 3D-printed XRF spectrometer (Fig.1) for Rare Earth Elements (REEs) analysis. Using standard solution materials, 10 μg of each element such La, Ce, Pr, Nd, Tb, Dy, Er, Yb and Y, was prepared to dry on polyester flat. We determined ng level (1 ppm) REEs at 100 mW X-ray tube power, and Fig.2 shows compared XRF spectra of the REEs samples.

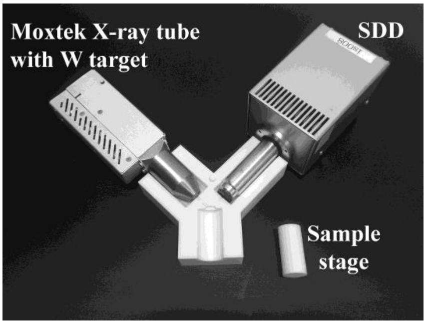

Fig.1. 3D-printed XRF spectrometer.

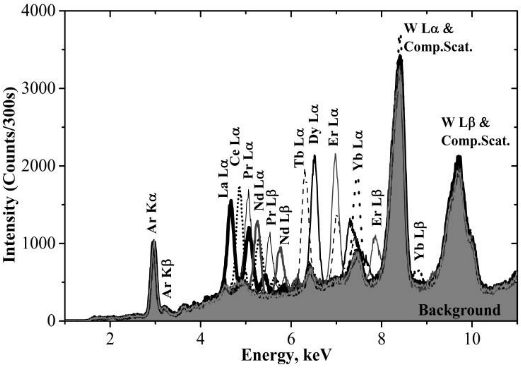

Fig.2. XRF spectra of REEs.

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Quantitative Analysis of Portable Polarized XRF

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A field of small X-ray instrument is moving towards a high sensitivity, three-axial, compact and simple operation [1-3]. Our group [4-5] assembled a low power three-dimensional X-ray fluorescence (XRF) spectrometer (Fig.1). In the present study, we evaluates analytical potential of the portable polarized XRF for elemental quantitative analysis. Under vanadium measurements, its detection limit was determined 29 ppm at 0.1 W and was improved to 1.6 ppm at 4.5 W of X-ray tube. A calibration curve of vanadium concentration is shown in Fig.2.

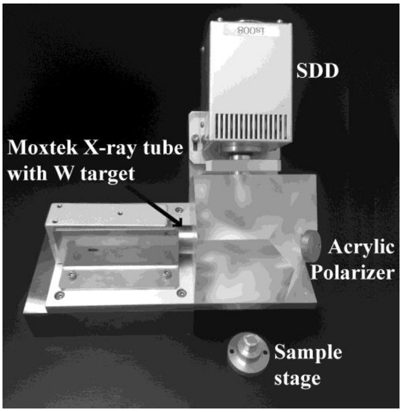

Fig.1. The polarized XRF spectrometer.

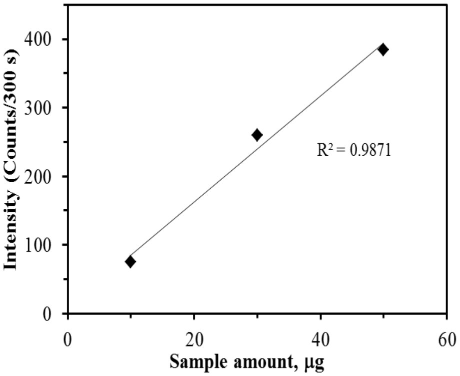

Fig.2. Calibration curve of vanadium.

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Performance assessment of portable XRF for measuring K and Rb in lithiniferous rocks

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With the latest emerging electric vehicle market and solar storage sector, the demand for rechargeable batteries has turned the focus of exploration and mining companies to metals such as lithium (Li) [1]. Techniques that provide the ability to collect in situ real-time multi-element geochemical data such as portable X-ray fluorescence (XRF) and portable Laser Induced Breakdown Spectroscopy (LIBS) are crucial to allow fast quantitative mineralogical screening and on-site decisions [2, 3].

However, XRF technique does not detect Li as it is a light element ($Z=3$), and, at low atomic numbers, the contribution of the X-ray fluorescence process is very low compared to the Auger process generated in the analytic material. Therefore, to use XRF for Li exploration, other target elements have to be used as proxy. The so-called path finder elements, give indirect information about Li content, while other elements give details about the alteration stage of the rock, that can result in a reduction of the concentration of Li to < 0.1 %, and deem the spot ineffective for extraction intended to battery use.

In this work, the performance of a portable XRF (Oxford Instruments X-MET7500) was assessed for measuring Rb, a pathfinder for Li, and K, a key element for determining the rock alteration stage. Several (n=15) powdered lithiniferous rocks were analysed, from which there was schists, pegmatites and aplite-pegmatites. These samples were purchased to LNEG (National Laboratory of Geology and Energy) and were previously analysed by a certified laboratory that reported Li concentrations measured by Inductively Coupled Plasma Optical Emission; K concentrations measured by Atomic Absorption Spectrometry; and Rb concentrations measured by XRF.

The bias in the measured values ranged from less than 10% to 50% (in rocks with K concentrations of around 1.1 %). Nonetheless, results showed a good linear correlation between the concentration measured values and the expected values, both for Rb and K. Correlation was also studied between the expected values and the area of the peaks detected for each element.

Using a prototype LIBS instrument that was recently developed for mining applications with quantification based on an artificial intelligence algorithm [4], relative concentrations of Li, K and Rb were measured and the results were considered fit for purpose. This is part of a preliminary study to enable the construction of the LIBS spectra knowledge data base to improve quantification methods in this type of systems.

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Study of Glass Reinforced Polyester Sculptures by Handheld XRF Spectrometer

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In the early 1960s, modern polymeric materials began to penetrate into the fine art in a great scale. Globally, polymeric materials began to particularly assert themselves in the arts in the second half of the 1960s. This is evidenced by contemporary art exhibitions in Europe and USA, where polymeric materials were used for most of the works. Artists begun to prefer mainly epoxy and polyester resins both for casted and laminated sculptures [1-3]. Artists in the former Czechoslovakia also captured this worldwide trend. During 1960s-70s, many significant outdoor sculptures have been created using mainly unsaturated polyester resins [4]. Unfortunately, many sculptures have not survived until nowadays. Only about 30 outdoor laminated sculptures can be found in the current Czech Republic. Moreover, many of them are in bad condition.

In the case of unsaturated polyester resins, the addition of a suitable catalyst leads to the formation of three-dimensional network of chemical bonds. In former Czechoslovakia in the early 1960s, only few catalysts worked at ambient temperature without an accelerator [5]. The common system included an accessible peroxide based catalyst and accelerator, which allowed to work at ambient temperature. A cobalt or vanadium based accelerators were optimal for the good quality of products. The normal amount of accelerator was hundreds of ppm [6]. Therefore, the aim of this work is to verify the possibility of the detection of Co or V in laminated polyester outdoor sculptures by a handheld XRF spectrometer and to find out if the specified amount of accelerator was added. For this reason, many samples with different content of Co accelerator and other fillers were prepared and tested by the handheld XRF spectrometer. The calibration for the content of Co in polyester samples was made and tested on real outdoor sculptures. It was shown that polyester and epoxide sculptures can be distinguish by fast and easy XRF analysis.

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10 Wednesday program

	Marmorna Hall 1	Marmorna Hall 2
	Chair: A. Karydas	
9:00	Invited: **X-ray Raman spectroscopy** *S. Huotari* (p. 219)	
9:30	Invited: **Evaluation of large x-ray spectral datasets from macro-scanning XRF** *P. Van Espen* (p. 220)	
	Session VI: SYNCHROTRON XRS, XAFS, HIGH RESOLUTION XES, AND RIXS Chair: A. Karydas	Session VII: XRS APPLICATIONS IN ART AND CULTURAL HERITAGE Chair: R. Cesareo
10:00	**XAS and RIXS spectroscopy of methanol** *F. Gelmukhanov* (p. 221)	**Reflection and Transmission mode MA-XRPD imaging: a comparison** *K. Janssens* (p. 227)
10:15	**Unveiling bonding schemes of nickel atoms at a Ni-MoS$_2$ metallic contact via microregional XAS** *W. Cao* (p. 222)	**A mobile Multi-Technique X-Ray scanner for a Real-time 2D and 3D Elemental Imaging of Artworks** *F. P. Romano* (p. 228)
10:30	Coffee Break	
11:00	**Operando XAS analysis of CuO/SiO$_2$ and CuO/CeO$_2$ catalysts** *I. Arčon* (p. 223)	**Study of two large dimension Murillo's paintings by means of Macro X-ray fluorescence (MA-XRF) imaging, point XRF analysis and stratigraphic studies** *A. Križnar* (p. 229)
11:15	**XAFS@BAMline: More than just Absorption** *S. Witte* (p. 224)	**Advantages and disadvantages XRF when applied to the investigation of cultural heritage objects** *A. Klisińska-Kopacz* (p. 230)
11:30	**X-ray fluorescence spectrometry beamline at Elettra Sincrotrone Trieste** *M. Czyzycki* (p. 225)	**Real-Time MAXRF Imaging of Egyptian Painted Wooden Coffers from the Tomb of Kha and Merit (1400 BC) at the Egyptian Museum in Torino** *C. Caliri* (p. 231)
11:45	**Characterization of titanium oxide nanoparticles in sludge from wastewater treatment plants from Mexico** *J. Reyes-Herrera* (p. 226)	**The Barberini harp: diagnostic investigations** *G. Marghella* (p. 232)
12:00	Lunch Break	
13:00	Conference Excursion	

X-ray Raman spectroscopy

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Non-resonant inelastic x-ray scattering from core-electron excitations is called x-ray Raman scattering (XRS – not to be confused in this context with x-ray spectroscopy in general). The process and information obtained from it is similar to that obtained by X-ray absorption spectroscopy (XAS) as well as by electron energy loss spectroscopy (EELS).

Soft-x-ray RIXS or XAS studies may sometimes encounter difficulties in certain cases when information from the bulk of materials, from buried systems is needed, or from samples that not compatible with vacuum. XRS spectroscopy offers alternative possibilities to study such cases. XRS lifts all constraints on the sample environment inherent to soft x-ray studies, and offers access to bulk-sensitive information on solids, liquids and gases as well as systems in enclosed sample environments such as high-pressure cells. For example, the microscopic structure of water within the supercritical regime has been recently studied using the oxygen K-edge excitation spectra measured by XRS, yielding new information on the hydrogen-bond network of water in extreme conditions [1]. Another important feature of XRS is that it allows for other than dipole transitions to be studied, thanks to a practically unlimited range of momentum transfer offered by hard x-rays. These higher order multipole excitations can yield novel information on the electronic structure [2], not accessible by many other spectroscopies. The availability of XRS instruments at third generation synchrotron radiation sources has made highly accurate XRS measurements possible. XRS can be even used as a contrast mechanism in three-dimensional X-ray imaging [3]. New beamline is now available for XRS studies at the European Synchrotron Radiation Facility [4,5]. The capabilities of XRS and recent examples of novel studies allowed by it will be reviewed.

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Evaluation of large x-ray spectral datasets from macro scanning XRF

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Scanning x-ray fluorescence with a submillimeter beam has proven to be a very valuable technique for investigating art objects, especially paintings. Information about the creation process, authenticity and previous restorations are readily obtained. New developments such as brighter sources and faster detectors make it possible to scan large areas of paintings in a reasonable amount of time[1].

Figure 1 shows the Pb Lα image of the painting "Venus Frigida" (P.P. Rubens, 1614). The scanning[2] of this masterpiece of 1850×1450 points resulted in ≈ 2.7 million spectra to be analysed. Storage, retrieval and more importantly evaluations of such large spectral datasets are a serious problem. Even if we spent only 0.2s on each spectrum, it would take us one week, 24 hours a day, to process the entire dataset.

Figure 1: Pb Lα image of P.P. Rubens "Venus Frigida", 1850×1450 pixels.

Just as people had problems storing and analysing tens of spectra with the first PC's 30 years ago we are again in the same situation! Some of the old solutions such as spectral compression might again become handy. Also the discussion between linear and non-linear methods of spectrum fitting is again relevant.

The spectrum evaluation process is reviewed in this context. What are limitations and pitfalls of the various linear and non-linear methods? A method called "hybrid fitting" will be introduced, basically solving the time problem while maintaining most of the benefits of the optimal, but slow, non-linear method. This method has been implemented in the software package bAxil.

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XAS and RIXS spectroscopy of methanol

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We overview our recent results in studies of X-ray absorption (XAS) and resonant inelastic X-ray scattering (RIXS) of gas phase and liquid methanol. The electronic transitions are studied with complementary computational methods including strict and extended second-order algebraic diagrammatic construction (ADC(2) and ADC(2)-x), restricted active space second-order perturbation theory (RASPT2), and time-dependent density functional theory (TDDFT)—providing a complete assignment of the near oxygen K-edge XAS. We show that multimode nuclear dynamics is of crucial importance for explaining the available experimental XAS and RIXS spectra. Multimode nuclear motions was considered in a developed mixed representation where dissociative states and highly excited vibrational modes are accurately treated with a time-dependent wave packet technique [1,2] while the remaining active vibrational modes are described using Franck–Condon amplitudes. Particular attention is paid to the polarization dependence of RIXS and the effects of the isotope substitution on the RIXS profile in the case of dissociative core-excited states. Our approach predicts the splitting of the 2a″ RIXS peak to be due to an interplay between molecular and atomic-like features arising in the course of transitions between dissociative core- and valence-excited states. It is shown the dynamical nature of the splitting of the 2a″ peak in RIXS of liquid methanol near pre-edge core excitation. The theoretical results are in good agreement with available experimental data.

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Unveiling bonding schemes of nickel atoms at a Ni-MoS$_2$ metallic contact via microregional XAS

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One of the key blockage for wide applications of the inorganic layered crystals (ILCs) stems from uncertain metal-semiconductor (M/S) contact modes, despite the ILCs' promising roles in future electronics, optics, and catalysis [1,2]. Reliable determination of M/S contact down to nanometer scale requires simultaneously microscopic and spectroscopic powers, yet, out of most authentic characterization abilities.

Herein, we report on an XAS study via X-ray photoemission electron microscopy (XPEEM) to evaluate the bonding mechanism of Ni-MoS$_2$ metallic contacts. By using the energy tunable synchrotron radiation photons as the incident light source, the electron microscope is empowered with the XAS measurements at specific microregions of the M/S joint [3]. Figure 1(a) is a typical XPEEM view of Ni-MoS$_2$ composite synthesized by ultrasonic assisted wet method [4]. A small region of interest is marked in the figure. By tuning incident photon energies from 845 eV to 875 eV, the XAS at Ni L$_{2,3}$ edges were obtained from this region (Fig. 1b). Besides the primary Ni 2$p_{3/2}$ and 2$p_{1/2}$ features, a significant peak emerges at 861 eV. The unexpected peak is out of the energy region due to chemical shift, and is ascribed to chemical bonding between Ni and S atoms but subjected to a quenched space [5]. The bonding between N-S contributes to metallization of the ILC part and results in a reliable metallic M/S contact [4].

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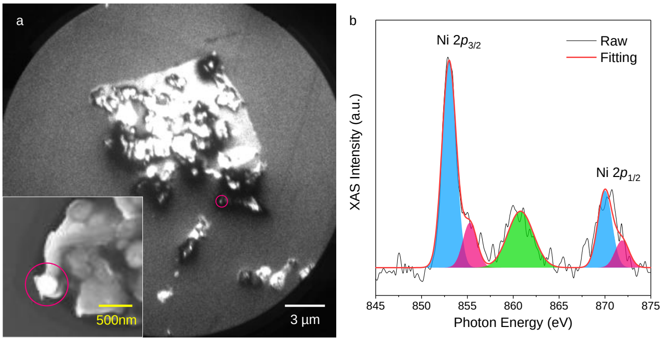

Figure 1. (a) An XPEEM view of Ni@MoS$_2$ composite. The round region marked in red circle was selected for XAS study. This region is more clearly shown in the inset. (b) XAS spectra collected from the selected region in (a).

Operando XAS analysis of CuO/SiO_2 and CuO/CeO_2 catalysts

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The possibilities of the operando XAS analysis of catalysts will be presented on two case studies of promising new catalytic materials: alkali doped nano-dispersed copper oxide clusters on ordered mesoporous SiO_2, which is highly active and selective towards propylene epoxidation [1], and nanoshaped CuO/CeO_2 catalysts used in N_2O decomposition reaction [2].

Operando Cu K-edge and Ce L3-edge XANES and EXAFS analysis was performed during catalytic reactions under controlled reaction conditions in a tubular reactor filled with protective He atmosphere at 1 bar. The spectra were measured before the reaction at RT, then during heating, and during catalytic reaction at 400 °C under controlled atmosphere.

Operando XANES analysis is used to monitor the changes in valence states and local symmetries of Cu and Ce cations in the catalysts. A partial reduction of Cu^{2+} to Cu^{+} and Cu^{0} and Ce^{4+} to Ce^{3+} species was detected during catalyst activation, and re-oxidation during catalytic reaction. Different dynamics of reaching a quasi-steady oxidation state were revealed as the tested catalysts approached the quasi-steady state after 300 min of reaction.

Operando EXAFS spectra are used to precisely determine local structure of Cu and Ce cations, to identify structural characteristics and changes of Cu and Ce species during the catalytic reactions. In this way, the active site in the catalytic reactions can be identified and the mechanism of the reaction clarified.

The results of operando XAS analyses are crucial to guide further material modification, to obtain more effective catalyst, and material which is more resistant to inhibiting effects that cause catalyst deactivation during catalytic reaction.

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XAFS@BAMline: More than just Absorption

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X-ray absorption fine structure spectroscopy (XAFS) is a frequently employed technique in order to investigate structural composition and change of chemical compounds such as catalytic species or corrosion processes. These structural properties are essential (i) to understand underlying reaction mechanism and (ii) to further improve the design of materials.

While XAFS measurements are usually performed with ionization chambers or simple fluorescence detectors, we at BAMline specialize in measurements with innovative set-ups that meet special requirements such as time resolution, (3D-) spatial resolution or demanding sample environments.

This contribution presents various available XAFS configurations with their corresponding applications. In particular, these comprise single-shot XAFS for time-resolved measurements, grazing-exit XAFS with energy and a spatially resolved detector for the characterization of thin films and an *in situ* grazing incidence setup for the characterization of corrosion layers. Additionally, the possibility of analyzing minute samples in total-reflection geometry is demonstrated.

X-ray fluorescence spectrometry beamline at Elettra Sincrotrone Trieste

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A new, advanced X-ray spectrometry beamline end-station [1] developed within a close collaboration between the Elettra Sincrotrone Trieste and the International Atomic Energy Agency has already completed three years of successful access provision to external users. The station is dedicated to X-ray fluorescence (XRF) and absorption spectrometry. Operating in vacuum in the energy range 3.6 - 14 keV the facility allows the XRF spectrometry under different alternative setup configurations, including either the conventional reflection (XRF 45/45) or the external X-ray total reflection (TXRF) geometry, but also allowing angle-dependent experiments, i.e. under grazing incidence/ exit angle (GI/GE-XRF), including also X-ray reflectometry (XRR). Being equipped with an advanced sample and detectors manipulation system the facility allows also for the complementary and synergistic application of different experimental strategies, e.g. a simultaneous GIXRF and XRR scan to investigate the structural features of nano-layered thin films or to perform X-ray absorption spectrometry (XANES) under TXRF geometry for trace elements speciation. In order to allow a user-friendly operation the instrumentation is controlled by the in-house developed software comprising Tango control system and a LabVIEW modular graphical user interface.

Every year within more than 60% of beamtime the community of external users exploits the instrumentation mainly for the environmental studies, including mostly air or water pollutants in different areas of the world, e.g. Saudi Arabia, Middle East, Asia Pacific region and South America. Other important application covers the issues related to medicine, life science and thin-layered materials characterization. By using well-characterized instrumentation, the facility is also used to deduce for some elements traceable datasets of X-ray fundamental parameters, thus evaluating the validity of various existing compilations and other theoretical databases.

The paper reports about the analytical performance of the instrumentation with a special emphasis towards the trace elements analysis. Exemplary applications on air pollutants characterization and the investigation of the in-depth distribution of deep-implanted heavy ion dopants into silicon wafers are discussed.

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Characterization of titanium oxide nanoparticles in sludge from wastewater treatment plants from Mexico

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Titanium oxide nanoparticles (TiO_2-NPs) are being increasingly used in many commercial products (e.g. sunscreens, cosmetics, paintings). 50,400 tons of TiO_2-NPs were globally produced in 2010 [1], making these NPs some of the most produced in the world. Thus, it is important to determine the harmful effects they may have on the ecosystems and health once released into the environment. Previous studies have shown that TiO_2-NPs induce genotoxicity in cells, mainly through the generation of oxidative stress [2]. In addition, the National Institute of Occupational Safety and Health (NIOSH) concluded that TiO_2-NPs are potentially carcinogenic (respiratory exposure) [3]. An important environmental concern is their release into wastewaters, ending up in the sludge produced in wastewater treatment plants (WWTPs) [4]. With the increasing use of WWTPs sludge as amendment in agricultural soils, a depth characterization of TiO_2-NPs in sludge samples is necessary for assessing potential environmental risks [5]. This work aims to the physical and chemical characterization of TiO_2-NPs present in the sludge of WWTPs.

The sludge samples were collected from WWTPs in the State of Chihuahua, Mexico. This state is territorially located in semi-desert zone, a climatic condition that causes the habit of the population to use sunscreen or moisturizers daily (often containing TiO_2-NPs). The samples were analyzed by X-ray fluorescence using different probe sizes, i.e. bulk (bulk-XRF), micro (μXRF) and nano (nXRF); also, by micrometric X-ray absorption near edge spectroscopy (μXANES).

Clear evidence of nanoparticulate Ti material was found in the sludge (Figure 1), along with other Cu and Zn particles with size distributions in the range of 100 nm, 200 nm and 300 nm. μXANES spectra from large particles (>3μm) corresponds to amorphous TiO_2 whereas smaller particles are mainly present in the anatase phase, which could correspond to engineered nanomaterials.

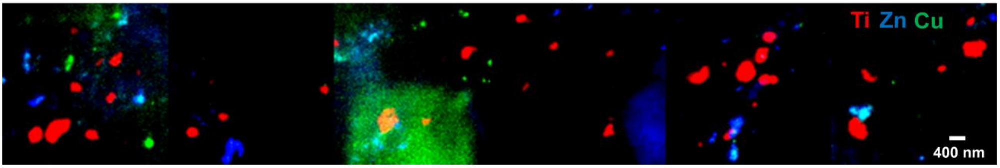

Figure 1. Nano-XRF map of a sludge sample.

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Reflection and Transmission mode MA-XRPD imaging: a comparison

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A microfocus X-ray source, equipped with Montel optics (yielding a 100x100 µm² beam) and a two-dimensional single-photon counting XRD detector were combined with scanning stages to create a transportable scanning macro X-ray powder diffraction (MA-XRPD) instrument. This device is capable of delivering large scale maps reflecting the distribution of crystal phases on/near the surface of quasi-flat (artistic) artefacts. By changing the geometry of the different components, imaging analyses can be performed both in transmission- and reflection-geometry. Simultaneous switching between a Ag-anode and a Cu-anode X-ray tube allows to collect either superficial or depth-averaged information.

Recently, several painted works of art from the 16-19th century have been investigated with this device in musea such as the Royal Museum of Fine Arts, Antwerp and the Musea Brugge (Belgium) and in the Rijksmuseum and Van Gogh Museum, Amsterdam, as well as in the Mauritshuis museum, The Hague (Netherlands).

When comparing the results produced by the MA-XRPD instrument with those obtained by means of other non-invasive methods such as macroscopic X-ray fluorescence analysis (MA-XRF) and various types of hyperspectral imaging, it is possible to pinpoint a number of strong and weak points of this method. Advantages include the high specificity with which mapping of crystalline paint components can be performed. Next to providing information on the distribution of the pigments employed by the artist, a marked advantage is that also information on degradation products can be obtained. The latter are formed *in situ* as a result of spontaneously occurring chemical reactions inside the paint, often induced by light. Limitations of MA-XRPD stem from the fact that the measurement time per scanning point is quite extensive (typically in the 1-10 s range) while in reflection geometry also a fairly large primary X-ray footprint (of the order of 0.1x1 mm^2) must be used. Both of these drawbacks cause the final image resolution to be limited. However, when MA-XRPD is combined with a less specific but faster imaging method such as MA-XRF, a number of the disadvantages can be compensated for.

The advantages and limitations of MA-XRPD in reflection and transmission mode will be illustrated with case studies involving non-invasive MA-XRF and MA-XRPD mapping of works of art by the 17th century painters Jan Davidsz. de Heem [2], Abraham Mignon and Johannes Vermeer and by 19th century artist Vincent van Gogh [3].

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A mobile Multi-Technique X-Ray scanner for a Real-time 2D and 3D Elemental Imaging of Artworks

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LANDIS-X is a mobile X-ray scanner based on a real-time technology providing macro-XRF (MAXRF), micro-XRF (MXRF), confocal-XRF (CXRF) analysis for the elemental 2D and 3D imaging of artworks.[1] The instrument is based on an Rh-anode microfocus X-ray tube, a polycapillary lens in the excitation channel and two SDD detectors placed in 45-90-45 geometry and operated in parallel. The spectrometric head is moved during the scanning by using a three-axis motorized stage presenting a 110×70×20 cm^3 range. A rotational scanning mode is also available for the elemental imaging of artworks presenting a three-dimensional geometry. The combination of the rotational scanning with a continuous translation of the spectrometric head along the vertical direction enables the unrolling of the curved sample surface providing the elemental distribution images over a 360 degrees view. The Z axis is dynamically guided with a laser sensor during scanning for keeping the spectrometer head at a fixed measurement distance.

MAXRF analysis is carried out by positioning samples out of the polycapillary focus with the primary beam presenting a spot size of few hundreds of microns. The full area of 110x70 cm^2 is covered in less than 2 hrs at 100 mm/sec. MXRF analysis is performed by positioning the sample at the focus where the beam presents a 50 μm spot-size. The real-time capabilities of the LANDIS-X scanner, allows us to achieve imaging details down to the micrometric scale within a macroscopic context. High definition elemental distribution images over 15 M pixels are obtained in 20 hrs. Finally, a conical polycapillary is installed on an ancillary SDD detector allowing the use of the CXRF set-up for the elemental depth profile of multilayered samples.

LANDIS-X is fully controlled by a custom-developed control processing unit. X-ray pixel spectra are processed in real-time by applying a least square fitting procedure; the deconvoluted elemental distribution images are elaborated during the scanning and are available in live mode to the users. A quantitative tool is also available in the instrument. A calibration procedure based on a fundamental parameter approach has been developed and verified in order to provide real-time quantitative images. Some examples concerning the analysis of large dimension paintings and of archeological gold objects with a complex shape are discussed.

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Study of two large dimension Murillo's paintings by means of Macro X-ray fluorescence (MA-XRF) imaging, point XRF analysis and stratigraphic studies

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During the recent restoration of two large dimension paintings by Murillo, entitled "Miracle of the loaves and fishes" and "Moses and the water from the rock of Horeb", several studies about the materials employed were carried out. Macro X-ray fluorescence (MA-XRF) scanning technique was performed on both works complemented by point XRF and stratigraphic analyses, in order to characterize the different elements of the paintings (ground layer, pigments and binders). The methods used during the study will be described in this work, with particular attention to the mobile MA-XRF device [1], which provides real-time elemental imaging of the paintings.

The results show that the ground layers were prepared in the usual fashion of the artist, using earths, calcium carbonate, iron oxide pigments and white lead. The polychromy is composed of lead white mixed with various pigments, depending on the color tone (red and yellow ochres, vermilion, azurite, smalt, lead-tin yellow, etc.). Other pigments from previous restorations were also found (zinc white, Prussian blue, etc.). MA-XRF mapping allowed determining the spatial distribution and the combination of these pigments along the surface of both works. Special mention should be made of the distribution of the smalt and its variable degree of degradation in the different areas of the paintings. During this work, it was also possible to obtain a graphic record of all the interventions made during the restoration process, principally due to the use of stucco for the reintegration of paint losses.

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Advantages and disadvantages XRF when applied to the investigation of cultural heritage objects

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X-ray based methods are powerful and well accepted for analysis of cultural heritage objects [1]. Non-destructive X-ray analytical methods include X-ray radiography and X-ray fluorescence (XRF) spectrometry. The structure of the whole object, which is characteristic of the artist's creative process is delivered by X-ray radiography, while XRF analysis allows to obtain a quick and accurate detection and identification of inorganic cultural heritage materials, especially pigments in a wide variety of objects including: watercolours, paintings, and polychromed sculptures, among many others. XRF analyses typically consist of point measurements, but in order to obtain more comprehensive information about the cultural object often times is necessary to perform analysis in several points throughout the object. The number of measurement points and the selection of measurement areas strongly depends on the analyst's experience. Macro XRF spectrometry (MA-XRF) is a more robust technique relative to point XRF providing more comprehensive information about either specific areas of the object or the entire object. MA-XRF analysis may be employed to collect elemental information from areas of an object and the results are visualized as chemical maps that show element distributions. Moreover, a new XRF imaging technique is being developed, i.e. full-field XRF (FF-XRF), allowing simultaneous projection of 10 ×10 cm area on the detector [2]. One of its main advantages is shorter measurement time and possibility of investigations of non-flat surfaces. Unfortunately, there are some disadvantages of XRF techniques. The elemental distribution images acquired by this method allow for the visualization of hidden paint layers and thus provide insight into the artist's creative process and the painting's conservation history. On one hand this is a clear benefit, but on the other hand especially in the case of paintings where XRF techniques provide information of the all layers of the painting this could be a problem.

This work presents and discusses XRF analysis conducted on the Medieval painting "*The Ecstasy of St. Francis of Assisi*" by El Greco from the collection of the Diocesan Museum in Siedlce. The advantages and limitations of the technique when applied to 19th and 20th century paintings by Maksymilian Gierymski, Henryk Siemiradzki and Zofia Stryjeńska will be discussed. Additionally, pigment mapping capabilities of new FF-XRF setup will be compared with commercially available systems, based on painting phantoms used as a test bed.

Part of this work was carried out thanks to the financial support of The National Centre for Research and Development within Applied Research Programme (project no. PBS3/A9/29/2015).

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Real-Time MAXRF Imaging of Egyptian Painted Wooden Coffers from the Tomb of Kha and Merit (1400 BC) at the Egyptian Museum in Torino

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The scientific investigation of paintings provides unique insights into nature of pigments, creative process and conservation state. X-ray Fluorescence (XRF) is a well-established method allowing in situ the non-destructive elemental analysis of samples. However, it is a spot analysis and its use for investigating complex painted materials can provide misleading information. This lack of information is remedied by the MA-XRF technique that provides the elemental distribution images of the pigments in the entire pictorial support [1-2].

To date MA-XRF have been applied mainly to historical and contemporary paintings. Its application to Archeology is still rare. In this work, we present the use of a mobile MA-XRF scanner based on a real-time technology for the imaging of Egyptian painted wooden coffers belonging to the funerary goods in the tomb of Kha and Merit (1428-1351 BC), today on view at the Egytpian Museum in Torino (Italy). Egyptian paintings are fascinating and complex materials to be investigated. Very often the use of the color is associated to symbolic meanings, especially when painted objects concern religious or mortuary use. From the technological point of view, various pigments and painting techniques were developed in ancient Egypt over a long period of time for decorating a number of supports.

The MA-XRF scanner (named LANDIS-X) was used in situ. It is composed of a spectroscopic head equipped with an X-ray tube focused with a polycapillary and two SDD detectors operated in parallel by a time-list event mode. The scanner operates a continuous scanning with a speed of 100 mm/sec. X-ray pixel spectra are processed in real-time and deconvoluted elemental distribution images are available to the users in a live mode.

The elemental maps obtained from the Egyptian coffers revealed the palette of pigments and gave new details on the painting technique and artistic style. Orpiment and/or Realgar, Egyptian Blu/Green, Red/Yellow Ochre and White chalk are the main pigments suggested by the elemental maps. Moreover, the use of an unusual manganese black was detected in different objects in combination with the more common organic black (sometimes in a mixture with a copper-based material). Finally, the presence of hidden “pentimenti” was identified in pictorial composition as well.

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The Barberini harp: diagnostic investigations

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In the frame of the COBRA project, funded by the Lazio Regional Authority, ENEA and the National Museum of Musical Instruments of Rome carried out a series of diagnostic investigations on numerous instruments of the museum's rich collection.

This paper presents the results related to the study of the conservation status of one of the rarest and most significant museum’s instruments, the Barberini harp, built between 1632 and 1633 on commission of Cardinal Antonio Barberini.

In order to study the original wood essence, the decorative apparatus, the integrity of the instrument structure and to assess its conservation status, two types of diagnostic techniques were used: X-ray radiography and observation of micro-samples under Scanning Electron Microscopy (SEM), coupled to elemental microanalysis.

In detail, micro-samples taken from the central column, from the gilding and from the sound chamber were observed for the identification of the materials, allowing to recognize the wood essence as maple (family of the angiosperms) and the gilding technique. Radiographic investigations showed that, during the realisation of the instrument, the modillion was strongly modified in the curvature, moving numerous anchorage holes of the strings pins and adding other wooden material to accentuate the curvature. The modillion’s grafts on the column and the sound chamber were also identified.

Both the analysis methods performed enlighten the realisation techniques and materials of the Barberini harp, as well as its state of conservation. The data collected from the diagnostic investigations, in particular those on the wood essence, will be useful for the realisation of modern instruments, having identical structural characteristics to the old ones, which could be played without the conservative problems connected to the handling of an instrument hundreds of years old, obtaining at the same time the same kind of sound.

11 Thursday program

	Marmorna Hall 1	Marmorna Hall 2
	Chair: P. Wobrauschek	
9:00	EXSA's Young Scientist Award 2018 ceremony	
9:10	Invited: **Grazing X-ray fluorescence techniques applied to nanometer-scale characterization applications** *Y. Kayser* (p. 237)	
9:40	Invited: **X-ray spectrometry in plant biology** *K. Vogel-Mikuš* (p. 238)	
	Session VIII: TXRF, GIXRF and related techniques Chair: P. Wobrauschek	Session IX: XRS applications in Life Sciences Chair: L. Carvalho
10:10	**Possibilities and drawbacks of EDXRF and TXRF for the determination of metallic traces in barite samples** *E. Marguí* (p. 240)	**Toxicity effects of SW-CNTS and crocidolite in human placental cells (BeWo) investigated by XRF microscopy** *A. Gianoncelli* (p. 251)
10:25	**Quantification of layers and implants using GIXRF in combination with TXRF standards** *D. Ingerle* (p. 241)	**Analysis of metal anti-cancer complexes and their interaction with DNA by means of X-ray spectroscopy** *J. Czapla-Masztafiak* (p. 252)
10:40	Coffee Break	
11:00	**Dual Energy Band Excitation for High Z and Low Z Elements by one Multilayer as Spectral Modifier** *J. Prost* (p. 242)	**A calibration procedure for a traceable contamination analysis on medical devices by combined X-ray spectrometry and ambient spectroscopic techniques** *B. Pollakowski-Herrmann* (p. 253)
11:15	**In-depth and dimensional characterization of nanolayers and 3-dimensional nanostructures using reference-free GIXRF-XRR** *P. Hönicke* (p. 243)	**The role of in vivo x-ray fluorescence in exploring a Strontium-health hypothesis** *D. Chettle* (p. 254)

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11:30	**Angle-resolved X-ray fluorescence spectroscopy in the laboratory** *I. Mantouvalou* (p. 244)	**Evidences of hepatic Gd retention and iron overload in pediatric oncologic patients revealed by a combination of micro-PIXE, LA-ICPMS and XRF** *L. Pascolo* (p. 255)
11:45	**TXRF, Chemometrics and Biology** *D. Eichert* (p. 245)	**Silver sub-cellular distribution and its impact on Hepatocyte functions revealed by nano-XRF microscopy** *V. Tardillo Suárez* (p. 256)
12:00	**Critical evaluation of the use of TXRF for the analysis of whole blood samples: Application to patients with thyroid gland diseases** *J. Jablan* (p. 246)	**Soft X-ray radiation damage on biological samples investigated with X-ray and FTIR microscopies** *D. Bedolla* (p. 257)
12:15	**One, two, three or four —- How many dimensions are there in the X-ray world?** *M. Krämer* (p. 247)	**Taking advantage of Compton-to-Rayleigh ratio in EDXRF spectra to recognize hydroxyapatite-based materials** *S. Pessanha* (p. 258)
12:30	Lunch Break	
	Chair: G. Pepponi	Chair: I. Arčon
14:00	Invited: **Physics interaction models and applications of PENELOPE in XRS and EPMA** *F. Salvat* (p. 239)	
14:30	**New Sample Carrier Modified with Low-Z Material Layer for TXRF Analysis** *K. Tsuji* (p. 248)	**Cadmium localization and chemical environment in a cadmium bioindicator Gomphrena claussenii** *P. Pongrac* (p. 259)
14:45	**TXRF analysis of uranium in acid elution solution model of soil** *H. Yoshii* (p. 249)	**Uptake, accumulation and translocation of metal and metalloid elements in plant seeds by μ-XRF and XANES** *L. Luo* (p. 260)
15:00	**Effect of the slag particle size in heavy elements releasing** *A. Riboldi* (p. 250)	**Combination of elemental and isotopic fingerprinting in food authenticity studies** *M. Nečemer* (p. 261)
15:15	Coffee Break	

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	Industrial session II. Chair: R. Tanaka
15:45	**High Performance Silicon Drift Detectors** *A. Pahlke, KETEK GmbH* (p. 263)
16:00	**Polycapillary X-ray Optics- The Driving Force of Advanced μXRF Analysis** *J. Sachs, XOS* (p. 264)
16:15	**Moxtek's Developments in Compact X-Ray Sources** *K. Kozaczek, Moxtek Inc.* (p. 265)
16:30	EXSA general assembly
⋮ ⋮ 18:00	Poster Session III.
20:00	Conference dinner

Grazing X-ray fluorescence techniques applied to nanometer-scale characterization applications

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Grazing X-ray fluorescence geometries, namely grazing incidence and grazing emission X-ray fluorescence, allow by the variation of the respective grazing angle tuning the probing depth within the sample from few nanometers to several hundred nanometers. Hence, both geometries are well suited for element-sensitive depth profiling measurements on samples with nanometer-sized features. Indeed, an accurate in-depth elemental characterization of nanoscaled systems is an important metrological challenge and requires further development of the current analytical techniques in view of the quickly increasing complexity of systems to be analyzed. Two recent developments were the introduction of a scanning-free methodology for grazing emission X-ray fluorescence (GEXRF) [1] and the application of reference-free grazing incidence X-ray fluorescence (GIXRF) towards structured surfaces.

The potential of scanning-free GEXRF in nanoelectronic, nanofabrication and quantum dot applications was demonstrated by characterizing the morphology of nanoparticles [2]. Furthermore scanning-free GEXRF can be readily combined with X-ray absorption spectroscopy (XAS) in order to expand the element- and depth-sensitive character of GEXRF by the chemical sensitivity of fluorescence detected XAS [3]. Indeed, the knowledge on the depth dependence of chemical states allows for a better understanding of the physical and chemical properties at the surface and thus to contribute potentially to the investigation of dynamical processes.

Reference-free GIXRF provides the possibility to validate and thus qualify artificial nanostructures as potential calibration samples for 3D analytical techniques as e.g. atom probe tomography [4]. Indeed, the physical traceability of the method allows, in combination with X-ray reflectrometry as a hybrid metrology approach, for a reliable quantitative in-depth characterization of nanoscale layers and layer stacks without requiring reference materials [5]. This allows supporting developments of increasingly complex nano-scaled materials as it enables a timely correlation of the actual functionalities with the underlying material properties.

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X-ray spectrometry in plant biology

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Trace elements are essential components of living systems, but at the same time they can be toxic at concentrations beyond those necessary for their biological functions. In addition, the toxicity can be extended to other non-essential elements of very similar atomic characteristics that can mimic the properties of a trace element.

Trace element malnutrition affects more than half of the world's population, while on the other hand industrialization, traffic and extensive use of fertilizers have resulted in exceedingly high concentrations of non-essential elements in food crops, posing risks to human health.

In order to be able to develop and improve phyto-technologies that enable production of safe and quality food, knowledge on the basic mechanisms involved in trace and non-essential element uptake, transport, accumulation and ligand environment in plants is needed.

Such studies are nowadays supported by highly sophisticated X-ray based techniques, such as synchrotron based X-ray fluorescence spectrometry, proton induced X-ray emission and X-ray absorption spectroscopy, enabling imaging of element distribution and determination of speciation and ligand environment of trace elements in biological tissues and cells with high spatial resolution and sensitivity.

Selected case studies of metal distribution and speciation in selected model and crop plants, achieved by interdisciplinary work, will be presented.

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Physics interaction models and applications of PENELOPE in XRS and EPMA

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The Monte Carlo method has proven to be a useful tool for the simulation of x-ray emission spectra in x-ray fluorescence (XRF) and electron probe microanalysis (EPMA). Accurate simulation of XRF and EPMA measurements is useful for optimizing the instrument parameters and for interpreting the measured spectra. Various Monte Carlo programs, with different capabilities and degrees of sophistication, have been developed over the years with the aim of facilitating the application of the method to XRF and EPMA. The accuracy of simulation results relies mostly on that of the adopted interaction models and atomic relaxation parameters. In this presentation, we will discuss the physics implemented in the general-purpose Monte Carlo code PENELOPE [1] and present applications of the code involving x-ray production and transport [2].

For photon interactions, the fundamental quantities are the cross sections for photoelectric absorption, incoherent (Compton) scattering and coherent (Rayleigh) scattering. The adopted cross sections are either calculated from first principles or taken from the LLNL Evaluated Photon Data Library (EPDL). The program may transport photons with arbitrary polarizations (defined by the Stockes parameters). The emission of characteristic x-rays from ions with inner-shell vacancies are simulated by using transition probabilities from the LLNL EADL, with approximate corrections for ions with multiple vacancies. In the case of electron interactions, the differential elastic cross sections are those in the NIST SRD 64 standard database. Inelastic collisions are described within the plane-wave Born approximation. Inner-shell ionization by electron impact is simulated by using the NIST SRD 164 database, which provides cross sections for the ionization of K, L, M-subshells. Finally, bremsstrahlung emission is described by means of numerical cross section tables that combine distorted-wave calculations and approximate high-energy theory.

Results from simulations with PENELOPE of x-ray spectra from EPMA and XRF measurements will be presented in order to illustrate the capabilities and limitations of the program. The main difficulty of these simulations is the long simulation time required, owing to the small solid angle covered by the detector and, in the case of x-ray emission, to the low probability of the interactions that originate x-rays. Simulations can be accelerated by using various variance reduction techniques implemented in the program.

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Possibilities and drawbacks of EDXRF and TXRF for the determination of metallic traces in barite samples

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Barite (BaSO4) is a mineral used in very diverse fields due to its high density. One of the important parameters that affects the properties and possible applications of barite, apart from particle size, is its chemical composition. For this reason, in addition to a good characterization of the purity of the barite samples, it is interesting to know the amount of minor and trace elements. The aim of the present work was to evaluate the analytical capabilities of low power EDXRF and TXRF for the determination of trace elements (Cd, Cr, Hg, Pb, Sb, As, Se) in barite samples. Both techniques allow the analysis of solid samples with a minimum sample treatment, which is advantageous in this application taking into account the difficult dissolution of barite matrix.

In order to work under conditions of maximum sensitivity, a carefully evaluation of the best sample preparation strategy (pressed pellet or suspension for EDXRF and TXRF analysis, respectively) as well as the instrumental conditions (excitation voltage, analytical lines, use of primary filters, measurement time) was carried out. In addition, in the case of TXRF analysis, a study of the shape, element distribution and layer thickness of the deposited residue on the reflector was performed by μ-XRF.

The use of several synthetic standards made of spiked pure barite appears to be an effective means to obtain reliable calibration curves with a good spread of data points over the working range (10-200 mg/kg). Internal standardization was also tested as quantification mode in TXRF analysis. However, the selection of a good internal standard (IS) was difficult since most of the elements commonly used in TXRF analysis were present in the barite matrix. Finally, taking into account that the TXRF system used in the present study was equipped with a W X-ray tube, molybdenum could be used as IS.

Using the best analytical and quantification strategies it was found that EDXRF shows a better performance for the determination of Se, Pb, As, Hg. The determination of Hg and As by TXRF at trace levels was hampered by volatility loses during the drying step on the reflector as well as the strong spectral overlap between Pb-L_α and As-K_α. However, limits of detection and accuracy for the determination of high-Z elements (Cd, Sb) were better when using TXRF analysis due to the possibility to determine these elements through K-lines. The quantification of Cr at trace levels (<100 mg/kg) was not possible using any of the XRF methods developed due to the severe interferences from Ba characteristic lines.

Quantification of layers and implants using GIXRF in combination with TXRF standards

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Grazing Incidence XRF (GIXRF) is a Total Reflection X-Ray Fluorescence Analysis (TXRF) related technique, which makes use 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 very small, i.e. in the order of only a few nanometers, the XRF spectra represent the elemental concentrations of this near surface region. Varying the angle of incidence in the grazing incident regime and collecting XRF spectra at several angle positions results in angle dependent intensity curves for each element. The shapes of these angle-dependent curves are correlated to the layer thickness, depth distribution and mass density of the elements in the sample. Furthermore, the measured intensities contain direct information on the number of deposited atoms per cm^2 of the respective elements, especially at larger angles, where the incident beam is fully penetrating the deposited layers or implanted regions.

In previous works the quantification of the elements in the sample, especially of implanted elements with no or limited influence on the refractive index, was performed by relative quantification to a standard material with similar but known composition [1]. It is obvious that this can be quite limiting for elements of which homogenous flat layers are difficult or even impossible to deposit. Another approach developed by Beckhoff et al. uses a fundamental parameter based methodology, which requires exact knowledge of the incident flux, the measurement geometry and the detector response function [2].

In order to simplify the quantification, we developed a new procedure, which uses liquid standards, as typically used for TXRF quantification, to obtain relative sensitivity factors in relation to the substrate material. For semiconductor samples, this is typically Silicon and Silicon Dioxide with well-known composition. The evaluation of the measured GIXRF data is performed by the well-developed methodology of fitting (also in combination with X-ray reflectivity data) with JGIXA [3], but additionally uses the curve of the substrate material as “internal” standard, in order to perform quantification with the previously obtained sensitivity factors. Results obtained with this approach will be presented and discussed, also in relation to previous data.

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Dual Energy Band Excitation for High Z and Low Z Elements by one Multilayer as Spectral Modifier

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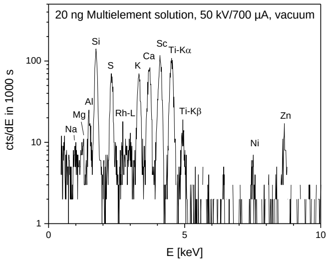
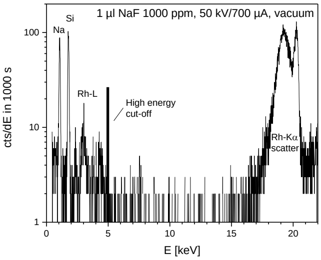
To efficiently excite a large number of elements ranging from carbon to uranium two different excitation energies are favorable, e.g. Cr-Kα for the light element range and Rh-Kα for higher Z elements. A TXRF vacuum chamber offering these two excitation conditions using two separate X-ray tubes is described in [1]. The spectrometer employs a silicon drift detector (SDD) with a 300 nm ultra-thin polymer window (UTW) including a magnetic trap, which acts as electron catcher. The setup allows the detection of both light and heavy elements. Monochromatization is done by an individual multilayer (ML) for each X-ray tube. The ML serves in both cases for the Rh and Cr anode tube as Bragg reflector adjusted to a fixed angle according to the desired energy and the 2d of the ML. Additionally, the ML always acts as a totally reflecting mirror due to its perfect surface quality. This means the reflected beam shows both the characteristic Kα line of the anode material and a low energy spectral distribution caused by the high energy cut-off effect. This idea to modify the spectrum is well-known and described in e.g. [2, 3]. So by intention, it is possible to create a dual energy band for the excitation of both low and high Z elements at a fixed angle of the ML. The Rh-L line series together with the low energy continuum is used for the low Z elements and the Rh-Kα line for the higher Z. The result is that one single X-ray source at one fixed angle can be applied for the excitation of two elemental regions. However, technical precautions have to be made: The beam path from the tube exit window to the sample inside the vacuum chamber must be evacuated to avoid air absorption. Results are shown for the technical solution of the design including beam path and vacuum chamber. Using an SDD with 8 µm Be window excellent results down to Na (Z = 11) were obtained. Measurements were performed in total reflection geometry (TXRF). Detection limits and sensitivities, calculated from SRMs and multielement standards, will be shown.





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In-depth and dimensional characterization of nanolayers and 3-dimensional nanostructures using reference-free GIXRF-XRR

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A reliable and non-destructive metrology of in-depth elemental distributions and dimensional parameters of nanoscaled layer systems and 3-dimensional nanostructures is an essential topic in many fields of research, especially the semiconductor industry [1]. With the decreasing minimal feature sizes and increasing complexity of the used structures, also the metrological challenges for a reliable characterization of such structures increase. As they must be characterized both with respect to their dimensional and elemental distribution parameters, a further development of the current analytical techniques is required.

A combined Grazing Incidence X-ray Fluorescence (GIXRF) and X-Ray Reflectometry (XRR) approach as proposed by de Boer [2] is well capable of contributing to the in-depth and the dimensional characterization of such nanoscale materials. In this work, XRR is combined with PTB's reference-free GIXRF [3], providing a direct access to the mass depositions (ρd) of the present materials. This allows for a significant reduction of the degrees of freedom within the combined GIXRF-XRR modeling and thus improves the characterization reliability of the methodology [4].

In this work, we will present how this combined reference-free GIXRF-XRR performs in the in-depth analysis of thin nanolaminate stacks of Al_2O_3 and HfO_2 layers with total thicknesses in the sub-10 nm regime. In addition, several 2D and 3D nanostructures are being characterized with respect to the dimensional properties and their in-depth material distributions [5,6]. For the GIXRF modeling of these nanostructures a novel approach for the calculation of the X-ray standing wave field intensity distributions is necessary (see fig. 1) and will also be presented.

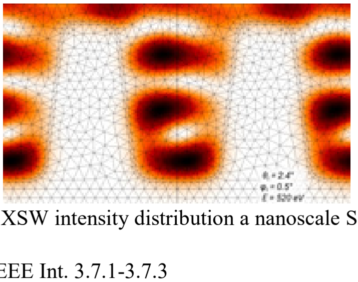

Figure 1: Calculated XSW intensity distribution a nanoscale S_3N_4 grating structure

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Angle-resolved X-ray fluorescence spectroscopy in the laboratory

Ioanna Mantouvalou[1], Veronika Szwedowski-Rammert[1], Jonas Baumann[1], Steffen Staeck[1], Malte Spanier[1,2], Daniel Grötzsch[1], Wolfgang Malzer[1] and Birgit Kanngießer[1]

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X-ray fluorescence spectroscopy (XRF) is a widely used method for the non-destructive analysis of elemental distributions of a wide variety of sample classes. By varying the angle of excitation or detection, the information depth can be altered and, thus, depth information can be gained additionally. Especially, for layered samples with one element in different layers or specimen with diffusion profiles, depth information is not accessible with conventional XRF, rendering angle-resolved XRF (ARXRF) into a valuable tool for analysis of technological samples. For specimen with sharp layer boundaries, interference effects either in the excitation channel (grazing-incidence XRF) or the detection channel (grazing-emission XRF) can enhance the sensitivity of the setup and give insights into the nature of nm-layered sample boundaries.

Usually, ARXRF experiments are performed at synchrotron radiation sources, because of the high brilliance, coherence and low divergence of the excitation radiation. In this presentation, we show different setups for ARXRF using laboratory equipment available at the Berlin Laboratory for innovative X-ray technologies (BLiX). A flexible high-vacuum chamber[1] is the heart of the experiments and different X-ray sources such as a laser-produced plasma source for the soft X-ray range[2] or X-ray tubes[3] as well as different detection schemes with SDD or CCD detectors can be utilized. We discuss challenges, limitations and advantages compared to setups at synchrotron radiation facilities and present the feasibility of compact adapted setups for selected applications.

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TXRF, Chemometrics, and Biology

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Total Reflection X-ray Fluorescence (TXRF) Spectroscopy is one of the most impressive analytical technique providing spectral signatures of materials that can be used to unravel their elemental composition. Within a few seconds and with limited sample preparation, a first characterization of qualitative character can be obtained, whereas thorough and quantitative information will require a full experimental design approach. A unique feature of fluorescence is its inherently multidimensional and multivariate character, containing e.g. chemical, physical and structural information of all sample components. In addition, differences between the samples or the samples analysis conditions may cause very slight spectral differences that may be difficult to distinguish and/or identify. As such, and despite its apparent versatility and ease-of-use, many issues remain opened in TXRF analysis. These are lying from sample preparation procedures (despite the minute amount of sample needed), experimental conditions to related data analysis.

Chemometrics [1] is a chemical discipline that uses mathematics, statistics, and formal logic i) to design or select optimal procedures and experiments, ii) to provide maximum chemical information by analyzing the data, and iii) to obtain knowledge about chemical systems to model and predict them. Thus, chemometrics tackles several areas such as design of experiments, information extraction methods (modelling, classification and test of assumptions) and techniques allowing the understanding of chemical mechanisms.

Associated to XRF, chemometrics may be the link connecting the state of a chemical system to the measurements of the system. Indeed, widespread problems in TXRF - and X-ray fluorescence in general - are i) the recognition of the elemental information from spectral data (classification), ii) quantitative analyses of elements in complex matrices (multivariate calibration), iii) determination of the origin of the samples (cluster analysis and classification), iv) prediction of the properties of the elemental compounds or materials (quantitative structure-activity-function relationships), or even v) modeling and optimization of syntheses, preparations, experimental conditions and ultimately process monitoring.

More research in this direction can result in developing new analytical methods which lead towards better laboratory practices, towards optimization and new definition of standards and standardization procedures, and towards process and quality monitoring. In particular, it can be applied to identify unique and specific sensor for monitoring, discriminating and screening, and to predict the quality parameters and processing operation in research, laboratory or industry.

These concepts will be illustrated via applications to e.g. nanomaterials, biological samples, and environmental issues.

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Critical evaluation of the use of TXRF for the analysis of whole blood samples: Application to patients with thyroid gland diseases

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Multielement analysis of whole blood can provide significant information for the evaluation of nutritional status, diagnosis of certain diseases as well as for the assessment of exposure to potentially toxic metals. However, the quantification of multiple elements in whole blood is not easy partly because of the wide variation in element concentrations (from ng/L to g/L) and the complex matrix. Since the publication by Prange et al. [1], total reflection X-ray fluorescence (TXRF) has been established as an effective tool for the analysis of trace elements in blood. However, most of the contributions dealing with this topic apply a previous digestion of the blood sample before the TXRF analysis. The aim of this work was to develop a fast, sustainable and reliable analytical method, in combination with low power TXRF, for multielement analysis of whole blood samples. For that, dilution is proposed as a sample treatment alternative.

Firstly, a set of experiments were carried out to select the best diluent type and dilution factor using the control material Seronorm^{TM} Trace Elements Whole Blood L-1. Results obtained showed that the best strategy to prepare the sample was a dilution 1:5 with Triton 1% (in water). A critical evaluation of the parameters affecting the sample deposition on the reflector (i.e. sample deposition volume and drying mode) was also carried out including a study of the shape and element distribution of the deposited residue on the reflector by micro X-ray fluorescence spectrometry. It was demonstrated that using a sample deposition volume of 10 µL and drying the drop under IR radiation a centred thin film is obtained which is the basis to perform the analysis under total reflection conditions.

Using the best analytical conditions and a measuring time of 2000s, limits of detection estimated were in the low mg/kg range (Ca, K: 14-25 mg/kg, Fe, Cu, Zn, Br, Rb, Cr, Ni, As, Se, Ag, Cd, Sn, Sb, Pb: 0.2-1.3 mg/kg) and similar to those obtained using more complex sample treatments such as digestion. Accuracy and precision of the results, evaluated by the analysis of the aforementioned blood control material, were in most cases acceptable (Recoveries: 89-102 %, RSD: 6-8%, n=5).

To prove the applicability of the method, several blood samples from control and thyroid diseases patients were analysed. Despite the fact that more samples need to be analysed, it seems that Zn and Br contents in some of the patients with thyroid diseases are significantly higher compared to control samples.

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One, two, three or four – How many dimensions are there in the X-ray world?

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The question which dimensions are important in an experiment often seems obvious, for example when radiation (wavelength 1D) from an X-ray source illuminates – at a distance f (1D) - a sample or optical device (typically surface 2D) and is measured by a detector (depending on type 0D, 1D or 2D). However, if we look closer this is often not a sufficient description. Even a microfoucus X-ray source is not infinitely small but has finite dimensions (2D or 3D) which have an influence on the focal beam size but also on the Bragg angle of reflection and thus the photon energy reflected from a monochromator mirror for example. Further, the bilayer thickness (1D) of a multilayer needs to be very precise not only in the layer stack (1D) but also laterally over the entire mirror surface (2D). Otherwise integral energy resolution or overall intensity may decrease significantly. Typical examples from multilayer optics in laboratory and synchrotron set-ups will be presented.

In another field of coating technology, the fabrication of ultrathin films, monolayers and “sub-monolayers”, the definition of a layer by its thickness (1D) may become inappropriate. Here, a relation has do be found between the (mathematically derived) thickness as used in the production process and the mass deposition (ng or atoms per mm², 0D or 2D) which is more common in surface analysis techniques such as TXRF. Several series of sub-nm layers have been fabricated and tested in various lab set-ups and at synchrotron sources of which results and evaluations are shown.

New Sample Carrier Modified with Low-Z Material Layer for TXRF Analysis

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Total reflection XRF (TXRF) is well known technique for trace elemental analysis. A small volume droplet of the sample solution is dried on a flat sample carrier. The dried residue is analyzed under total reflection condition. Quantification is performed by standard addition technique. However, the size and shape of the dried residues still influence on the quantitative values. It is difficult to control the size and shape of the dried residue. If the size of the dried residue is large, self-absorption affect the quantification. To solve these problems, Prof. Fittschen et.al developed a picoliter solution deposition technique using an ink-jet printer [1,2]. The size and height of deposits was reduced. It is also reported that shading effect is important for TXRF analysis of residues [3]. They confirmed the shading effect directly by using a color x-ray camera under total reflection condition

We tried to prepare a film type residue. For this purpose, a glass substrate was modified using photoresist pattern [4]. A structure of parallel crosses shape was produced by photolithography, as shown in Fig.1. A 10 µL volume of the standard solution (including Ti, Cr, Ni, and Pb) was dropped on the resist pattern substrate. The dried residue was obtained in a relatively large area of 3-4 mm in diameter. The surface morphology was observed by a laser 3D microscope. The thickness of the residue was thin less than 1 µm. We also tried to use a simple carbon layer instead of the resist layer. The experimental results will be shown at the conference.

TXRF analysis was performed at a glancing angle of 0.05 degree by using NANOHUNTERTM, (Rigaku Co.). An x-ray tube with Mo target was operated at 50 kV and 0.6 mA. A repeatability and RSD values of quantitative results were improved by applying this new sample preparation.

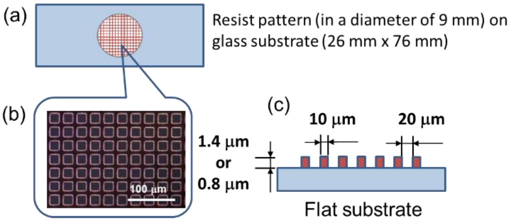

Figure 1 Glass substrate with parallel cross resist pattern [4].

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TXRF analysis of uranium in acid elution solution model of soil

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In the decommissioning field of the Fukushima Daiichi Nuclear Power Plant, several kinds of waste contaminated with radionuclides were discharged. Although uranium has not been detected in the waste till now, there is a possibility of finding uranium on the surface of the waste in the near future. Because radioisotopes of uranium rarely emit easily detectable α- and γ-rays, quantification of uranium in the waste by radiation measurement is difficult. It is thought that the most suitable method for this purpose is mass analysis of an acid elution solution of waste by inductively coupled plasma mass spectrometry (ICP-MS). Total reflection X-ray fluorescence analysis (TXRF) is another potential technique to estimate uranium in an acid elution solution of waste. Although ICP-MS has higher detection sensitivity than TXRF, the time-consuming ashing process, which is required for decomposition of organic matter in the pretreatment for ICP-MS analysis, is not required for TXRF analysis. In the present study, TXRF analysis of uranium in a model of acid elution solution of waste was performed, and the potential of TXRF as a screening method for contamination level of uranium in the acid elution solution of waste was discussed.

Uncontaminated dried soil, with diameter less than 2 mm, was employed as a model of dried sludge. Accurately metered dried soil was added to uranium-containing nitric acid, the uranium concentration of which was set to 1 ppm. After 30 min of shaking, the solution was filtered. Thus, a model of acid elution solution of uranium-contaminated waste could be produced. Uranium in the model solution was extracted by chromatography resin separation. A small amount of the sample solution was placed on a glass sample holder after mixing with indium standard solution employed as an internal standard and was subjected to TXRF measurement using a benchtop type TXRF spectrometer, NANOHUNTER-II (Rigaku, Japan).

In the measured TXRF spectrum, the peaks of U Lα and Th Lα were found, because thorium can also be extracted by chromatography resin separation. The net peak intensities were obtained by Gaussian fitting. The measured uranium concentration in the sample solution was 1 ppm, same as that of the uranium-containing nitric acid, which implies that the collection rate of uranium was approximately 100%. The detection limit of uranium was calculated as 5 ppb. Hence, this method can be useful for screening of uranium contamination level on the surface of nuclear waste.

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Effect of the slag particle size in heavy elements releasing

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For the reduction of the environmental impact, the utilisation of by-product materials has a primary role. Steelmaking industries are one of the most widespread activities in the world and, in particular, Italy is the second steel producer in the European Union (UE). Electric arc furnace (EAF) slags are a by-product and can be considered as igneous rocks. Steel slag outputs are approximately 20% by mass of the steel output. Due to its mechanical characteristics, the utilisation for road construction and concrete aggregate is a common practice in many Countries. However, hydraulic mineralogical phases, as Larnite (2CaO SiO2), can pollute soils and water by releasing heavy metals, especially Mo, V, Ba, and Cr [1]. To increase the chemical stability of EAF slags, silica can be added during the deslagging stage.

SLAG NEW LIFE is an National Interuniversity Consortium for Materials Science and Tecnology (INSTM) project co-financed by Lombardia Region and Consortium Company for Environmental Research for Metallurgy (RAMET) (http://slagnewlife.vpsite.it/). The aims of the project are the evaluation and comparison of conventional tests to evaluate the environmental impacts of different uses of these materials.

In this work, two EAF samples, with and without adding the silica during the deslagging stage, were analysed and leaching tests have been performed according to EN 12457-2 and EN 12457-4 standards. The eluates have been analyzed by ICP-MS. To investigate the effect of particle sizes on leaching test results, the samples have been sieved in nine granulometric fractions. Leaching tests of the nine subsamples of each sample were performed and analyzed by total reflection X-ray fluorescence [2]. The correlation of the heavy metals concentration in the eluates of the subsamples will be discussed. Relevant correlations have been identified, that allow to foreseen the belonging to the elements to different phases.

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Toxicity effects of SW-CNTS and crocidolite in human placental cells (BeWo) investigated by XRF microscopy

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BeWo cells have been demonstrated to be a good *in vitro* model for placental functions, also for studying the ability of environmental and/or manufactured particles, fibres and nanotubes (CNTs) to translocate across the placental barrier [1,2].

Several studies indicate that this ability depends on their type, size and surface modification, and may cause complications to the reproductive system and the fetus. Among these, only a few studies report on the exposure of the human placenta to asbestos fibres, as well as carbon nanotubes. We recently reported that these two nanomaterials cause a similar iron-related response in a mesothelial (MET) cell model [3] by applying a combination of advanced synchrotron-based X-ray microscopy and fluorescence techniques (µXRM and XRF). Here we show the results obtained with the same approach on BeWo cell model exposed to asbestos and raw single-walled carbon nanotubes (SW-CNTs).

X-ray Fluorescence microscopy in mild and soft X-ray regimes was used to map the distribution of P, S, Ca, Fe and C in exposed and control cells while absorption and phase contrast imaging (soft X-ray Microscopy) provided simultaneous morphological information. In addition AFM analyses were performed to identify nanomaterial penetration inside the cells [4].

The findings show that there is a marginal increase of intracellular iron, also confirmed by the stimulation of ferritin, after the exposure to both crocidolite and SW-CNTs. However the cellular iron changes in the BeWo model appear much lower then in MET cells, suggesting different toxicity mechanisms.

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Analysis of metal anti-cancer complexes and their interaction with DNA by means of X-ray spectroscopy

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It is predicted that the number of diagnosed cancer cases, both for men and women will reach almost 200000 cases/year until 2025. Therefore, it is beyond doubt that the effective prevention, diagnostic and therapy are needed. The development of new anticancer drugs is also forced by the strong side-effects and chemoresistance, both being induced when commonly used platinum-based chemotherapeutics are applied. Thus, new platinum and non-platinum metal complexes are being explored. The cytotoxic mechanism of action of anticancer drugs can be divided into separate steps: cell entry, drug activation, DNA binding and cellular responses. The efficiency of the drug can be seen as efficiency of each of these stages. Therefore, the detailed knowledge about these mechanisms is of the primary interest when new anti-tumor compounds are studied.

Herein, we report a strategy to follow the chemical changes in the structure of metal complexes during hydrolysis and coordination to DNA under physiological conditions, namely by means of *in situ* resonant X-ray emission spectroscopy (RXES). The spectroscopic method proposed by us was successfully used to validate the mechanism of action of cisplatin [1, 2] as well as elucidate the DNA binding of Pt103 compound that exhibits cytotoxic activity [3]. Moreover, we showed that RXES can be used to unveil the electronic structure of metallodrugs with high resolution and sensitivity and to disentangle differences in the electronic structure of the metal center induced by a secondary ligand stereochemistry [2, 4]. Additionally, the development of laboratory-based X-ray spectrometer for biological applications will be presented.

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A calibration procedure for a traceable contamination analysis on medical devices by combined X-ray spectrometry and ambient spectroscopic techniques

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There is a strong need in the medical device industry to decrease failure rates of biomedical devices by reducing the incidence of defect structures and contaminants during the production process. The detection and identification of defect structures and contaminants is crucial for many industrial applications. The present study exploits reference-free X-ray fluorescence (XRF) analysis as an analytical tool for the traceable characterization of surface contaminants of medical devices, in particular N,N'-ethylene-bis(stearamide), an ubiquitous compound used in many industrial applications as a release agent or friction reduction additive.

Reference-free XRF analysis as primary method has been proven to be capable of underpinning all other applied methods since it yields the absolute mass deposition of the selected N,N'-ethylene-bis (stear-amide) contaminant whilst X-ray absorption fine structure analysis determines the chemical species. Ambient vibrational spectroscopy and mass spectroscopy methodologies such as Fourier transform infrared, Raman, and secondary ion mass spectroscopy have been used in this systematic procedure providing an extensive range of complementary analyses.

The calibration procedure was developed using specially designed and fabricated model systems varying in thickness and substrate material [1]. Furthermore, typical real medical devices such as both a polyethylene hip liner and a silver-coated wound dressing have been contaminated and investigated by these diverse methods, enabling testing of this developed procedure. These well-characterized samples may be used as calibration standards for bench top instrumentation from the perspective of providing traceable analysis of biomaterials and surface treatments. These findings demonstrate the potential importance and usefulness of combining complementary methods for a better understanding of the relevant organic materials.

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The role of *in vivo* x-ray fluorescence in exploring a Strontium-health hypothesis

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In excess, Strontium is damaging to bone. There are also data to suggest that low Sr levels are harmful. Sr supplements administered to people diagnosed with osteoporosis resulted in reduced fracture risk[1], but there were also cardiovascular side effects.

An *in vivo* x-ray fluorescence system, using photon emissions from an ^{125}I brachytherapy source and a Si(Li) detector was used to monitor bone Sr in a group of people self supplementing with Sr. Over a period of up to four years, all subjects showed an increase in bone Sr, but the extent of that increase varied widely, from a factor of ten to a factor of one hundred[2].

In a convenience sample of adults not taking Sr, it was found that amongst people residing in Canada, those of East Asian origin had three times the bone Sr of Caucasians[3]. Amongst studies of hip fracture risk in different countries, the risk in East Asian countries is two to three times lower than that in North America or Western Europe[4].

An hypothesis is that modest levels of Sr, perhaps acquired through diet over a lifetime, are protective against osteoporosis, whereas supplementing with Sr after diagnosis of osteoporosis can be characterised as too much, too quickly, too late.

In vivo x-ray fluorescence can play two types of role. First is in the basic testing of this hypothesis. In an ageing population, one would predict (a) that bone Sr would vary with ethnic origin (and probably diet) and (b) the prevalence of osteoporosis would also vary with ethnic origin. *In vivo* bone Sr measurements are required to test the bone Sr levels. Secondly, if this hypothesis were to be confirmed, it would become important to be able to monitor bone Sr routinely, especially if the *in vivo* bone Sr system could be made quick and easy to use.

The present *in vivo* bone Sr measurement takes 30 minutes. A limitation is the count rate throughput for the Si(Li). A further limitation is that absolute quantification is impeded by the need for correction for soft tissue overlying the bone, an issue being investigated by Gevaert[5].

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Evidences of hepatic Gd retention and iron overload in pediatric oncologic patients revealed by a combination of micro-PIXE, LA-ICPMS and XRF

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Gadolinium based contrast agents (Gd-CAs) are extremely important diagnostic drugs formulated to have a rapid clearance upon administration, which assures innocuous use in MRI procedures [1]. However, in the last ten years important concerns on the safety of Gd-CAs have been raised. The most important alarm comes from the discovery of the Nephrogenic Systemic Fibrosis (NSF) syndrome, linked to Gd-CAs administration in renal patients and causing invalidating fibrosis of skin and connective tissues [2]. More recently, FDA issued a new alarm on the risk for occasional occurrence of Gd precipitates in the brain after repeated Gd-CAs administrations [3]. In addition, we recently reported that iron overload condition in oncologic and hematopoietic stem cell transplant pediatric patients causes a long lasting Gd retention in the liver and kidney after Gd-CAs administrations [4]. For further investigating this new toxicological evidence, we decided to combine different chemical imaging techniques to study the cellular distribution of Gd and its relation with iron or other trace and endogenous elements in the liver. The bioptic samples were collected from six hemato-oncologic patients having advanced hepatic iron overload and that received MRI procedures with contrast agents 3-4 months before. Samples were rapidly frozen, cut to 30 µm cuttings and freeze-dried. Alternatively, the samples were fixed in formalin, included in paraffin and histological 5 µm cuts were prepared. The air-dried cuttings were first imaged by a fully quantitative micro particle induced X-ray emission (micro-PIXE, JSI) with 1µm lateral resolution and 3 MeV proton beam. Afterwards, laser ablation inductively coupled plasma mass spectroscopy was employed for imaging of Gd distribution. Finally, paraffin included samples were analysed by synchrotron XRF microscopy at 7.3 keV and 0.5µm resolution. Due to very low Gd concentrations (on average 0.3 µg/g) Gd was successfully detected in all samples only by LA-ICP-MS. XRF confirmed the results detecting intracellular Gd traces only in one sample. PIXE and XRF described at different resolution levels the distribution of Fe and other trace and endogenous elements, allowing proper co-localization analyses. The results showed that LA-ICPMS was the best method to detect trace levels of Gd. Conversely, micro-PIXE and micro-XRF are fast and fully quantitative techniques offering insights into liver ionome in pathology.

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Silver sub-cellular distribution and its impact on Hepatocyte functions revealed by nano-XRF microscopy

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Ag-nanoparticles (AgNPs) are amongst the most frequently used nanomaterials due to their antibacterial properties. However, their widespread use as a biocide has raised concern towards their environmental and health effects. AgNPs toxicity has been studied in cells and animals. In the latter, it has been shown that AgNPs accumulate in several organs, mainly in the liver upon chronic oral exposure [1]. At the molecular level, their toxicity is due to the release of Ag(I) ions from AgNPs [2, 3]. However, the mechanisms of AgNPs absorption and ion release in cellulo, as well as their impact on hepatocyte functions are not yet well understood. In this context, we studied the fate of AgNPs in human hepatic cells (HepG2). By performing X-Ray Fluorescence (XRF) microscopy in the state-of-the-art nanoprobe ID16B-NA (ESRF), we could observe Ag sub-cellular distribution with resolution down to 100 nm. Moreover, coupling Transmission Electron Microscopy (TEM) and Nano-XRF microscopy allowed us to propose that AgNPs enter the cell through endocytosis, forming vesicles where AgNPs dissolve, resulting in the release of ions in the cellular cytoplasm. By mapping elemental distributions in thin (400 nm) cell cuts under chronic exposure to low AgNPs concentrations, we highlighted the presence of Ag(I) in cell nuclei. This novel finding might lead to the understanding of the observed disruption of metal homeostasis, especially that of Zn and Cu, vital ions for the well-functioning of the cell. Finally, we used spheroids (cells grown in 3D) in order to mimic a liver-like structure and study the excretion process of Silver in Hepatocytes.

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Soft X-ray radiation damage on biological samples investigated with X-ray and FTIR microscopies

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Radiation damage is an issue to be considered when working with soft X-rays. Damage at this energy is worse than with hard X-rays because of their increased ionizing power [1] especially for biological samples. Cellular components can be ionized by X-rays inducing breaking of molecular chemical bonds and indirectly promoting the formation of water derived radicals that may react with nearby molecules. Radiation damage can be manifested as a variation in mass density, as a reorganization of the fine morphological features of the samples, and eventually mass translocation and possibly elemental re-distribution, especially in hydrated samples [2,3,4]. The extent of the damage will depend on exposure dose, wavelength, sample preparation and environment.

In a previous work [5], the damaging effect was generated on formalin-fixed single cells by soft X-ray Microscopy (TwinMic beamline, Elettra Sincrotrone Trieste, Italy) and assessed by using two non-destructive techniques: atomic force microscopy (AFM) and FTIR microspectroscopy. Results showed that the ionizing radiation damaged the formalin-fixed cells by inducing extensive oligomerization of bio-macromolecules resulting in a complete disintegration of the vibrational architecture. In a recent work [6], the study was concentrated on paraffin-embedded tissues, where different fixation protocols were compared by using FTIR microspectroscopy. In this investigation, a loss in structure on the proteins was observed by following its vibrational bands, similarly to what observed in [5]. On the other hand, in this study, not only the tissues were examined, but also the substrate and the embedding medium, giving a clear message that not only the biological matrix but also the substrates can play an important role.

In this work, an overview of these experiments will be presented with more detailed information on the process a sample is undergoing while being exposed to soft X-ray photons.

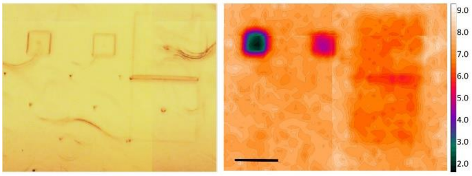

Figure 1. Ultralene foil exposed to different doses of soft X-rays. A) Visible light microscope image. B) Corresponding FTIR chemical image obtained by integrating the asymmetric CH_3 band (2960 cm^{-1}); color bar indicates the values in a.u. Scale bar: 50μm.

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Taking advantage of Compton-to-Rayleigh ratio in EDXRF spectra to recognize hydroxyapatite-based materials

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In this work, we established a methodology for the analysis and characterization of hydroxyapatite-based materials using X Ray Fluorescence. There are several animal hard tissues (ivory, antlers, bone) that can be recognized regarding the relative amounts of hydroxyapatite (HAp) and collagen using vibrational spectroscopy. The same principle can be applied within dental tissues to distinguish between enamel, dentine and root. Regarding X Ray Fluorescence spectra, only the inorganic part can be identified and, sometimes, only Ca can be detected due to elevated limits of detection for P.

This way, we have established a methodology for hydroxyapatite recognition using reference samples in order to obtain a calibration curve of the ratio of the Compton and Rayleigh scattering of the Ka characteristic line of the anode material as a function of the effective atomic number of the sample. The reference samples consisted on different proportions of Hap [$Ca_{10}(PO_4)_6(OH)_2$] and Boric Acid [H_3BO_3] reference materials in order to obtain an effective Z range of 7 to 14.

Calibration curves were developed for three different X Ray Fluorescence setups, with different characteristics, and applied to different materials: Ivory jewelry and decorative objects from African and Asian origin, with the purpose of establishing differentiation markers; human teeth tissues before and after erosion processes for demineralization assessment.

Cadmium localization and chemical environment in a cadmium bioindicator *Gomphrena claussenii*

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Cadmium (Cd) is toxic to plants in very small concentrations, i.e. above 5-10 mg kg^{-1} dry matter. There are, however, few plant species that are tolerant to Cd tissue concentration above 100 mg kg^{-1} dry matter. Some of these (hyper)tolerant plants can either accumulate Cd in their aboveground biomass in a linear relation with increasing Cd in the soil (bioindicators) or accumulate great Cd concentrations even at small Cd supply (hyperaccumulators). A recently discovered Cd bioindicator plant, *Gomphrena claussenii* accumulates up to 280 mg Cd kg^{-1} dry matter under field conditions, while hydroponically grown plants, exposed to 100 µM Cd, accumulate up to 1,000 mg Cd kg^{-1} dry matter in their shoots, in a typical indicator-like response [1,2]. The majority of the accumulated Cd in stems and leaves localised in numerous calcium oxalate crystals as revealed using cryo-scanning electron microscopy-energy dispersive X-ray fluorescence and micro-particle induced X-ray emission, however Cd binding in these oxalate crystals remained unresolved [2].

Using synchrotron radiation X-ray fluorescence mapping avoiding potassium interference we confirmed localization of Cd in oxalate crystals of hydroponically grown *G. claussenii*. In addition, using synchrotron radiation X-ray absorption near edge spectroscopy we demonstrated that in oxalate crystals majority of Cd is bound to oxygen ligands in oxalate (>90%) and the remaining Cd is bound to sulphur ligands. Cadmium binding to oxalate did not depend on the amount of Ca supplied or on the aboveground organ (stems and mature leaves). By contrast, roots contained no oxalate crystals and therein, Cd was bound predominantly to sulphur ligands.

The potential to remove Cd by extraction of Cd-rich oxalate crystals from plant material should be tested for application in phytoremediation strategies.

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Uptake, accumulation and translocation of metal and metalloid elements in plant seeds by µ-XRF and XANES

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The distribution of the metal and metalloid elements in plant tissues is closely correlated with the biological functions and the alterations of the functions. Among the correlations, a key is the distribution of the elements in the tissues during seed germination. In the study, the metal and metalloid elements in seeds during germination were determined and the distribution patters compared to evaluate the effects of the elements in seeds on the biological functions,

The maps of location of the elements in the seeds during germination were obtained by *in vivo* micro X-ray fluorescence (µ-XRF) scanning with a 20 µm each step. The species of the elements were analyzed by X-ray absorption near edge structure (XANES). The main results are as follows.

First, the distribution pattern of the elements by the µ-XRF maps was different from each other after the uptake of the elements by the vegetable seeds during germination. In the spinach seed, for example, Ca accumulated in a circle in the middle of the seed, and Pb located mainly in the root, as shown in Fig 1(left). Secondly, the translocation of the elements was different among different species of the vegetables, as shown in Fig. 1. Besides most of Pb accumulated in the roots, K, Ca and Cu translocated and accumulated in different parts in the seeds and shoots. The different distribution patters of the elements in seed germination reveal the different biological functions. Thirdly, the species of the elements determined by XANES revealed the mechanism of uptake, accumulation and translocation of the elements in seeds during germination.

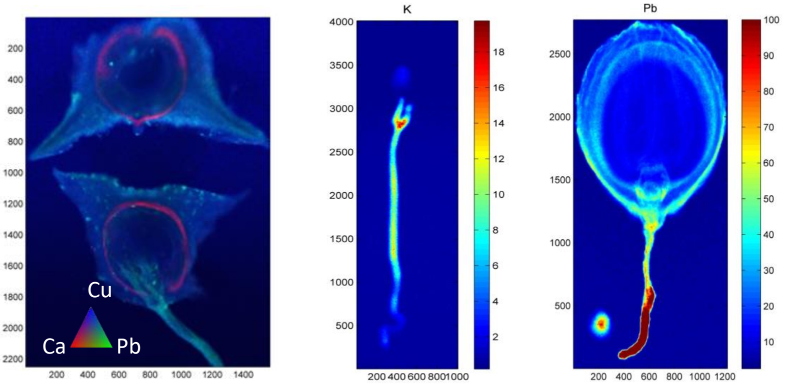

Fig. 1 The distribution of Ca, Cu and Pb in seeds of spinach (left), celery (middle), and coriander (right) during germination.

Combination of elemental and isotopic fingerprinting in food authenticity studies

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Elemental and isotopic fingerprinting, either single or in combination, is a very powerful analytical tool widely applied in food authenticity investigations.[1] The main issues are food provenance, traceability of food commodities, species, botanical, geographical origin, discrimination among organic and conventional food production, food adulteration, etc. In this work, capacity of Energy Dispersive X-ray Fluorescence Spectrometry (EDXRF) and Isotope Ratio Mass Spectrometry (IRMS) in combination with chemometry are presented as a rapid, inexpensive, robust and efficient screening methodology suitable to tackle food authenticity, quality and safety. The developed procedure involved determination of multi-element (P, S, Cl, K, Ca, Mn, Fe, Zn, Br, Rb, Sr) and isotopic (δ^{13}C, δ^{15}N, δ^{18}O, δ^{34}S) parameters and further processing of obtained data set by multivariate discriminant analysis. The proposed methodology was successfully applied in two food provenance studies, Slovenian milk, cheese, and vegetables. In the first study, our aim was to distinguish between species and geographical origin of Slovenian goat, sheep and cow milk and cheese, with the emphasis on EU Protected Designation Origin label (PDO) Bovški and Kraški sheep cheese and Tolminc cow cheese. In the second one, we were looking for the best statistical model to distinguishing lettuce, sweet pepper, and tomato samples available at Slovenian market according to their given country of origin (i.e., Slovenia, Austria, Spain, Morocco, Italy, Greece), and thus ensuring their traceability in terms of their authenticity.

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High Performance Silicon Drift Detectors

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KETEK is the world market leader for Silicon drift detectors (SDDs). Among all market competitors KETEK offers by far the largest product variety associated with SDD modules, operating electronics and detector accessories. The focus on market needs and the traditionally close collaboration with its customers allows KETEK to develop products of highest performance and quality. In this talk we present our latest developments in SDD technology.

Mobile XRF systems need to be optimized for low power consumption and very reliable operation in harsh environment at temperatures up to +50 °C. For such applications KETEK developed a new generation of SDD modules capable of continuously operating the detector chip at temperatures down to -60 °C for heat sink temperatures up to +65 °C. Permanent storage even at ambient temperatures up to +80 °C is possible without any long term degradation of detector performance. For operation at heat sink temperatures of + 20 °C, we succeeded to halve the power consumption of our modules down to <1 W, while still reaching optimum chip operating temperatures of -60 °C.

KETEK serves not only the XRF but also the EDX market, where applications, e.g. in SEM or TEM systems, require the detection of low energy X-rays <1 keV. Our latest module generation tailored for such applications combines the new cooling technology with a standard polymer (AP3.3) window and a Xenon gas fill. In contrast to the Nitrogen fill used before, Xenon dramatically reduces heat transport via the filling gas within the encapsulated module. The new design allows for excellent low energy X-ray transmission while achieving a cooling performance comparable to that of conventional vacuum encapsulated detectors.

The new cooling technology is available for all our vacuum encapsulated modules having collimated chip sizes from 7 to 150 mm² (active area 12 to 170 mm²) and for our Xenon filled TO8 modules having chip sizes from 7 mm² to 50 mm² (active area 12 to 65 mm²).

For best cooling and spectroscopic performance in EDX and XRF analysis KETEK offers in-house developed and patented carbon windows as an alternative to AP3.3 and Beryllium windows. The carbon windows are compatible to our TO8 vacuum encapsulation process and are fully inert and non-toxic. Both the AP3.3 and the Beryllium replacement have an X-ray transmission surpassing that of their conventional counterparts and excel in light tightness as well as in mechanical stress. KETEK’s new carbon windows will raise spectroscopic detector performance to an unprecedented level.

The technological superiority of KETEK products is also acknowledged by JPL, with whom KETEK is successfully collaborating in the Mars 2020 mission. Here, KETEK is currently working on the integration of two 50 mm² modules into the next Mars rover.

Polycapillary X-ray Optics- The Driving Force of Advanced µXRF Analysis

Jared Sachs and Ning Gao, XOS, East Greenbush, NY, USA

XOS is the leading global manufacturer of polycapillary X-ray optics. These state-of-the-art optics capture a large solid angle of X-rays from an X-ray source and redirect them to a micron-sized focal spot or highly collimated beam. The use of polycapillary optics have been successfully used to significantly enhance the performance of X-ray analysis in many applications, including X-ray fluorescence (XRF) and X-ray diffraction (XRD).

In this presentation we will highlight both the performance capabilities of polycapillary optics for the use in XRF and XRD and the complete solution configurations XOS offers. The complete solution, fleX-Beam, is a unique, compact X-ray generator that combines a low-powered X-ray source with a custom polycapillary x-ray optic. This complete solution can be used in a lab environment or integrated into an OEM system.

Moxtek's Developments in Compact X-Ray Sources

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Manufactures of XRF and XRD benchtop instrumentation face increasing demand for lowering detection limits, decreasing the sampling time, increasing accuracy and/or precision of measurements. The x-ray tube is a vital component of XRF and XRD instruments, which affects the aforementioned characteristics. There are several ways of addressing these needs; increasing the x-ray flux, conditioning the x-ray beam in terms of the size and energy spectrum, and increasing the high voltage which increases the activation energy. We will present the on several different prototype x-ray tubes developed at Moxtek which address performance needs of modern XRF/XRD spectrometers:

1. The high power conical (HPC) tube, which is a compact 75 kV tube with both a 150 Watt and 350 Watt package. This x-ray tube provides an unprecedented x-ray flux from a compact, air cooled device.
2. A microfocal x-ray tube, with a 100 microns or less focal spot size.
3. A portable and compact 120 kV & 5 Watt x-ray tube and high voltage power supply, an air cooled device in a hand size package.

In this presentation we will cover some of the basic functionality of each one of these sources, as well as some of the advantages for their intended x-ray applications.

11.2 Poster session III

11.2.1 TXRF, GIXRF and related techniques

13 **Hollow Fiber Liquid Phase Microextraction (HF-LPME) combined with Total Reflection X-ray Spectrometry (TXRF) for the determination of trace level inorganic arsenic species in waters**
Santanu Majumder, Eva Marguí, Gabriela Roman-Ross, Debashis Chatterjee and Manuela Hidalgo (p. 285)

14 **Trace determination of uranium preconcentrated using graphene oxide by total reflection X-ray fluorescence spectrometry**
Hiroaki Takahashi, Yukie Izumoto, Tsugufumi Matsuyama and Hiroshi Yoshii (p. 286)

15 **Alterations in Mammary Cells Exposed To Radiation Doses Used In Screening Mammography**
Carla L Mota, Andrea Mantuano, Arissa Pickler, Camila Salata, Samara C Ferreira-Machado and Carlos E Dealmeida (p. 287)

16 **Total Reflection X-ray Fluorescence Analysis of Poultry and Swine Mechanically Separated Meat (MSM)**
Rogerta Dalipi, Renato Berneri and Emanuele Sangiorgi (p. 288)

17 **Detection limit in XRF and TXRF: pitfalls and special cases**
Dmitrijs Docenko and Juliette Vandermeer (p. 289)

18 **TXRF quantification of gold nanoparticle uptake in cancer cells: optimizing measurement time and comparison with ICP**
Gabriella Mankovskii and Ana Pejovic-Milic (p. 290)

11.2.2 XRS applications in life sciences

19 **Advances in the Histopathological Characterization of Breast Tissue using Combined XRF and XRD Data in a Multivariate Analysis Approach**
Erica Dao, Eric Johnston, Soo Hyun Byun and Michael Farquharson (p. 291)

20 **TXRF analysis of trace metals in gingival fluid of patients with dental implants and different prosthetic materials**
Miriam Grenón, David Fucks, Manuel García, Fabiana Oliva, Juan Ibañez, María Ibañez, María Juaneda, Carlos Pérez and Héctor Sánchez (p. 292)

21 **IN VIVO EDXRF-ANALYSIS OF LOW Z CHEMICAL ELEMENTS IN FINGERNAILS**
Roberto Cesareo, Alfredo Castellano, Sergio Mascarenhas and Iana Mizumukai (p. 293)

22 **XRF Analysis of Correction Factors for Soft Tissue Equivalents**
Julia Gevaert and David R Chettle (p. 294)

23 **Multielemental Analyses of *Lonomia obliqua* (Lepidoptera, Saturniidae) Caterpillar Using XRF and NAA Techniques**
Cibele Zamboni, Dalton Giovanni,
Vera Salvador, Ivone Sato, Ronaldo Mendonça, Fan Wen and Simone Simons (p. 295)

11.2.3 XRS applications in earth and environment

11.2.4 XRS applications in industrial quality and process control

11.2.5 WDXRS, XRD and other

Ultra trace Determination of Uranium in Water Samples by Total Reflection X-ray Fluorescence Spectrometry

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Trace and ultra trace determinations of uranium (U) in water samples is of utmost important as the intake of U contaminated water by human and animals lead to several diseases e.g. failure of kidney, cancer, neurological disorders, etc. Determination of U in water samples at ultra trace levels is required for its quality control and remedial action. In order to know the concentration of U in water samples at such low concentration levels, a suitable analytical technique is required. Total Reflection X-ray Fluorescence (TXRF) is a well-established technique for trace determinations in water samples [1]. However, there are certain problems associated, such as increase in spectrum background due to the presence of high matrix in real water samples and common interference with Rb Kα (13.39 keV) and Br Kβ (13.29 keV) with U Lα (13.60 keV) which is normally used as analytical line for trace determinations of uranium. The increased background and spectral interferences make trace and ultra trace determinations of uranium in water samples difficult. In some parts of India, contamination of water bodies with U has been reported [2].

In present work, we report developments of a TXRF methodology for ultra trace determinations of U in water samples. The methodology involves preconcentration of the water samples by evaporation, redissolution of the residue obtained in 4M HNO_3 followed by selective extraction of U using an organic extractant, 30% tri-n-butyl phosphate (TBP) in dodecane. After selective extraction of uranium in the organic phase, it was back extracted in the aqueous phase using Milli-Q water. A constant amount of Y internal standard was added to this aqueous solution. The sample solutions were analyzed by the low power Low Z - high Z TXRF spectrometer and Rh Kα excitation source [3]. An aliquot of 50µL of the sample was pippetted out and deposited on quartz sample support. A calibration plot was made by plotting intensity ratios of (U Lα / Y Kα) obtained from the TXRF spectra of U standards having U concentrations in the range of 5 ng/ml to 50 ng/ml prepared by diluting MERCK single element U standard. A linear plot having regression coefficient of 0.997 and calibration equation $y = 0.001x + 0.003$ was obtained. The detection limit for U obtained using this method was 0.39 ng/ml (1σ). Different water samples e.g. tap water samples spiked with U in ng/mL level concentrations, U solutions and natural water samples contaminated with U were analyzed using the above calibration equation. The average precision obtained was 4% and the TXRF determined concentrations deviated from the expected concentration by 15%.

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Possibility of Elemental Determinations in Plutonium Samples by Total Reflection X-ray Fluorescence Spectrometry

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Total reflection X-ray fluorescence spectrometry (TXRF) is being used in different areas of science and technology for chemical compositional characterization of materials due to its different advantageous features. Due to requirement of very small amount of sample (in ng level), multielement analytical capabilities and excellent detection limits, the technique is well suited for analysis of radioactive, forensic, hazardous and precious materials for their compositional characterization[1]. Plutonium (Pu) is a technological important, precious and radiotoxic material finding its applications in nuclear industry. For its application as fuel of a nuclear reactor, chemical analysis of Pu fuel is required at various stages of fuel fabrication. For Pu based samples, in order to take care of the spreading of radioactivity in environment, sample preparations are normally done inside glove box or fume hoods. Due to the requirement of very small amount of sample and other advantageous features of TXRF, the radioactive samples can be fixed on TXRF sample supports and analyzed without touching these sample spot on the specimen in ambient atmosphere. This feature of TXRF makes it a better technique for Pu sample analysis compared to other conventional techniques e.g. Inactively Coupled Plasma Atomic Spectrometry (ICP-AES), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), etc where the sample amount required is comparatively large and therefore the instrument has to be put inside a glove box for such analysis. Handling of the instrument outside a glove box avoids complicated and time-consuming maintenance and operation of the instrument.

In our laboratory, we have developed a methodology for fixation of Pu based samples on TXRF sample support so that it can be utilized for major as well as trace determinations. The methodology involves pippeting out 2 µL (containing <100 ng of the Pu) Pu sample solutions at the center of quartz sample support and drying it completely. The Pu sample dried residue was further covered with 10 µL of collodion solution in amyl acetate solution and dried. The sample preparation activities were carried out inside a radioactive fume hood. Finally, the surface areas of quartz support, not containing the sample spot, were wiped carefully using a wet tissue in order to remove any loose contamination. After checking the alpha activity of these specimens and ascertaining that these are fit to be handled in ambient atmosphere and there is no loose contamination, the specimens were loaded inside the spectrometer. The TXRF measurements were carried out using the low power Low Z - high Z TXRF spectrometer and Rh Kα excitation source [2]. All the specimens were measured for a counting time of 2000s. This approach is being used for the major as well as trace elemental determination of Pu based solution samples. For trace determinations, separation of the major matrix (Pu) is essential. The details of this methodology shall be presented in this paper.

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Challenges of the pharmaceutical industry: TXRF analysis of catalyst and nutrient elements

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It is a serious challenge to develop an analytical chemistry method which meets the growing demand in increasingly regulated areas, such as the detection of metal contamination or monitoring of catalyst elements in pharmaceutical production according to the new EU and US Pharmacopeia standards [1]. First, the method has to fulfill the analytical requirements, e.g the limits of quantification, accuracy and precision of the analysis. Second, the analytical performance has to be validated by well documented processes and quality control procedures. In the EUPh and USP standards ICP-OES and ICP-MS are already listed as accepted methods. But in production and smaller research facilities the use of any ICP is restriced or impossible due to missing laboratory infrastructure. Benchtop TXRF might be an attractive alternative for such laboratories.

In this presentation the prove of Total Reflection X-Ray Fluorescence (TXRF) spectrometry for pharmaceutical applications will be described. Applying a dual tube system with Mo (17,5 keV) and W-Brems (35 keV) excitation the quantification of catalyst elements like V, Ni, Rh, Pd and more will be shown in detail.

In the second part the production of biopharmaceuticals in the pharmaceutical industry will be explained. Today, biopharmaceuticals are part of standard life-saving medication for the treatment of diabetes, cancer or multiple sclerosis.

During the production process mammalian cell cultures are grown in bioreactors producing the target pharmaceutical substance. The yield of this process strictly depends on the special recipe of the cell culture media.

Applying a TXRF spectrometer with Mo and W-L (8,4 keV) excitation all nutrient elements of the cell culture media are quantified at highest precision. Details of the sample preparation and the analytical process will be presented in this paper.

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The effect of freeze-thaw cycle on cerebrospinal fluid using multielemental quantification with TXRF

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Amyotrophic lateral sclerosis (ALS) is a motor neuronal disease which causes weakening of the muscles ultimately leading to paralysis. Diagnosis of the illness typically relies on observations of physical symptoms such as muscle atrophy and speech impairments which indicate advanced progression of the diseases. As such, there is a need for diagnosing the onset of the illness prior to neuronal degeneration [1]. Recent interest in using TXRF for finding biomarkers of ALS [2, 3] in cerebrospinal fluid (CSF) warrants investigations of sample storage conditions. This becomes particularly relevant when multiple samples must be tested over a period of time or when the samples have to be shipped for inter-laboratory measurements.

In this work, we investigate the effects of freeze-thaw cycles on CSF samples from healthy human donors. Measurements were performed using a commercial TXRF spectrometer (S2 PicoFox, Bruker-AXS, USA) coupled to a molybdenum target X-ray tube and SDD detection system. CSF samples were purchased from Innovative Research (Michigan, USA). The CSF samples were measured upon arrival and stored at -20 ˚C and -80 ˚C for a period of 14 days. The frozen samples were thawed to room temperature and were measured at 7 and 14 days using quartz sample carriers. At each time point, two sample preparation methods were investigated. In the first method, the sample was measured in its native state. In the second method, the sample was processed using nitric acid to digest the organic matrix and reduce background contributions. Multielemental quantification was achieved using lanthanum and yttrium as internal standards to examine the effects of storage temperature, time and freeze-thaw cycle on the CSF samples.

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Total reflection X-ray fluorescence analysis of uranium in immersion liquid of demolition waste using benchtop-type device

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In the accident at the Fukushima Daiichi Nuclear Power Plant of the Tokyo Electric Power Company in March 2011, nuclear fuels were cooled by water. Therefore, water contaminated with the nuclear fuel material (i.e., uranium and plutonium) will be found at and around the reactor during the decommissioning process in the near future. When the contaminated water is effused as drainage water, the concentrations of uranium and plutonium must be determined. Generally, radiation measurement methods (e.g., α-, β-, and γ-spectrometry) are applied to analyze radionuclides. However, because uranium (mainly ^{238}U and ^{235}U) rarely emits α- and γ-ray, it is difficult to determine the uranium concentration in the contaminated water using α- or γ-spectrometry. Therefore, we proposed a new methodology for uranium quantification by using total reflection X-ray fluorescence (TXRF) analysis [1]. Measurement of uranium content in model drainage water was also performed using a portable-type TXRF device [2]. In this study, we employed the benchtop-type TXRF device to perform a more sensitive analysis for uranium quantification in model drainage water. To produce model drainage water, a uranium-containing multi-element standard solution was added to the immersion liquid of the debris collected in the demolition field of the old building in our institute. The final concentration of uranium was set to 0, 0.05, 0.1, 0.5, and 1 ppm. A standard solution of indium was added to the samples as an internal standard. The prepared samples were dropped onto a substrate, and TXRF measurements were performed using a benchtop TXRF device NANOHUNTER-Ⅱ(Rigaku, japan). The obtained calibration plot illustrating the relationship between uranium concentration and relative signal intensity (U Lα / In Kα) was linear over the entire range of uranium concentration employed in the present study. The minimum detection limit of uranium in this method was low enough to ensure a regulated value as per the Japanese Water Pollution Prevention Law.

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Determination of trace amounts of gold in aqueous samples by ligandless surfractant assisted emulsification microextraction and TXRF analysis

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Because of their unique physical and chemical properties, the use of gold nanoparticles (AuNPs) has considerably increased in various fields last years. This fact has promoted the inevitable release of these nanomaterials into the environment and an increase of gold concentration in environmental samples arising from the dissolution/transformation of AuNPs into ionic gold (Au^{3+}). Therefore, at present, there is an increasing interest in methods enabling the selective determination of trace amounts of gold in environmental samples.

In this contribution, for the first time, a novel and quick ligandless surfactant assisted emulsification microextraction (LL-SAEME) approach for the quantification of gold ions in liquid samples by total reflection X-ray fluorescence spectrometry (TXRF) is proposed. The method is very simple and it is based on the formation of a gold hydrophobic compound with the cationic surfactant cetyltrimethylammonium bromide (CTAB) which is extracted in few microliters of 1,2-dichloroethane. After swirling the solution by hand for 5 seconds, the mixture is centrifuged for 3 minutes at 2000 rpm and 5 μL of the organic phase containing the gold ions are deposited on a quartz reflector to carry out the TXRF analysis. Variables affecting the extraction process and measurement conditions were carefully evaluated to obtain the best sensitivity for gold determination. Moreover, the influence of the presence of other ions, AuNPs and dissolved organic matter in the water samples was also studied to demonstrate the selectivity of the method for ionic gold (Au^{3+}) determination.

Under the best analytical conditions the limit of detection for gold was 0.05 μg/L and a good linearity (R^2>0.99) was assessed in the range of 1-500 μg/L. Precision of the obtained results was evaluated by replicate analysis of gold aqueous standards at the level of 1 and 50 μg/L. In both cases, the calculated relative standard deviation of the results was lower than 4.5% (n=5). Finally, accuracy of the method was studied by analysing several spiked water samples including sea, tap, mineral, river, waste waters at the level of 5 μg/L of gold. Recoveries in all cases were in the range of 94.9-101.5 %, even for the analysis of salty water samples such as sea water. As study case, the developed LL-SAEME-TXRF method was applied to monitor AuNPs stability in soils by means of Au^{3+} monitoring overtime.

To sum up, the proposed method is fast, simple and involves low operating costs and low consumption of reagents in comparison with other spectroscopic methods for gold determination at trace levels.

3D-printed TXRF

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In recent years, the miniaturization of analytical equipment has been remarkable, and spectrometers with components made by 3D printer have been reported [1-3]. The CAD data used in the 3D printer have the same format as those used in machining, *i.e.*, the 3D printer can be directly and easily replaced the conventional way. Combined with the conventional machining, 3D printer should promote making lightweight portable spectrometers.

With the use of 3D printers, we assembled TXRF spectrometer and assessed its applicability to spectroscopic analysis. 3D-printed TXRF spectrometer is shown in Figure. Detection limit of ng order was achieved for vanadium by the simple spectrometer. The 3D-printed resin holders of X-ray tubes and detectors could reduce interference peaks generated in a metallic equipment.

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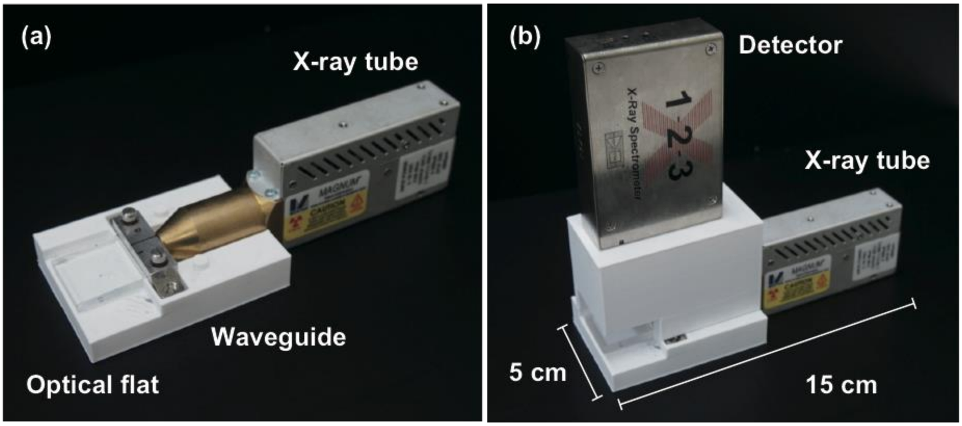

Figure. 3D-printed total reflection XRF spectrometer. (a) Lower part of the spectrometer. An X-ray tube, a waveguide, and an optical flat can be attached. (b) Overview. The size of the spectrometer is length 15 cm, width 5 cm, and height 15 cm.

GIXRF-based elemental analysis of sequentially infiltrated Al_2O_3 in self-assembled block copolymer films.

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The sequential infiltration synthesis (SIS) process, which is derived from atomic layer deposition (ALD), is based on the sequential and self-limiting exposures of polymer layers to gaseous precursors in order to infiltrate the polymer with inorganic materials. SIS is often used to harden lithographic resists [1], to produce inorganic nanostructures within block copolymer (BCP) templates [2] or to obtain conformal coatings with low refractive indexes [3]. Despite the development of a large number of applications, the mechanism behind this synthesis process is still discussed [4].

A better understanding of SIS can be achieved by means of grazing incidence X-ray fluorescence analysis (GIXRF), which can address many open questions on this technique. By a combined modeling of GIXRF and X-ray reflectometry (XRR) data, it is possible to determine the changes of the elemental depth profile of the infiltration inside the polymer. Moreover, the employment of calibrated instrumentation allows for reference-free GIXRF [5,6] and thus for a quantification of the elemental mass deposition of the inorganic material.

GIXRF and XRR analysis was performed on various polymer layers (PMMA, PS-*r*-PMMA and PS-*b*-PMMA) treated with 1 to 10 cycles of Al_2O_3 ALD using TMA and H_2O precursors.

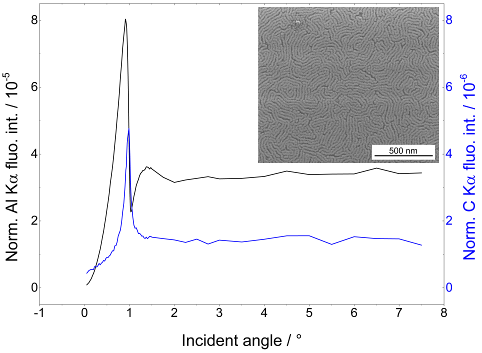

Figure 1 - The Al-Kα and C-Kα layer-like fluorescence angular profiles are shown for the PS-*b*-PMMA layer infiltrated with 10 cycles of Al_2O_3 ALD; the profiles at low glancing angle give an indication of the mass deposition of Al on top and inside the C layer. The SEM micrograph of the sample is shown in the inset.

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Total Reflection X-ray Fluorescence of Lithium Ion Battery Electrolytes from Field-Tested Electric Vehicles

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The lithium ion battery (LIB) is addressed as the key technology for the success of the electro-mobility, due to its high energy density and sufficient power density. The state-of-the-art LIB consist of a negative and positive electrode, whereas carbonaceous materials and lithium transition metal oxides (e.g. lithium nickel manganese cobalt oxide ($Li_1Ni_{0.x}Co_{0.y}Mn_{0.z}O_2$; XYZ=1)) are used, respectively. Furthermore, a combination of different cyclic and linear organic carbonates are used, in which the lithium conducting salt (e.g. lithium hexafluorophosphate ($LiPF_6$)) is dissolved to ensure lithium ion conductivity.

However, these materials suffer from severe capacity fading especially at elevated charge cut-off voltages or charging rates, which causes are still a matter of discussion in literature.[1,2] This becomes of major importance in the case of electric vehicles (Evs) due to the need of fast charging and long battery lifetime. Thus, these cell degradation - often referred to as cell aging - needs to be understood in detail with respect to al cell compenents.

Focusing on lithium transition metal oxide cathode materials, several degradation mechanisms were previously reported, however, lacking in reliable quantification of the transition metals in either electrolyte solutions or on carbonaceous anodes.[3] The suitability of TXRF in the field of battery research was already shown in previous publications[2,4], focusing on TM detection on carbonaceous anodes. However, the quantification of electrolyte solutions was yet not accomplished, due to excessive salt fractions from the conducting salt and organic solvent/surface tension.

In this study, we used total reflection X-ray fluorescence (TXRF) for the quantification of dissolved transition metals in electrolyte solutions extracted from different field-tested electric vehicles. Furthermore, a nanoliter-droplet approach was applied and verified to the extracted electrolyte to circumvent excessive backgrounds during measurements. The transition metals were further monitored and compared with each field-tested EV electrolyte to gain information about dissolution properties of the cathodes. Additionally, gas chromatographic analysis was conducted to elucidate the electrolyte composition as well as the degradation of the respective electrolyte to get a complete picture of the cell aging.

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Total-Reflection X-Ray Fluorescence Analysis (TXRF) of Airborne Particulate Matter at Atominstitut – Overview of Recent Activities

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The Atominstitut X-ray group has been working on airborne particulate matter (APM) for several years using both TXRF and classical energy-dispersive XRF. In a recent paper a quantitative analysis method for TXRF of APM was presented. [1] This method uses a three-stage Dekati cascade impactor (cut-off diameters 10, 2.5 and 1 µm, backup filter for particles < 1 µm) equipped with 30 mm Vaseline coated quartz reflectors. After sampling 5 ng Y are added centrally to each sample and the Vaseline layer is removed by cold plasma ashing for 30 minutes. For each stage an individual calibration curve had to be established, as the spot patterns produced by the impactor extend over the area seen by the detector. To this end the spot patterns were simulated using droplets of multielement standard solutions applied with the Atominstitut Nanoliter Deposition Unit. [2] In January 2017 an outdoor sampling campaign was carried out during 10 days. Samplings were carried out hourly with a sampling time of 45 minutes. The size fractions collected on quartz reflectors (i.e. > 1 µm) are dominated by crustal elements such as Ca, Ti, Fe and Sr as well as Cl coming from de-icing salt. The backup filters were changed weekly and analyzed by conventional EDXRF. This size fraction is dominated by anthropogenic particles forming from combustion processes, typically containing S, K, Zn and Pb. Quantitative results of this sampling campaign will be shown and discussed.

To assess the sub-µm fraction also with TXRF, a four-stage Sioutas impactor was used (cut-off diameters 2.5, 1, 0.5 and 0.25 µm) in a sampling campaign in October 2017. Sampling was performed for 90 minutes on 1" Si wafers greased with Vaseline, with a quantitative analysis procedure similar to the one described above. Results agree very well with the January results with the anthropogenic particle fraction having its maximum in the 0.25 µm stage.

Furthermore, a comparative study was carried out by parallel sampling with the Dekati impactor as well as a two-stage Gent sampler [3], which separates the particle size fractions 2 to 10 µm and < 2 µm from each other, particles > 10 µm are removed in a pre-impaction stage. Particles are collected on filters for subsequent EDXRF analysis. For this method a calibration, verified using *NIST SRM 2783 Air particulate on filter media*, is available. Results will be presented and discussed.

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Using a portable total reflection X-ray fluorescence system for a multielement analysis of swiss mice brains with experimental Alzheimer's disease induced by AβOs.

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Alzheimer's disease (AD) is a progressive and irreversible disorder whose pathological features include β-amyloid plaques, neurofibrillary tangles, neuronal and synaptic loss. The cause of AD is still not fully understood, however, the discovery that soluble β-amyloid oligomers (Aβos) are potent neurotoxins for the central nervous system has led to a new perspective on the pathogenesis of AD. Besides that, metals such as Fe, Cu and Zn are all increased in the brains of elderly, and these patients with AD have higher concentrations of them. Recently, several groups have raised the “metal hypothesis” of AD. This hypothesis is mainly based upon experimental results. These metal ions can interact with Aβ, resulting in the promotion of Aβ deposition and plaque formation a hallmark of AD. Thus, altered metals homeostasis may result in the development of AD. Total Reflection X-Ray Fluorescence (TXRF) is a multielement analytical technique that can be used to analyze trace elements, and which is capable of yielding quantitative information on the elemental composition of a variety of materials. The TXRF technique is very important in this analysis, because can be used to identify and quantify trace elements present in the sample at very low concentrations ($\mu g g^{-1}$). In this work, to evaluate the concentration of metals in the brain regions of swiss mice three groups of females and three groups males were studied: control, DA10 and DA100. The groups AD10 and AD100 were given a single intracerebroventricular injection (icv) of 10 pmol and 100 pmol of Aβos respectively to be induced AD. Seven days after the icv was carried out craniectomy and subsequently evaluated six brain compartments: frontal cortex, temporal cortex, hypothalamus, hippocampus, cerebellum and substantia nigra. All samples were submitted to acid digestion (HNO_3 + H_2O_2). After that, were diluted with Milli-Q water and added an internal standard (Ga). The TXRF measurements were performed using a portable total reflection X-ray fluorescence system developed in the Laboratory of Nuclear Instrumentation (LIN/UFRJ) that uses an X-ray tube with a molybdenum anode operating at 40 kV and 500 µA used for the excitation and a detector Si-PIN with energy resolution of 145 eV at 5.9 keV . It was possible to determine the concentrations of the following elements: P, S, K, Fe, Cu and Zn. Results showed differences in the elemental concentration in brain regions between the AD groups and the control group. The findings in this study showed differences for P, K, Fe and Cu levels for the hippocampus and hypothalamus. Although the cerebellum is the major repository of metals, where large amounts of Fe, Cu, and Zn are located, the findings shows statistically significant differences between the groups only for P, S and Fe in this tissue, differently than believed. The results suggest an association between AD and changes in the homeostasis of these elements.

Sample preparation for TXRF analysis of ovarian cyst fluids.

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Total reflection X-ray fluorescence (TXRF) spectrometry is fast, simple and cost-effective technique for multi-elemental analysis of biological samples, including human fluids such as blood, serum and urine. For this method are certain benefits such as the small amounts of samples, simple preparation and quantification by internal standardization. The aim of this study was to optimize the procedure of preparing samples for elemental analysis of fluids from human cysts.

The samples designed to elemental analysis were taken intraoperatively from cyst fluids of different degrees of malignancy. The ovarian samples were collected from 12 patients. The samples after the surgery were frozen in -80°C. Sample preparation consisting of suspending about 100 ml in 300 ml of distilled water showed to be the most suitable for this kind of sample. However for comparison purpose, an acidic digestion procedure was also applied. Also three different procedures of drying of sample deposit were evaluated: at room temperature in laminar flow chamber and under vacuum and drying on the hot-plate. For the quantification, 1000 ug/g gallium (Ga) internal standard was added. The measurements were performed with use the Rigaku Nanohunter II spectrometer. In the measurements Mo X-ray tube was used. The operating voltage and current of the X-ray tube were 50 kV and 12 mA, respectively. Time of measurement of each sample was 2000s.

The TXRF technique revealed that elements such as K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Se, Rb and Sr were present in all neoplastic fluids analysed. Accuracy, precision and relative standard derivation were calculated. Using the collected spectra the values of the Method Detection Limit (MDL) were also determined.

Hollow Fiber Liquid Phase Microextraction (HF-LPME) combined with Total Reflection X-ray Spectrometry (TXRF) for the determination of trace level inorganic arsenic species in waters

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Natural arsenic contamination of drinking water resources is a serious threat to human health around the globe. Arsenic naturally occurs in the environment in inorganic as well as organic forms, being inorganic As predominant in water. It is generally known that the inorganic As species Arsenite (As(III)) and Arsenate (As(V)) are the toxic forms of arsenic that are bioavailable and can cause adverse health effects. Therefore, although measuring total arsenic is useful for screening and in comparing the results to regulatory limits, speciation studies are needed for risk assessment.

Arsenic speciation is usually determined using sophisticated hyphenated analytical techniques as LC-ICP/MS (liquid chromatography inductively coupled plasma mass spectrometry). However, these techniques are expensive and sometimes suffer from matrix effects. This limitation can be overcome by using efficient sample preparation/preconcentration methods combined with atomic spectrometry. Hollow fiber liquid phase microextraction (HF-LPME) has evolved to be a viable alternative to conventional sample preparation, and has been used in the extraction of a wide range of compounds, including metals ad metalloids.

In the present study, and taking into account the microanalytical capability of total reflection X-ray spectrometry (TXRF), we investigated two liquid-phase microextraction systems (two and three phase HF-LPME) combined with this TXRF for the determination of trace amounts of inorganic As species in waters. For each of the LPME studied configurations, the influence of the relevant experimental parameters affecting As extraction (i.e. extractant type, organic solvent, pH conditions and extraction time) was evaluated. It was found that As(III) was more efficiently extracted by the ion exchanger Aliquat 336 at pH 13, whereas optimum pH for As(V) extraction was 8.5. The obtained results showed the three phase system as more suitable to be used in combination with TRXF than the two phase configuration, since higher sensitivity and better precision for As determination can be attained. Moreover, the limits of detection achieved using the best analytical conditions meet the requirements of current legislation and allow the determination of inorganic As (V) and As(III) in water. The proposed method was applied to the determination of trace inorganic As species in different environmental waters.

Trace determination of uranium preconcentrated using graphene oxide by total reflection X-ray fluorescence spectrometry

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The leaching of actinides from the fuel debris that has arisen from the severe accident at the Fukushima Daiichi Nuclear Power Station (1F NPS) was inferred from leaching experiments of simulated fuel debris into seawater [1]. The leaching ratios from the simulated fuel debris were reported in the order corresponding to U > Np ≈ Am ≈ Pu [1]. For the radiological characterisation of contaminated material and waste from the 1F NPS, it is quite important to measure the concentration of actinides, especially uranium with a high leaching ratio.

Since uranium has lower α specific radioactivity than the other actinides, it is difficult to detect uranium dissolved in water by α counting. As the total reflection X-ray fluorescence (TXRF) spectrometry is useful for the determination of uranium, we studied a fast and simple analytical method of trace determination of uranium in a multi-element solution which contains 4 ng mL^{-1} each of 6 elements: Co, Cs, Cu, Th, U and Rb.

The method was based on TXRF and dispersive micro-solid phase extraction (DMSPE) using graphene oxide (GO) as a solid adsorbent whose maximum uranium adsorption capacities were higher than any of the reported nanomaterials [2, 3]. In this method, the suspension of GO was injected into a multi-element solution to adsorb uranium. After the adsorption period, uranium adsorbed on the GO nanosheets was separated from the solution by vacuum filtration and soaked to elute in a small volume of internal standard solution of 2 mol L^{-1} HNO_3 mixing with indium internal standard. The 10 µL of the eluents was deposited onto a glass reflector and dried over 5 min, and their TXRF spectra were measured for 5 min.

Since rubidium was effectively removed from the uranium-containing solution by the DMSPE-GO method, the interference of Rb Kα peak against U Lα peak was avoided in the TXRF spectrometry. The recovery efficiencies of uranium from a dilute multi-element solution by the GO were high, however, they slightly decreased with increasing of the ion strength from 0 to 1 mol L^{-1}. Our findings demonstrate that the TXRF spectrometry followed by preconcentration and Rb removal by DMSPE using GO could be used as a fast and simple analytical method for trace determination of uranium concentration in contaminated water.

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Alterations in Mammary Cells Exposed To Radiation Doses Used In Screening Mammography

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The risks and benefits of mammography breast screening (MBS) are under constant study [1]. Controversy exists regarding the biological effectiveness of low energy x-rays used for MBS. Recent radiobiology studies have provided compelling evidence that these low energy x-rays may be for times more effective in causing mutational damage than higher energy x-rays [2]. Studies indicate changes in the concentration of certain elements in different tumor cell lines, after different treatments, using the TXRF method [3, 4]. This demonstrates the importance of the application of this methodology in the present study. We analyzed the elemental composition of human breast tumor cells (MCF-7) and non-tumor cells (MCF-10), subjected to doses used in MBS. The different cell lines were exposed to low (LD) (17 mGy) and high radiation (HD) doses (2 Gy). Cells were prepared to TXRF analysis, according literature [5]. The trace elements (S, K, Ca, Cr, Fe and Zn) were quantified using TXRF line D09B of LNLS (Laboratório Nacional de Luz Síncrotron, Brazil). The results showed statistically significant differences of all the analyzed elements among control (non-irradiated) and irradiated samples for both tumor and non-tumor cell groups. In HD non-tumor cells, the concentration of S, K, Cr are lower when compared to control. On the other hand, S, K, Ca, Fe and Zn concentrations are higher in HD tumor cells when compared to control and LD groups. For both tumor and non-tumor groups the trace element profile changed after high radiation doses exposure, and this profile only changed for non-tumor cells after low radiation dose exposure. This can indicate that tumor mammary cells are more radioresistant than healthy mammary cells. All the studied elements play important role on the cell maintenance. Ca is one of the main responsible for signal transduction pathways, while K is the major cation inside animal cells and its balance with Na causes a difference in electric potential between the inside and outside of cells, known as the membrane potential. Zinc participates in the regulation of cell proliferation, Fe in involved in the regulation of cellcycle progression and angiogenesis ans Sulfur in present in most of the essential amino acids in the human body. The study of this elements can help to better understand how the ionizing radiation changes the cell metabolism, prevent the possible damage caused by radiation on healthy mammary cells, an enhance the effects caused on tumor cells.

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Total Reflection X-ray Fluorescence Analysis of Poultry and Swine Mechanically Separated Meat (MSM)

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Mechanically separated meat (MSM) is a specific aspect of meat production and is usually produced from poultry and swine carcasses. The microbial risk grows with the muscle fiber degradation. For this reason, identification of a meat product obtained from MSM is very important from food quality and safety point of view. Important chemical parameters that could be used to distinguish MSM from non-MSM products are the content of calcium and iron [1,2]. Therefore, reliable and cost-effective analytical methods are needed to determine the chemical composition of these foods.

In this study, we have developed an analytical method for elemental analysis of poultry and swine meat samples. A low power benchtop total reflection X-ray fluorescence (TXRF) system equipped with Mo X-ray tube was used. Samples were prepared by suspending the grinded meat sample in disperser agent solution. Different types of meat: fresh, meat with different percentage of MSM, pure MSM and meat products prepared with MSM were analyzed. Accuracy evaluation was performed by comparing the obtained results with those obtained with inductively coupled plasma mass spectrometry (ICP-MS) analysis. Results show that, K, Ca and Fe are the most important parameters for differentiation of fresh meat from meat with MSM and meat products.

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Detection limit in XRF and TXRF: pitfalls and special cases

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According to the ISO 11929:2010 standard [1], "detection limit" (DL) is the "smallest true value of the measurand which ensures a specified probability of being detectable by the measurement procedure". In case of XRF and TXRF, the "measurand" is typically concentration of an analyte or its absolute quantity, layer thickness, or, in general, any other measurable quantity. IUPAC [2] definition of "limit of detection" (LOD) has similar meaning.

In literature [3,4,5,6], there are several derivations and different expressions for computing the detection limit. For the analyst, it is often confusing and unclear, which procedure to use and what is the meaning and limit of applicability of the selected approach.

In this presentation, I will clarify meanings of different expressions used in practice and then focus on specific topics of interest for the DL estimation:

1) Dependence of the DL on the analyzed sample composition and structure;
2) Effect of the region of interest of the analytical line in presence of overlaps;
3) Estimation of the DL with and without blank sample spectra. Reliability of DL estimate from routine sample spectrum;
4) Estimation without specific region of interest for the analytical line, e.g., in the full spectrum fitting or in spectrum simulation;
5) Estimation for very low number of background counts (of interest for TXRF or short integration time measurements). Influence of Poisson statistics in general.

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TXRF quantification of gold nanoparticle uptake in cancer cells: optimizing measurement time and comparison with ICP

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Recent interest in gold nanoparticles (AuNPs) as contrast agents and radiosensitizers in cancer therapy and research warrants careful examination of their uptake to determine efficiency and cytotoxicity [1]. Current quantification approaches are based on inductively coupled plasma (ICP) methods, which require extensive sample preparation and large sample volume. Following our group's development of TXRF-based AuNP quantification [2], in this work we optimize measurement time and compare the refined protocol with established ICP techniques.

A commercial TXRF spectrometer with a molybdenum target X-ray tube, SDD detection system and quartz sample carriers (S2 PicoFox, Bruker-AXS, USA) was used to quantify gold in breast (MDA-MB-231) and prostate cancer (PC3) cells using lanthanum as an internal standard. Optimization experiments were performed using certified reference gold solution (Ultra Scientific, USA). Each cell line was doped with concentrations varying from in-vitro (0.05 ppm) [3] to in-vivo (10 ppm) applications [4], and measured for 30, 60, 300 and 600 sec per sample. For comparison with ICP, each cell line was incubated with 50 ppm of 10 nm reference material AuNPs (NIST, USA) and prepared according to ICP sample preparation protocols to allow for direct comparison with TXRF. Spectra obtained from TXRF were analyzed using PyMCA and the recovery rate was compared with that of ICP.

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Advances in the Histopathological Characterization of Breast Tissue using Combined XRF and XRD Data in a Multivariate Analysis Approach

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Breast cancer is the most frequently diagnosed cancer among women worldwide, affecting approximately 1.7 million new women each year[1]. During the treatment of breast cancer, tissue is often removed from the patient and sent to a histopathologist for classification, after which a proper treatment plan can be tailored for the patient. In some cases, repeat tissue resectioning surgery is required to remove tumourous tissue leading to further risk and stress to the patient.

Previous studies have shown that the combination of x-ray fluorescence and x-ray diffraction data can be used as a histopathological characterization tool for breast tissue[2-4]. While this technique has shown promising results, it requires access to a synchrotron x-ray source, limiting its practical uses. However, recent advances in energy-dispersive x-ray fluorescence techniques have allowed for benchtop systems to produce useful results in a reasonable time frame, allowing for clinical implementation to be realized. Using a polarized energy-dispersive x-ray fluorescence and energy-dispersive x-ray diffraction system optimized for measuring soft tissues, 38 breast tissue samples (19 normal, 19 diseased) were examined. The measured elemental concentrations and adipose and fibrous tissue contents were used in a principal component analysis study to determine the variables that produced the most differentiation between the normal and diseased tissues. These variables were then utilized to create classification models using partial least-squares regression models. The results of classification models utilizing only x-ray fluorescence data, only x-ray diffraction data, and both data will be presented. The usefulness of each classification model will be discussed.

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TXRF analysis of trace metals in gingival fluid of patients with dental implants and different prosthetic materials

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Titanium dental implants are implanted in an electrolytic hostile media composed by bacterial colonies and gingival fluid. It triggers an electrochemical degradation process known as corrosion. During this process, different ions are released to the media and to the organism from the implant. This can result in the degradation of the implant surface, i.e., increase of the roughness and decrease of the TiO2 protective layer. Corrosion is often associated with tissue inflammation but, nowadays, it is not clear if the media changes due to inflammation triggers corrosion processes, or on contrary, corrosion leads to cytotoxic responses and causes inflammatory processes and pathological conditions such as peri-implantitis.

Trace and ultra trece elements present in gingival fluid can be studied using very specialized spectrochemical techniques like total-reflection x-ray fluorescence analysis induced by synchrotron radiation (SR-TXRF).

In this paper, studies of metals in gingival fluid of patients with dental implants and different prosthetic materials were performed by SR-TXRF. Prosthetic materials based in zirconium, noble metals and nickel-chromium alloys were considered.

The results indicate that concentrations of Ni, Cu, and Zn in gingival fluid of patients with implants with prosthetic components of nickel-chromium alloys and inflamed gums are higher than those of patients with healthy gums. Similar (statistically) results were found for the same elements and vanadium when the prosthetic material was noble metals. In the case of prostheses made in base of zirconium, the only element with a significant statistical difference was titanium.

Based on these results it is possible to infer the real origin of the corrosion of dental implants.

These results also indicate the importance of metal release to the organism and the influence of it on the prosthetic restoration. Moreover, further research is needed regarding the release of metals by dental implant and prostheses in order to obtain clinical applications.

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IN VIVO EDXRF-ANALYSIS OF LOW Z CHEMICAL ELEMENTS IN FINGERNAILS

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In humans, a nail is a horn-like envelope covering the tips of the fingers. It is composed of various parts, of which the hardest and largest (of about 10 x 15 mm^2) is made of layers of translucent tough protective protein called keratin, which contains sulfur.

A person's nails composition depends on many parameters, such as the sex (women are more subject to osteoporosis, which implies a general decrease of calcium) ; age (calcium content halves between 20 and 80 years) but also on the food input and on the environment. Nails are surely one of the best non invasive bioindicators of metal exposure. Further, nails mineral content could be utilized as one of the indicators of bone mineral metabolism .

Mean composition values of several low Z chemical elements in nails are :Sulfur ~ 0.34% ; Chlorine : ~ 1000-3600 ppm ; Potassium : ~ 360-2800 ppm ; Calcium : ~ 370-3400 ppm .

Nails composition can be determined "in vivo" and "in situ" in a rapid (25 s), non-destructive and non-invasive manner by using a portable equipment for energy-dispersive X-ray fluorescence (EDXRF), characterized by a X-ray tube working at low voltages, and properly filtered. In particular, low atomic number elements, such as P, S, Cl, K, Ca can be detected and quantitatively evaluated (Figure 1). Of special interest will be the quantitative evaluation of calcium, especially if the content of this element could be related to bone density.

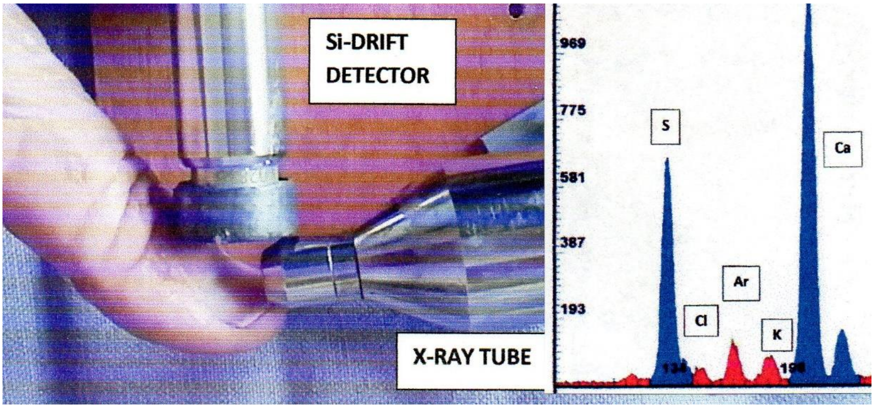

Figure 1 – EDXRF-experimental set-up during a measurement of fingernail composition. X-ray beam from the tube, which works at 10 kV and 50 µA, is collimated and filtered, while the detector entrance is filtered and shielded The X-ray spectrum is also shown on the right, with the X-ray peaks of S, Cl, Ar, K and Ca. For quantitative evaluation, the peaks are normalized to the scattered radiation.

XRF Analysis of Correction Factors for Soft Tissue Equivalents

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X-Ray Fluorescence (XRF) is a widely used method for in-vivo elemental analysis. Particularly for bone, it is a non-invasive technique that provides information on composition without significant risk to the patient[1]. Although toxic elements, such as lead, are the focus of research efforts, XRF also contributes a capability for measuring elements beneficial to human health, such as Strontium. This is a proposed supplement that has been shown in clinical trials to reduce fracture risk in people diagnosed with osteoporosis[2].

While XRF is a viable method for quantifying bone Strontium, there are still factors that constrain its effectiveness. X-ray attenuation through overlying soft tissue decreases the signal, consequently requiring correction before estimating the true concentration of Strontium in bone. A correction factor can be applied to account for the reduced signal, but an accurate measurement of overlying soft tissue thickness is required. Existing methods for this, such as ultrasound, are time consuming and consistency across subjects is hard to achieve. In a study done by Nie L et. al., an alternative method is proposed which uses the correlation between soft tissue thickness and Compton peak count rate[3]. Measurements were taken using Lucite as a soft tissue substitute overlying lead-doped plaster of Paris bone phantoms. Here, the Compton correlation method was shown to be equivalent to the ultrasound measurements (intraclass correlation coefficient, ICC = 0.82)[3]. Lucite is commonly used as a soft tissue substitute, however, its mean atomic number is appreciably lower than soft tissue, somewhat limiting its applicability.

This study tests the feasibility of using cellulose or cotton filter papers within the 0.5-4mm range as a substitute for overlying skin to perform XRF analysis of Strontium-doped hydroxyapatite bone phantoms. Cellulose papers have the advantage of containing Oxygen, and are easily manipulated to achieve desired thickness. Mass attenuation coefficients are shown to be closer to those of soft tissue (ICRU 4-component) than Lucite, and the Compton correlation is used to estimate thickness as a correction factor to quantify true Strontium concentration.

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Multielemental Analyses of *Lonomia obliqua* (Lepidoptera, Saturniidae) Caterpillar Using XRF and NAA Techniques

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The elemental composition of the *Lonomia obliqua* caterpillar Walker, 1855 (Lepidoptera, Saturniidae) was investigated using X-Ray Fluorescence (XRF) and Neutron Activation Analyses (NAA) techniques. The need of this study is related to morphological changes (mainly size and color) observed in some caterpillars used for preparation of antiveneom (*antilonomic* serum). This species is poisonous and has the ability to cause serious and fatal hemorrhagic effects in humans after contact characterized by hemorrhage, disseminated intravascular coagulation, and acute renal failure [1, 2]. The first case of poisoning (registered in Brazil) occurred in 1989 and the average number of accidents is closer to 500 / year [3]. To reverse these effects, a specific antivenom (*antilonomic* serum) is currently produced by Instituto Butantan (Research Center at São Paulo city).

For this investigation, the samples were classified as healthy (caterpillars of control) and unhealthy (caterpillars visibly modified). The XRF measurements were performed in an EDXRF Spectrometer SHIMADZU Co. model Rany 720 and the NAA measurements in the IEA-R1 nuclear reactor (both facilities of IPEN, Research Center at São Paulo city).

The results show significant differences (high concentration) for several elements in unhealthy caterpillars that can affect the development of this specie as well as the quality and yield of the antiveneom. Furthermore, the elemental characterization of this species can also contribute for the understanding the potential pharmacological (pro-coagulant and anti-thrombotic) in the prevention of life-threatening blood-clots.

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Elemental Caracterization of the Extract of Propolis Produced by *Scaptotrigona Aff postica* Bee from Brazil Using EDXRF and INAA Techniques

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The *Scaptotrigona Aff Postica* bee is an insect stingless belonging to Apidae family and subfamily Meliponinae. This genus occurs throughout in Neotropics. In Brazil, it is found in the northeastern mainly in the Barra do Corda County (Maranhão). Specifically, the extract of propolis produced by this bee have several medical applications. It is used in the healing of wounds with an inflammatory process and in treatment of prostate tumors as well as food supplement [1-3].

Considering its importance in medicinal use and the great variability in relation to botanical origin, its standardization in relation to the dosage of ions and metal is important to meet the different medical applications. The objective of this investigation was to perform a multielemental characterization using Energy Dispersive X-Ray Fluorescence (EDXRF) and Instrumental Neutron Activation Analysis (INAA) techniques. The neutron activation measurement was performed in the nuclear reactor (IEA-R1, 3-4 MW, at IPEN) and XRF data were obtained using a mini - X Ray spectrometer with Ag and Au targets.

These data increase the knowledge of its inorganic components and can introduce improvements in the production these the extracts, mainly as regards to toxicity. Moreover, considering that the demand for natural products has increase (Brazil stands out as world exporter of honey and derivatives), these data also contributes for checking the quality and food safety.

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Ionomic and metabolomic changes in mercury and selenium exposed plants and animals by X-ray and FTIR spectrometry

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Organisms are a dynamic system that responds to environmental changes in biologically important ways with an infinite number of possible variations. Primary concern in plant physiology is the search for mechanisms, responsible for mobilisation of low soluble metals from soil, their translocation within the plant, and sequestration of metal ions in cytosol or in cellular compartments [1,2]. Mineral ion uptake, bioavailability, ligand environment and accumulation can be addressed by X-Ray Absorption (XAS) and Fluorescence Spectroscopy (XRF) techniques. Plant defence mechanisms against heavy metal stress which result in changes of metabolome can be further studied by complementary Fourier transformation infrared (FTIR) spectroscopy [2]. With these different approaches (analytical methods) we can investigate interactions between a set of total element concentrations (multi-element concentration fingerprint, also referred to as ionome) and metabolomic profiles of experimental organisms under different environmental stressors [2,3].

The aim of our study was to explore possible correlations between ionomic and metabolomic changes in lettuce *(Lactuca sativa)*, grown on mercury (Hg) contaminated soil, and to check the impact on primary consumers of contaminated lettuce, the slugs *(Arion sp.)*. As selenium (Se) could prevent Hg induced stress in plants and animals [4], one half of experimental plants was foliarly sprayed with Se solution during the growth period and fed to the slugs.

The results show that addition of Hg as well as Se interferes with ionomic and metabolic pathways and a combination of Hg and Se alleviates Hg caused stress in plants and slugs. Metabolomic changes detected by FTIR were noticeable already at 1 μg/g of Hg in the soil, while ionomic changes were not as prominent, although showing a dose dependent response.

Since changes in ionomic and metabolomic profiles appeared between Hg and Hg+Se treatments, ligand environment of Hg in lettuce roots was additionally examined by XAS (SR facilities of ELETTRA (beamline XAFS, pr. 20165258 and 20170045)). The measured spectra show that ligand environment of Hg changes in case of foliar Se spraying compared to only Hg treated lettuce.

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Recognition of different types of ovarian cancer tissues by X-ray fluorescence imaging

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The histopathological diagnosis is well known that it is inherently affected by the human factor and the sampling procedure, leading to a considerable ambiguity in the final assessment of the grade of malignancy. For this reason any method that can narrow down the uncertainty of diagnosis is desirable. Our study is an attempt to answer the question whether the spatial distribution of minor and trace elements in the interface between tumour and surrounding stroma can be used for differentiation of stromal and neoplastic areas of human ovarian tissue. The samples designed for the elemental analysis were taken intraoperatively from the patients with the ovarian cancer tumours requiring surgical intervention. The samples were prepared and diagnosed at the Department of Pathology, Jagiellonian University Medical College in Krakow. For each sample two subsequent slices were cut: one for the histopathological analysis and the second one for the elemental imaging. In our investigation 18 samples were used. The experiment was conducted at the International Atomic Energy Agency end-station at X-ray Fluorescence beamline of Elettra Sincrotrone Trieste facility [1]. A bichromatic exciting beam was delivered by the RuB_4C multilayer monochromator at the energies of 1.6 keV and 10 keV respectively. . The beam spot size and step size was 250x120 μm^2. The fluorescence radiation was detected with a SDD detector with ultra-thin polymer window in 45°/45° geometry. The experiment was performed in vacuum ($2 \cdot 10^{-7}$ mbar). The time of the measurements was 5 s per pixel and the average scan area was 30 mm^2.
The elemental maps of C, N, O, Na, Mg, P, S, Cl, K, Ca, Mn, Fe, Cu, Zn, Se and Br were used as an input data for two statistical methods to achieve the image segmentation: K-means clustering and positive matrix factorization . The results of the differentiation were compared with the results of the histopathological examination.

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Feasibility of whole-body in vivo X-ray Fluorescence of Lead in Bone in Mice

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Lead (Pb) is a toxic metal with effects on human health that include IQ [1], blood pressure [2] and early menopause [3]. While Pb exposure in North America has fallen dramatically in the last two decades, incidents like Flint, Michigan, show that children are still at risk. Data show an association between Pb exposure and IQ, but there is no technology and methodology to assess effects such as de-myelination in brain in vivo and link them to long-term exposure. We are developing a mouse model for Pb exposure and report here the feasibility of an in vivo x-ray fluorescence (XRF) system for the measurement of Pb in the skeleton of whole mice.

^{109}Cd XRF has been used to study Pb in human bone non-invasively for decades [4]. The ^{109}Cd K XRF system has a normalization that means accuracy is independent of bone shape, size, density, subject motion and tissue overlay thickness. Precision, of course, varies with these factors. To date no-one has assessed the feasibility of measuring the whole mouse in vivo.

Calibration was performed using standard addition Plaster of Paris phantoms mimicking human bone doped with Pb concentrations ranging from 0 to 100 ppm. Detection limits for the bone phantoms, were found to be 1.52 µg Pb/g plaster for 1 hour measurement. By comparison, using 2 strains of Pb free mice, CD-1 and C57BL/6J, we determined MDLs of 3.88 - 4.74 µg Pb/g and 4.58 - 5.82 µg Pb/g for whole mice (with skull and hind facing the detector respectively) for a 3-hour measurement. We will discuss data acquired using mouse-mimicking Plaster of Paris phantoms to show the effect of variations in Pb distribution across the mouse; the applicability of the normalization in mice and the effects of mouse orientation. We conclude that we can proceed to *in vivo* measurement of Pb dosed mice.

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Feasibility of dose enhancement assessment: preliminary results by means of Gd-infused polymer gel dosimeter and Monte Carlo study

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This work reports the experimental development of an integral Gd-infused dosimeter suitable for Gd dose enhancement assessment along with Monte Carlo simulations applied to determine the dose enhancement by radioactive and X-ray sources of interest in conventional and electronic brachytherapy. In this context, capability to elaborate a stable and reliable Gd-infused dosimeter was the first goal aimed at direct and accurate measurements of dose enhancement due to Gd presence. Dose-response was characterized for standard and Gd-infused PAGAT polymer gel dosimeters by means of optical transmission/absorbance [1]. The developed Gd- infused PAGAT dosimeters demonstrated to be stable presenting similar dose-response as standard PAGAT within a linear trend up to 13 Gy along with good post-irradiation readout stability verified at 24 and 48 hours. Additionally, dose enhancement was evaluated for Gd-infused PAGAT dosimeters by means of Monte Carlo (PENELOPE) simulations considering scenarios for isotopic and X-ray generator sources [2,3]. The obtained results demonstrated the feasibility of obtaining a maximum enhancement around of (14±1)% for 192Ir source and an average enhancement of (70±13)% for 241Am. However, dose enhancement up to (267±18)% may be achieved if suitable filtering is added to the 241Am source. On the other hand, optimized X-ray spectra may attain dose enhancements up to (253±22) %, which constitutes a promising future alternative for replacing radioactive sources by implementing electronic brachytherapy achieving high dose levels.

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Monte Carlo optimization of a secondary targeting EDXRF system for increment the limit of detection of gold, silver and gadolinium nanoparticles in tissue

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Recently, gold, silver and gadolinium nanoparticles have been functionalized to act as tumor markers as well as to be simultaneously applied on highly localized treatments. In this work we optimizing the amount of X-rays photons with energies near to the absorption edge of gold, silver and gadolinium from a common emission spectrum of a mini-X-rays tube, with the purpose of to improve the limit of detection of this nanoparticles into tissue samples. For this, we used the secondary target technique where the primary radiation from the X-ray tube excite a target which emits a secondary radiation that is used as a source to excite the sample. Monte Carlo simulations by code Penelope and XMIM-SIM was used to simulate the interactions and study the spectrum of each target and sample [1,2]. Three differents compositions of secondary targets were modeled for each metallic nanoparticle of interest, in order to find which is the one that improves better sensitivity (reducing the background and increasing the characteristic peak of interest). Filters of Ni, Cu and Zn were studied like secondary targeting for improve the excitation of the L edge of Gd nanoparticles, Sr, Y and Zr filters for excite the L edge of Au and Sb, I and Ba filters for excite the K edge of Ag. The results obtained shown improvements up to 140% in the limit of of detection using secondary target of Y for the measurement of Gold nanoparticles and using secondary target of Zn for the measurement of Gd nanoparticles instead the primary radiation of the X-ray tube.

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Confocal high energy EDXRF of metallic nano biomarker for detection and simultaneous treatment of cancer

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A new methodology for the EDXRF detection and simultaneous treatment of tumors is presented. The method is based on a 3D scanning by means of convergent X-ray beam[1] irradiating phantom/patient containing targets with biomarker of heavy atomic number nanoparticles, Gd and Au, in certain concentration levels previously studied by other authors.

Confocal detection of the point scanning allows reconstruction of a 3D image aimed at mapping tumor cells, while a second convergent beam scanning slightly out of phase operates in treatment mode to eliminate the tumor. It is proposed that simultaneity between target location and treatment irradiation may avoid the mismatches between actual and practical target.

Monte Carlo simulations carried out adapting subroutines in FLUKA and PENELOPE main codes demonstrated the feasible of the proposed method. Current efforts are devoted to design and built a laboratory prototype to validate the proposed methodtext of your abstract should be entered here.

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Alternating PM_{10} and $PM_{2.5}$ sampling with an inlet switching system for an online XRF spectrometer

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The Xact®625i Ambient Metals Monitor collects ambient aerosols of one given cut-off size (PM_{10} or $PM_{2.5}$) with time resolutions from 15 to 240 minutes. Following the experiences in [1], an inlet switching system was designed and built that allows for alternating sampling of PM_{10} and $PM_{2.5}$ ambient aerosols. While this approach causes a 50% loss in time resolution of the measurement for each particle size class, it doubles the information gained by alternating sampling of two sizes. The distinction between coarse and fine particles helps in the identification of aerosol sources.

The system was deployed in a field campaign in Beijing, China, in the fall of 2017. It was in continuous operation from 5 November to 12 December 2017, with a time resolution of 1 h. After a sample was complete, the mass concentrations of 31 elements were determined with X-ray fluorescence (XRF) spectrometry, while the next sample was collected. More than 1000 samples were collected and analyzed during the campaign.

The results show that pollution episodes alternated with episodes of relatively clean air. The diurnal variations showed relatively weak amplitudes, as pollution episodes were dominated by a quasi-steady increase of concentrations over several days, independent of the time of day. The $PM_{2.5}/PM_{10}$ ratio of the averages varied between 0.05 and 0.99, depending on the element. A ratio of 1 means that all PM is in the fine mode. Crustal elements occurred mainly in the coarse mode, while elements related to coal combustion belonged predominately to the fine mode.

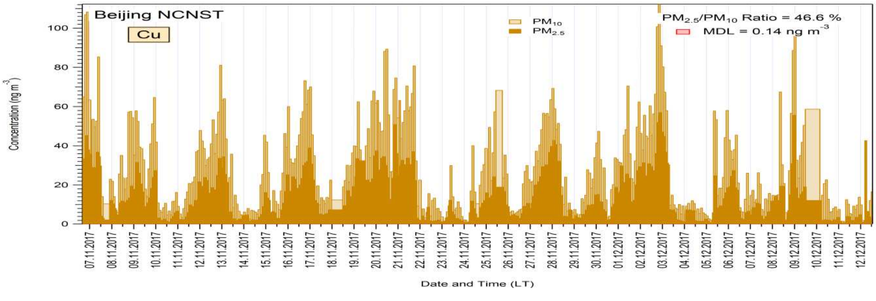

Fig. 1: Time series of PM_{10} and $PM_{2.5}$ concentrations of Cu at Beijing National Center for Nano-Science and Technology (NCNST). MDL = minimum detection limit.

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Determination of EDXRF Detection Limits of Air Samples with Custom Low-Loaded Multi-Elemental Reference Materials

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The new approach to generate and utilize multi-elemental reference materials (MEs) on PTFE filters with mass loadings as close to estimated Method Detection Limits (MDLs) as possible, is presented in this study.

The MEs containing 28 elements are generated using aerosol deposition system at the University of California-Davis (UCD)[1,2]. The derived EDXRF (Panalytical Epsilon5, Almelo, The Netherlands) MDLs based on MEs (MDL_{ME}) and calculated laboratory blanks-based MDLs (MDL_{LB}) are reported and compared based on the following methodology:

1. The laboratory blanks-based MDL (MDL_{LB}) is initially calculated using Eq.1:

$$MDL_{LB} = \overline{X_{LB}} + t_{(n-1,1-\propto=0.99)} \times SD_{LB} \quad (1)$$

where, $\overline{X_{LB}}$ is the mean of n laboratory blanks (208 blanks in this study), SD_{LB} is sample standard deviation of those results, and $t_{(n-1,\ 1-\alpha=0.99)}$ is the student's *t* value appropriate for a 99% confidence level with *n*-1 degrees of freedom (2.326).

2. Multiple MEs are generated at loadings 3 to 5 times higher than MDL_{LB}. These MEs are analyzed on different days, and ME-based MDL (MDL_{ME}) is calculated using Eq.2:

$$MDL_{ME} = t_{(m-1,\ 1-\propto=0.99)} \times SD_{ME} \qquad (2)$$

where m is the number of replicated measurements of MEs (m=10)

3. The higher value of MDL_{LB} and MDL_{ME} is reported as MDL.

The proposed methodology yielded similar MDL_{LB} and MDL_{ME} (abs. relative difference ≤ 25%) for Co, Ni, As, Se and Pb. The MDL_{LB} was lower than MDL_{ME} for Na, Mg, S, and V. whereas was higher for Al, Ca, Cr, Mn, Fe, Cu, Zn and Sr, due to random contamination on blanks and variable spectral contamination from analyzer's components.

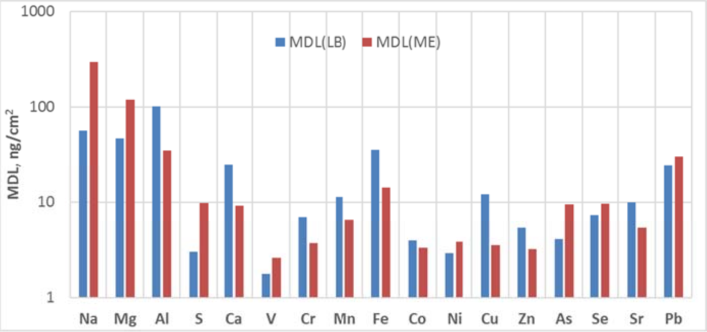

Fig.1. MDL_{LB}s and MDL_{ME}s for selected elements calculated following the proposed methodology.

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Quantitative assessment of mercury and other heavy metals on freshwater fish and vegetation collected in areas of gold mining in Brasil

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Brazilian *garimpos* are gold (or any other precious mineral) mines operated by people working with rudimentary pans, shovels and sluice boxes that have been used for centuries. The recovery of gold is done through gold panning, looking for gold nuggets, but also by mixing sediments with mercury to obtain gold, after the amalgamation and evaporation of mercury by heating. Regardless of the method, this mining technique is dirty, dangerous and often illegal. Clandestine gold mining, without any kind of control is still frequent, and is a major concern because it causes degradation to the surrounding environment. The main risk is associated to contamination of fish, water, air and soil not only by mercury but also by other heavy metals.

Energy Dispersive X-ray Fluorescence (EDXRF) measurements and fundamental parameters calculations were carried out for the analysis of freshwater fish and several types of edible vegetables, existing in two different *garimpos* areas from the region of Ouro Preto, Minas Gerais, without any sample treatment. The experimental EDXRF setup used is not sensitive enough for Hg detection and therefore this element has been studied by Atomic Absorption Spectroscopy (AAS) using an instrumentation specifically designed to determine total mercury content both in solids and liquids, without sample pre-treatment or sample pre-concentration (Advanced Mercury Analyzer system - AMA).

The obtained results show very high concentrations of heavy metals, reaching 2% of Fe and 150 $\mu g.g^{-1}$ of Cr in vegetables. Mercury has only been detected in the vegetables root in the order of 200 $\mu g.kg^{-1}$. Concerning fish, high levels were detected, with Fe concentrations reaching 10%, Cr 270 $\mu g.g^{-1}$ and Ni 60 $\mu g.g^{-1}$ in fish with guts. Metals concentration in fish muscle are not so high, however in many cases the fish is eaten whole.

Concerning Hg in fish the levels were between 30-300 $\mu g.kg^{-1}$ in muscle and 900 $\mu g.kg^{-1}$ in complete fish, being this last value close to the maximum allowed value in several official food regulations.

Characterization of a sustainable porous material designed for air particulate matter trapping

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Adverse health effects of air pollution may be attributed to the presence of suspended particulate matter (PM). Although there is still a lack on specific toxicological mechanisms, metallic components are known to exert major health problems [1, 2, 3]. PM sampling is routinely performed on different membrane filters such polycarbonate, cellulose acetate, polytetrafluoroethylene or Teflon^{TM} (PTFE) using air pumps [4] or passive sampler [5] exposed in indoor or outdoor environment. This study aims to characterize a new porous material designed to trap air PM, for passive sampling, and to compare the performance with respect to conventional filtering membranes. The novelty of this work is the material production process, based on environmental friendly gel-casting procedure, of mixed industrial by-products, like silica fume, and low cost materials such as sodium alginate. The variable porosity of this material offers the capability to trap PM with different size. In order to get information on a wide range of PM masses and sizes, different sources were considered: diesel exhaust fumes, incense smoke, working environment in an industry steel alloy, highway, and courtyard. X-Ray Diffraction (XRD) was employed for structural analysis of the material. While, the composition of the material and trapped PM was performed by Total reflection X -Ray Fluorescence (TXRF), focusing on: K, Mn, Fe, Ni, Zn, As, Se, Br, Rb, Sr and Ba as representative of different sources. Results show the highest metal concentration in samples exposed in the highway and the industry steel plant, highlighting the good ability of this new porous material to trap PM. However, the variable composition of the raw materials used, make it difficult to achieve reproducible data, and state the need of further studies to assess a suitable procedure for determining the amount of trapped PM.

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Radiological assessment of bottom sediment samples from East Black Sea Region, Turkey

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In this study, sea sediment samples taken from 16 different locations in the Eastern Black Sea Region were investigated for radioactivity analysis. This analysis has been performed using an HPGe detector (Ortec Model) gamma spectroscopy system. According to results of analyses, the concentrations of the radioactive isotopes ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs were determined. In order to assess the radiological hazards resulting from natural radioactivity, radium equivalent activities (Ra_{eq}), absorber dose rate (D), internal (H_{in}) and external (H_{ex}) index, annual effective dose rate (AED) and Excess life time cancer risk ($ELCR$) were calculated and compared with recommended values of international organizations.

Analytical capabilities of EDXRF and TXRF for multielement analysis of marine sediments

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Environmental studies to evaluate sources and destination of metals are heavily dependent on quantitative measurements of the amounts and distribution of these contaminants in environmental samples, leading to the necessity of simple and cost-effective analytical techniques.

The purpose of this work is to evaluate the possibilities and drawbacks of benchtop energy dispersive X-ray fluorescence (EDXRF) and total reflection X-ray fluorescence (TXRF) for a rapid and cost-effective multielement analysis (Al, S, Cl, K, Ca, Ti, V, Cr, Mn, Ni, Cu, Zn, Ga, As, Br, Rb, Sr, Y, Zr, Pb, Sn) of marine sediments collected in the Gulf of Guacanayabo (Cuba) with a minimum sample treatment.

In the case of EDXRF analysis, 5 grams of sample were added to 0.4 g of Elvacite® (plasticizer) to prepare stable pressed pellets of 40 mm in diameter. On the contrary, TXRF analysis was performed by preparing a homogenous suspension weighing 20 mg of sample in 1 mL of a dispersant solution (1% Triton® X-110 in water) and depositing 10 µL of the suspension on a reflective carrier. In both cases, instrumental conditions such as the excitation voltage, use of primary filters and measurement time were optimized to work under conditions of maximum sensitivity for the elements of interest. External calibration using a set of certified reference materials with a matrix similar to the sediment samples was used as quantification approach in EDXRF analysis. In the case of TXRF analysis, quantification was carried out in a simpler and faster way by internal standardization using Rh.

Analytical parameters for both XRF methods were evaluated by analysing a certified marine sediment reference material (PACS-2). Limits of detection (LODs) were significantly better for light element determination ($Z<19$) when using EDXRF highlighting the benefits of working under vacuum conditions in comparison with the TXRF system. For heavier elements, LODs were also slightly better (EDXRF:0.9-15 mg/kg, TXRF: 3-70 mg/kg) but it is interesting to remark that the sample amount to carry out the EDXRF analysisis 250 times larger. EDXRF shows a better performance in terms of accuracy and precision of the results for multielement analysis of marine sediments as well. However, the direct analysis of soil suspensions by TXRF could be interesting to get a first idea of the multielement composition of the sediment, above all for mass-limited samples, when certified reference materials are not available for quantification purposes.

Elemental Distribution Analysis of Copper-based Preservative-treated Woods by Micro XRF Method

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A wood has been used as a construction material, but wood is vulnerable for decay and insect damege. An injecting copper-based preservative treatment is effective for this. An analytical method for investigating the injection amount of copper in a non-destructive and non-contact manner is required. In this study, we attempted to acquire elemental distribution in wood by using micro XRF method.

Oshu Akamatsu wood treated with copper-based preservative chemicals was measured by micro XRF instrument in the laboratory. The elemental distribution of Cu was measured on the surface and cross section of the wood sample. In addition, the detection efficiency of Cu fluorescent X-rays were calculated according to Lambert-Beer's law and compared with the experimental result.

It was found that the distribution of Cu was uneven in wood. Figure 1 shows experimental and theoretical curves of Cu Kα intensity as a function of analyzing depth. The vertical axis is the detection efficiency (the product of the transmittance of fluorescent X-ray of Cu and the transmittance of fluorescent X-ray of Mo), and the horizontal axis is the analysis point (depth) in wood. The detection efficiency by actual measurement was lower than the value in the simulation. This is because fluorescent X-rays of Cu were absorbed by trace elements in wood.

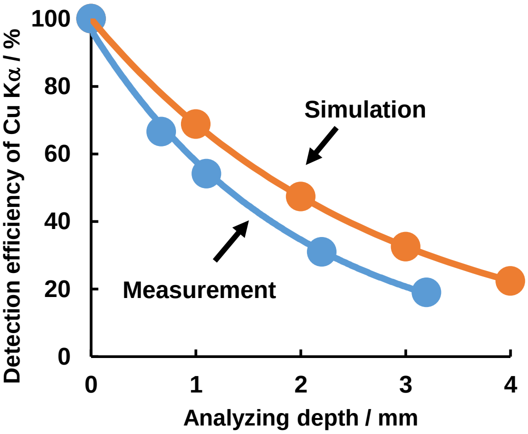

Figure 1 Detection efficiency of Cu Kα in wood.

Acknowledgement: This work was supported by JSPS KAKENHI Grant Number 17H01481

Profiling of Air Particulate Matter at Manila and Valenzuela, Philippines using EDXRF

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Air particulate matter pollution is a serious and continuing problem in urban/industrialized areas in the Philippines, such as in the cities of Manila and Valenzuela, resulting to visibility degradation, environmental impact and health effects. Air particulate matter (PM_{10}, fractionated as coarse [$PM_{10-2.5}$] and fine [$PM_{2.5}$]]) samples were collected using Gent air samplers at Pamantasan ng Lungsod ng Maynila Campus in Manila City (PLM) and at an EMB air monitoring station in Valenzuela City (VB) for a two-month period in 2017. About fifty percent or more of PM_{10} and $PM_{2.5}$ daily levels are in exceedance of the WHO 24-hr guideline values indicating the ambient air quality in the Manila and Valenzuela sites as unhealthy for both PM_{10} and $PM_{2.5}$ by the WHO standards. Black Carbon, a fingerprint of incomplete combustion products, can go up to about 50% of $PM_{2.5}$. Elemental levels (Na, Mg, Al, Si, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, and Pb) in air particulate samples were determined using non-destructive nuclear related analytical technique using Panalytical Epsilon 5 Energy Dispersive X-ray Fluorescence Spectrometer (E5 EDXRF). Spectra were fitted, and results were calculated using the software package Quantitative X-ray Analysis System (QXAS) developed by the IAEA, which is an integrated system for the quantitative evaluation of spectra measured with the XRF system. Quality assurance for the XRF results was observed with the use of NIST SRM2783, a multi-element standard on filter medium. Elements such as S, Zn, and Pb have been predominant in both sites that may indicate the presence of the vehicular emissions and industrial emissions from source/s which are proximate to both sites. Pb levels in VB's ambient air is 5 times higher than that of PLM's and BC levels in VB is almost 2 times higher than that of PLM's. RCM calculations of PM have shown that soil has the highest contribution to the coarse fraction. On the other hand, BC has the highest contribution to fine fraction at both sites. The use of XRF in this study affords a better understanding of the air particulate pollution at these urban study sites.

Comparison of laboratory WDXRF and handheld XRF for analysis of lake sediments

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Lake sediments are one of the most popular geological history archives in the Holocene environmental and paleoclimatical research. Organic and non-organic analysis, sedimentology, paleoecology are some of the multiple methods commonly used in the recent studies. Non-organic analysis, especially those aiming at the determination of the elemental concentrations, can be used to help the reconstruction of both anthropogenic effects (like heavy metal pollution, mining, deforestation) and natural processes (such as change in weathering and conditions of sediment formation). The most important challenge in these studies is to find the balance between the temporal resolution and the frequency of core sampling. Lot of sampling points results in better temporal resolution but in lower sample amounts due to the limitations of a sediment core. Thus we have to be extra careful when selecting the appropriate methods and instruments for elemental analysis because as low sample amount as possible can be only used for them.

In this study, we have compared the laboratory WDXRF and handheld EDXRF analysis of CRM standard reference materials and lake sediment samples. We have tested the effect of different sample preparation methods (non- disturbed sample, powdered sample, and pressed powdered samples with and without binding agent) on the measured elemental concentrations. We have also compared different calibration options as well; two FP (fundamental parameter) calibration (Environment and Mining) and a standard calibration based on the analysis of large number of certified reference materials.

The lake sediment samples were collected from the Lake Bolatau-Feredeu. This small but notable lake is located in the East Carpathian Mountains, Romania, Central Europe. Our objective was to find anthropogenic signals in the elemental compositions of layers from the last 500 years. The lake surface is 0.3 ha and its maximum depth is 5.1 m. [1] The chronology is based on AMS radiocarbon analyses which was supplemented by Pb-210 isotope analyses. The total sediment core represents ~ 6000 years. [2,3]

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Localization and species of Pb in Moss Collected from a Pb-Zn Mining Area by μ-XRF and XANES

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Moss is an important biological indicator and hyperaccumulator since its high tolerance and accumulating capacity to heavy metals. The root of moss mainly plays a role for supporting the whole plants and can hardly absorb nutrients from soils. On the countrary, its main absorption pathway is leaves. Thus, we use the special physiological structure of moss to study the transport characteristics of atmospheric pollution of heavy metals in mining areas.

In this study, the localizations of heavy metal elements and some nutrition elements in moss sampled from a lead-zinc mine was analyzed by X-ray fluorescence spectrometry. The speciation of lead was analyzed by X-ray absorption near edge spectroscopy.

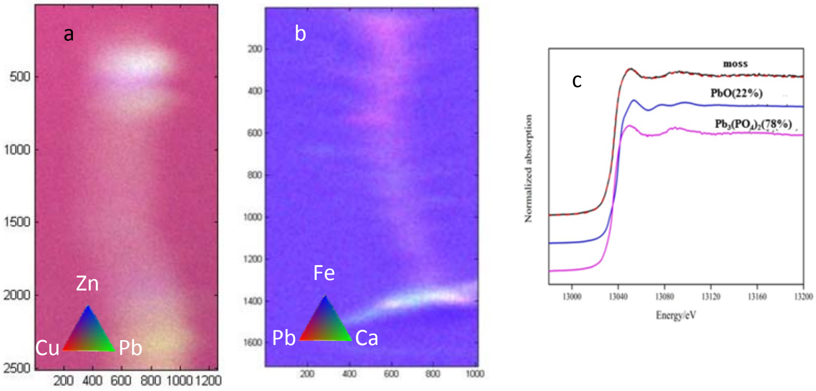

Fig.1 Localizations of Cu Pb and Zn in two moss species: *Hypnumplumaeforme(a)* and *Brachytheciumprocumbens(b)* collected from Pb-Zn mining, and Pb species in moss(c)

Research showed that the concentrations of Pb, Zn, Cd and As in the moss samples collected from the mining area were extremely high. The white color parts for 2D mapping(fig.1-a, b) showed that all three elements were extramally high in these areas. It can be observed that Fe and Ca mainly localized in root and bottom of dichasial branch. The shoots, especially the new tissues of the moss, were the major sites for accumulation and storage of heavy metals like Zn Pb and Cu. The micro-distribution characteristics varied between *Hypnumplumaeforme* and *Brachytheciumprocumbens*, indicating differeces in absorption pathway, accumulation and tolerance mechanisms for heavy metals between these two different moss species. Linear combination fitting results indicated that the main lead speciation in moss was $Pb_3(PO_3)_4$ and PbO, which suggested that the precipitation of $Pb_3(PO_3)_4$ might be the main mechanism of tolerance for moss(fig.1-c).

Bioaccumulation of heavy metals in Epiphytic Lichens: an emerging biomonitoring tool for assessing atmospheric pollution

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Alarming rise of gaseous particulate matter together with heavy metals in air has grossly deteriorated the environmental quality. The foremost step to assess the air quality of a place is to evaluate the status of the pollutant load in the environment, using tools and strategies where conditions and resource use continue to meet human needs, without undermining the integrity and stability of the natural systems. Biomonitoring is one such tool offering cost-effective and simple ways for evaluating the shift in environmental equilibrium. This work describes the potential of epiphytic lichens in accumulating trace elements and heavy metals from ambient air.

The lichen samples collected from the barks of roadside trees from different locations in and around Kolkata were subjected to elemental profiling using atomic techniques viz. Energy Dispersive X Ray Fluorescence (EDXRF) and Proton Induced X Ray Emission (PIXE) spectroscopy. Concentrations of elements like Fe, Ni, Cu, Zn and Pb are correlated with the pollution status of the respective sampling locations. The sites that are away from the city show comparatively less elemental accumulation than the ones prone to increased anthropogenic activities. The change in lichen abundance and diversity over a period of five years is distinctly noticeable. The mechanism of metal accumulation in the lichen thalli and its effect on the surface morphology of the concerned lichens are explored using scanning electron microscopy. Distortions and plasmolyses of photobiont cells together with concomitant increase in intra-cellular entrapment of particulate matter in the mycobiont component of the lichens are observed. The work highlights the importance of elemental profiling of epiphytic lichens and their physiological reactions in response to the accumulated heavy metals. The potential of these lichens as biomonitors and metal hyper-accumulator is discussed in the light of pollution mitigation vis-a-vis ecosystem homeostasis.

Evaluation of temporal evolution of Atmospheric Particulate Matter deposition on Built Heritage by means of Energy Dispersive X-ray fluorescence imaging

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Nowadays anthropogenic air pollution represents a serious risk for the preservation of Cultural Heritage, particularly for the ones located outdoors. The huge increase in automobile traffic and other emission sources has promoted a considerable rise in the levels of O_3, NO_x and Atmospheric Particulate Matter (APM). Dry deposition of suspended compounds in atmosphere over building materials is one of the most dangerous events that can promote different degradation processes on them. The sampling and collection of APM can be performed following different methods, as for example cascade impactors, which allow separating APM according to their size. However, in general terms, these devices are expensive and require regular maintenance. In addition, the study of APM deposition effects on buildings do not require APM separation by size.

In this work, an economic methodology to evaluate the impact of APM on Built Heritage has been developed using sample retainers usually devoted for the analysis of liquids by means of X-ray fluorescence spectrometry. The ability of this kind of surfaces to adsorb APM through months of exposure to the atmosphere has been explored. Different units of the retainer were mounted on a wood surface, previously covered by Mylar in order to prevent from contaminations, which was fixed to a wall of a construction with high historic and cultural value, Punta Begoña Galleries Getxo (Basque Country, North of Spain). The passive sampler was set the 1st of November 2016, and although the first retainer was collected 15 days later, one sampling was conducted each month until March 2017. Since then, one sampling per two months was carried out until September 2017. In each sampling, three retainers were randomly collected in order to have different replicates in each sampling. The collected filters were measured by means of µ-Energy Dispersive X-ray fluorescence spectrometry following an imaging strategy. Concretely the whole surface of each retainer was mapped at down to 25 µm of lateral resolution. In each cellulose filter, a square area of 33 x 33 mm^2 was analyzed. Once the square area was measured, the circular area of the filter was selected to eliminate part of the measured PET ring, and to obtain the sum spectrum of that circular area. With the spectral information, Fundamental Parameters-based quantification method was applied to extract the concentration of each element detected. With this information, it was possible to approach not only the semi-quantitative value of the concentration arriving per area of building, but also the temporal variations and tendencies of the deposited elements during almost one year of exposure to the atmosphere.

Characteristics of Aerosol Pollution in the Vicinity of an Oil Refinery near Rijeka, Croatia

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Fine aerosol pollution is one of the most important factors in air pollution monitoring. Industrial facilities are often significant sources of aerosol pollution in their areas, and therefore it is important to understand their impact on air quality.

In order to investigate contribution to the air pollution coming from the oil refinery, $PM_{2.5}$ (particulate matter with aerodynamic diameter smaller than 2.5 μm) samples were collected in the vicinity of oil refinery during one-year period. At the same time, $PM_{2.5}$ was sampled at an urban site in the city of Rijeka, Croatia, at a distance of about 10 km from the refinery. This site was used as a reference location. The sampling was performed with two cyclone samplers on thin polytetrafluoroethylene (PTFE) filters. Aerosols were sampled for 24 h every other day, simultaneously at both locations. In total, more than 350 samples were collected.

The samples were analyzed with X-Ray Fluorescence (XRF) and Particle Induced X-ray Emission (PIXE) to obtain concentrations of 22 elements from Na to Pb. Additionally, concentrations of black carbon were determined using Laser Integrated Plate Method (LIPM). It was found that concentrations of S, V and Ni, elements that are characteristic for oil burning, were substantially higher at the refinery sampling site in comparison to the reference location.

Obtained concentrations were statistically evaluated by performing Positive Matrix Factorization to obtain relative contributions of major pollution sources at both locations.

Effects of red mud on metals bioaccumulation in earthworms

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Red mud is a byproduct of bauxite refinement using the Bayer process in order to produce alumina. It is created in large quantities, which makes finding a location for storage problematic. Although it is not considered a hazardous waste by the US Environmental Protection Agency, it should be analyzed before use or deposition because of its high alkaline pH, high salinity, heavy metals content and possible increased radioactivity. Sometimes red mud is added to soil in order to modify its chemical and physical properties or even to immobilize toxic chemical elements in polluted soils. In this research we have investigated how the red mud amended soils affect earthworms, which are often examined as bioassays organisms in environmental studies. Tests were performed in laboratory conditions by using red mud originated from waste disposal sites in Croatia and Hungary in order to compare their effects on earthworms exposed to soil containing different quantities of red mud. Earthworm excretion and tissues were analyzed along with the content and bioavailability of elements in different soil/red mud combinations by using energy dispersive x-ray fluorescence. Excrements were collected from the moist filter paper and were mixed with double distilled water and filtered. Tissues were prepared by centrifuging the earthworms and collecting the residue. Bioavailable elements were analyzed after mixing the soil sample for 24 hours, separating the supernatant, lowering its pH, adding APDC and filtering.

Aerosol Metrology for Atmospheric Science and Air Quality: the AEROMET Project

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The EMPIR AEROMET project has the overall aim of developing and demonstrating methods for traceability and calibration of different aerosol instruments, with emphasis on environmental regulatory measurement. The relevant particle size range is from several nm up to 10 µm, mass concentrations (0.1 µg/m³ to 1000 µg/m³), number concentrations up to 106 particles per cm³ and airborne particle composition for such components as metals, anions, cations, elemental carbon and organic carbon. This involves the development of reproducible reference methods for PM10 and PM2.5, including the design and building of a demonstration aerosol chamber. Moreover, calibration procedures are going to develop for Mobility Particle Size Spectrometers (MPSS) for ambient measurements in the size range up to 1000 nm.

A key issue is to apply mobile x-ray spectroscopy techniques combined within particle sampling techniques to quantify particle compositions in the field in real time. The reference-free synchrotron-based Grazing Incidence X-Ray Fluorescence (GIXRF) methodology qualifies as a traceable reference for quantitative chemical aerosol analysis mobile and bench top GIXRF instrumentation. Full traceability is achieved by the use of fabricated micro and nanostructures. Additionally, traceable validated methods such as are established for the determination of major components of particulate matter such as elemental and organic carbon (EC/OC), total carbon, anions and cations and major metals (e.g. arsenic, cadmium, mercury, nickel), in order to meet the data quality objectives of current regulation. The presentation will aim to summarize the goals and challenges of the project, which is currently in its early stages, in order to encourage contributions from the wider community.

Bulk and Single-Grain Analyses of Thorium- and Uranium-bearing Mineral Allanite from Palawan, Philippines

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Uranium- and thorium-containing minerals serve as natural "analogues" of long-term nuclear radiation effects in high-level nuclear waste form [1]. The alpha-decay of thorium and uranium in the mineral can cause metamictization or degradation of the mineral's crystal structure and may affect its physical integrity and stability [2]. A better understanding on the structural properties of a natural analogue, particularly the long/short-range disorder due to alpha-irradiation effects in the mineral can provide useful information for studying long-term alpha-particle damage accumulation. Allanite (chemical formula: $(Ca,REE)_2(Fe^{2+},Fe^{3+})(Al, Fe^{3+})_2O[Si_2O_7][SiO4](OH)$; REE stands for rare-earth elements, La, Ce, Nd, Th and U), found in Palawan, Philippines was the natural analogue investigated in this study.

Mineral grains were carefully selected and grinded into powder for bulk analysis. Bulk techniques included Gamma-Ray Spectrometry, X-Ray Fluorescence Spectroscopy (XRF), and Inductively-Coupled Plasma Mass Spectrometer (ICP-MS) to determine chemical composition and correlated with the geological age; structural properties and degree of crystallinity was investigated by Powder X-Ray Diffraction (XRD), Fourier Transform InfraRed (FTIR), Mossbauer Effect Spectroscopy (MES), complemented by Scanning Electron Microscope (SEM).

For micro- or single grain analysis, sample grains were polished and prepared into thin sections. X-ray microprobe analysis was performed at the microXAS beamline at the Swiss Light Source (SLS). Micro-XRF and micro-XRD were simultaneously done on single grains to correlate the spatial composition with the crystallinity.

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Rapid analysis of minerals in breakfast cereals by Energy Dispersive X-Ray Fluorescence.

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Energy Dispersive–X-Ray Fluorescence (ED-XRF) is a well spread near-line analytical technique, suitable for easy and rapid measurement of major elements and/or trace elements especially in many different food matrices [1] such as infant cereals, milk based powders, powdered cocoa drinks, bouillons cubes, dry pet food and premixes.

This study intends to demonstrate the fitness for purpose of this method to ensure the correct addition of minerals during breakfast cereals production. Indeed, variations in process and in raw material mineral compositions may lead to values out of legal tolerance and thus quality controls need to be regularly performed as release criteria. Using such analytical technique close to production can allow controls that are more systematic as well as avoiding the shipment of numerous samples for reference method analyses to external laboratories. Thus, ED-XRF allows to ensure finished products compliance versus fortification declarations.

An ED-XRF commercial device from PANalytical (Epsilon 3XLE) was used during this study. With 7 minutes of analytical time for 2 replicates per sample, the developed method gave accurate results for the quantification of Na, Mg, Ca, Fe and Zn in breakfast cereals without any systematic and proportional biases between ED-XRF and reference method (Inductively Coupled Plasma- Atomic Emission Spectrometry) results.

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Capabilities of EDXRF for the determination of trace amounts of sulfur in biodiesel

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Knowledge of sulfur concentration in petroleum products is necessary for processing purposes since the quality of these products is affected by the amount of sulfur present. Bio-based fuels (biodiesel) are a promising alternative to fossil fuels due to their low-sulfur content, among other advantages. For sulfur determination in petroleum products, some standard methods are available such as the one recommended by the American Society of Testing Materials (ASTM D4294), which is based on the direct analysis of 5 mL of the liquid petroleum product in a disposable cell for the subsequent energy dispersive X-ray fluorescence (EDXRF) spectrometry analysis.

The aim of the present work is the development of a faster, simpler, more sensitive and more sustainable EDXRF method for the determination of trace amounts of sulfur in biodiesel samples. In this method, the deposition of several microliters of sample onto an organic thin layer and the analysis of the resulting dried biodiesel spot by benchtop EDXRF is proposed.

A careful study was performed to select the volume and the best solid support to deposit biodiesel samples, including filters made of different materials (glass fibre, Nylon, cellulose, paper) and a commercial disposable absorbent pad (UltraCarry, Rigaku). A critical issue that limits the use of most of these solid supports was the relative high background signals that hamper the determination of sulfur at trace levels. Finally, it was found that best strategy was the deposition of 50 µL of biodiesel on the UltraCarry sample retainer. Operating conditions for EDXRF measurements were also evaluated to obtain the best instrumental sensitivity for sulfur determination (Excitation: 20 kV, no primary filter, measurement time: 300s).

Using the best analytical conditions the detection limit of the method was 9.6 mg/kg of sulfur. This value is similar to the one reported in the ASTM D4294 method (LOQ: 16.0 mg/kg) but using a sample amount 100 times smaller. The linearity was confirmed in the range of 10-100 mg/kg by analysing a set of B100 biodiesel standards (CONOSTAN B100). Accuracy and precision of the results, evaluated by the analysis of calibration check samples at the level of 20, 40 and 75 mg/kg of S, was acceptable (Recoveries: 94.3-110.6%, RSD: 10.8-13.6%, n=3) for the intended purpose.

Overall, the performance of the method developed is promising and it could be used to determine trace amounts of sulfur in biodiesel samples in a simple, sustainable and cost-effective way. Furthermore, its non-destructive nature enables further analyses to be carried out.

ED-XRF determination of trace elements in vegetable raw materials and other light matrices for cosmetic applications

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The demand for natural ingredients in cosmetic products has grown significantly in the last decade and especially in the last few years. Marine algae, plant extracts and grinded leaves have become common ingredients of cosmetic formulations in make-up, skincare, coloration and haircare. These natural vegetables can naturally contain trace elements that have been taken up from their culture media (soil, water, sediment…) during their growth.

In order to guarantee formulator and consumer safety, cosmetic raw materials are monitored to verify that unavoidable trace element contents are as low as reasonably achievable. The techniques of choice for these elemental analysis are commonly ICP-OES/MS or FAAS combined to well-defined sample preparation methods. Although quite expensive and time-consuming, these techniques are well-suited for the analysis of synthetic raw materials since there is very little variation in the batch quality and random sampling is usually sufficient to guarantee quality control. On the other hand, the monitoring of trace elements in vegetable raw materials is complicated by the fact that the quality of batches can significantly vary as a function of the harvesting site, the nature of the soil or the quality of irrigation water. ED-XRF is particularly suited for quality control of vegetable raw materials in industrial applications, since it can provide a rapid, robust and precise enough method for the determination of trace elements with minimum sample preparation and little expertise required. Moreover, because of the organic nature of the matrix, sensibility is enhanced and inter-elemental interferences can be reasonably corrected.

This study focuses on the determination of trace element contents in several batches of Indigo, Cassia, Henna and algae extracts using an ED-XRF (SPECTRO XEPOS HE) by means of an excitation with a tube power of up to 50 W and a tube voltage of up to 60 kV. In order to increase the accuracy of the method, a first series of samples have been analyzed by ICP-MS and employed in calibration and a second set of samples with known concentrations have been used for validating purposes. This fast evaluation methodology can be applied for the control of other light-matrices used in cosmetic formulations.

Crude Oil Analysis By X-Ray Scattering Technique

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Composed of hydrocarbons and other substances, petroleum is classified as a non-renewable source of energy. In its unrefined form, it is called crude oil. Currently, its derivates are widely used in domestic and industrial environments, with the greatest exponent being motor fuels and lubricating oils [1-2]. Due to the overwhelming demand, new oil wells in the pre-salt region of Brazil are going to be drilled, which will, in its turn, increase the demand for analysis and require the use of less costly technologies. X-ray scattering is a technique that shows a high precision and accuracy in the quantitative analysis of low-Z elements in materials. As very low atomic number produce much Compton scattering, while elements of higher atomic number produce a larger proportion of Rayleigh scattering, the intensity ratio of the Rayleigh to Compton scattering (R/C) should be sensitive to small changes in the composition of samples [3]. The purpose of this paper is to present an experimental method that aims at characterizing crude oil samples through their X-ray scattering profiles without any chemical preparation, which enables this method to be used for analyzing samples just after their extraction. For the experiment, a portable X-Ray scattering system composed by an X-Ray tube (silver anode) and a SiPIN detector were used in order to analyze samples from different wells. The process consisted in establishing a linear relationship between the effective atomic number and the ratio between peak intensities of Compton and Rayleigh scattering from known density samples.

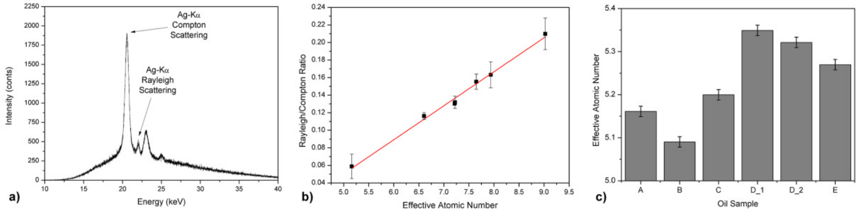

Figure 1 - a) Scattering spectrum, b) Linear correlation between the effective atomic number and R/C ratio and c) Characterization of the oil samples through their effective atomic number.

The linear function was then applied to samples of crude oil and the results showed that it is possible to characterize them based on the Rayleigh to Compton scattering ratio. After the analysis, a compatibility test performed on the samples proved that, through this methodology, it is possible to differentiate samples of different proveniences and to verify the compatibility of samples extracted from the same well.

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Applications of reference-free X-ray spectrometry towards the development of 3D heterogeneous integration technology

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The 3D integration of circuits and devices is one of the key topics in today's microelectronic industry and future development in this sector require for advanced metrology tools. At the Physikalische-Technische Bundesanstalt, Germany´s national metrology institute, reference-free X-ray spectrometry methodologies [1,2] are applied to different metrological aspects from the field of 3D systems integration.

One example is metal to metal wafer bonding, which is a key technique from this field and requires clean and oxide free metal surfaces. In Under Bump Metallization (UBM) processes in which the die is connected to the substrate, the possible formation of voids, observed for Cu, can affect the reliability of the electronic package. Co and Ni, on the other hand present a lower yield in stacking experiments due to incomplete bonding to or easier debonding from the wafer. A possible reason is the formation of metal oxides prior to the bonding which hinders the formation of an intermetallic compound (IMC). In this view the oxidation over time of Co, Ni and Cu surfaces was studied using a variety of X-ray spectrometry techniques. Reference-free XRF was used to quantify the amount of O at the metal layer surface, the distribution of the O atoms can be modeled using results provided by GIXRF and the oxide formed at the surface can be studied using the results from XANES measurements at the metallic L-edges and comparing them to calculations in order to reveal the metallic oxidation state. Finally, the combination of all the three named methodologies is expected to provide a full characterization substrate and die interfaces.

Considering the non-destructive character of the X-ray spectrometric techniques, the presented experiments will demonstrate the potential to contribute eventually to the metrology for in-line process control measurements for the different 3D integration technologies.

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Elemental analysis of powdered dietary supplements by X-ray spectroscopy techniques

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During recent years, consumption of healthy food, and medicinal products, such as dietary supplements, obtained from plants or other natural resources has increased in almost all the countries in Europe. Nowadays, the utilization of multivitamins or multimineral preparations is widely spread in order to increase the daily intake of essential micronutrient. In the United States, it has been estimated that approximately 45% of the population consumes vitamins and/or mineral preparations.

Dietary supplements are defined as products that increase the total dietary intake of minerals, essential elements, vitamins, amino acids and mixtures or any metabolite helpful to human health. These products can be found in the form or gelcaps, tablets, liquids, capsules or powders. These dietary supplements are generally used without prescriptions, proper counselling or any awareness of their health risk. Most of these products that are on the market contain between 8 and 12 different chemical elements such as calcium, iron, manganese, zinc, copper, chromium, magnesium, phosphorus, potassium, magnesium, molybdenum, selenium and iodine. Also additional elemental impurities can be found.

Most of these elements (i.e. Ca, Fe, Mn, Cu and Zn) are of great importance to our daily body functions due to their physiological and biological roles, by its role as cofactor of a larger number of enzymes, or by their implication in the prevention of specific diseases. Some other elements (such Mo, Se or Cr) are essential minerals, involved in the production of antioxidant enzymes. However, an increase or chronicity in intake above recommended limit and daily allowance (RDA) may result in toxic effects, producing weakness of the immune system, neurotoxic threat and other pathological effects.

The current study aimed at analysing the elemental chemistry of powdered dietary supplements consumed in Spain and Portugal, using different X-ray based spectroscopy methods (EDXRF, TXRF, XRD) for a faster, simpler and sensitive multielemental analysis of powdered dietary supplements.

X-ray excited optical luminescence analyzer for on-line analysis of nonmetallic inclusions in steel

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The analysis of nonmetallic inclusions in steel is important to ensure its quality because nonmetallic inclusions lead to various defects such as breakage of steel wires during drawing, hydrogen-induced cracking, and fatigue failure[1]. An analytical method combined with optical microscopes and electron probe microanalysis (EPMA) is conventionally used for the analysis of nonmetallic inclusions. This analysis is the time-consuming process in the steelmaking because it takes approximately 1 week to complete this analysis for a single sample. In the present study, we applied X-ray excited optical luminescence (XEOL) phenomenon, that is light emission from materials as a result of X-ray irradiation, to the analysis of nonmetallic inclusions in steel[2]. XEOL analysis has potential in the on-line analysis of nonmetallic inclusions because XEOL can be performed in air, which would contribute to the reduction of the analysis time of nonmetallic inclusions. A model sample containing $MgAl_2O_4$ and Al_2O_3 inclusions was measured using an XEOL analyzer shown in Fig. 1 because $MgAl_2O_4$ and Al_2O_3 generate are one of the most harmful inclusions in steel. The voltage and current of the X-ray tube was set to 20 kV and 150 μA, respectively. The sample was prepared by pressing mixture of copper, $MgAl_2O_4$ and Al_2O_3 powder reagents into a form of disc. XEOL image of the sample was captured with a digital single-lens reflex camera equipped with a zoom lens for 30 s. We detected particles emitting green or blue luminescence as shown in Fig. 2. The particles producing green and blue luminescence were confirmed to be $MgAl_2O_4$ and Al_2O_3, respectively, by energy-dispersive X-ray (EDX) point analysis. This result indicates that XEOL analysis can detect nonmetallic inclusions in air.

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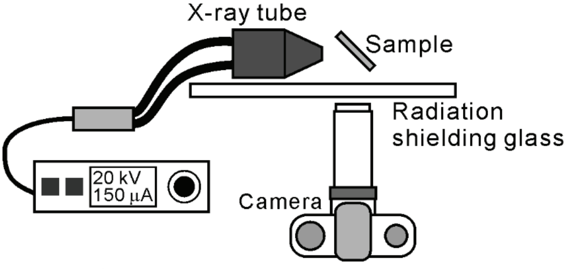

Figure 1. Schematic view of XEOL analyzer.

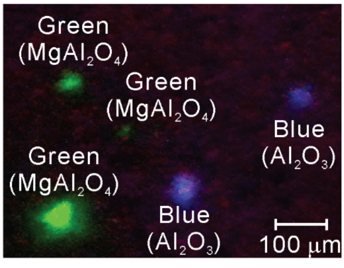

Figure2. XEOL image of the sample.

Evaluation of Valence Identification Performance of Polychromatic Simultaneous WDXRF and Application to Lithium-ion Batteries

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A polychromatic simultaneous WDXRF spectrometer is a new scanning-free WDXRF spectrometer for laboratory use, which possesses a high energy resolution of 3.9 eV for Fe $K\alpha_1$, and is capable of valence identification of 3d transition elements [1]. The authors evaluated the valence identification precision of the spectrometer with three different valence manganese oxides. After confirming that the same performance can be obtained for lithium manganese oxides used in manganese-based lithium-ion batteries (LIBs), it was applied to the evaluation of valence change depending on charge and discharge of the LIB.

All experiments were performed under vacuum with an X-ray tube of 20 kV and 100 mA. The standard deviation for five measurements was calculated, and used for the error bar. As shown in Figure 1, the Mn $K\beta_{1,3}$ peak energies of manganese oxides were negatively proportional to the valence, and those of lithium manganese oxides also showed a similar relationship. Based on these data, the valence change of a LIB was investigated. Figure 2 shows that the valence of Mn in $LiMn_2O_4$, which is the raw cathode material for LIBs, increases depending on the state of charge (SOC) of the LIB.

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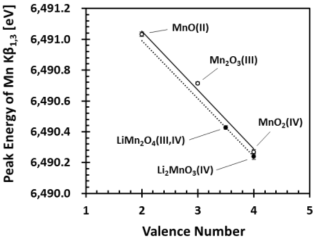

Figure 1. Dependence of Mn $K\beta_{1,3}$ peak energy on the valence number.

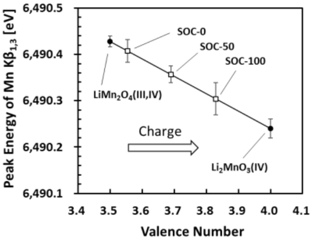

Figure 2. Valence change of Mn in a LIB cathode material depending on the state of charge (SOC).

Using of SK$\alpha_{1,2}$ and SK$\beta_{1,3}$ lines chemical shift for routine sulfur speciation analysis by WDXRF

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Besides the determination of total elemental concentrations, XRF method can be efficiently used for the sulfur speciation in samples of environmental and geological interest using measurements of the changes in the intensity of satellite lines relative to the diagram lines [1-3]. Measurement of line intensities ratios need no high resolution instrumentation and can be carried out using conventional XRF spectrometer. However in sulphide ore analysis spectral overlap of lead spectrum M-series lines can significantly distort analytical. The chemical shift significantly decreases accuracy of XRF determination of total sulphur, and nevertheless it can be used for the sulphur chemical state determination. For the SK$\alpha_{1,2}$ and SK$\beta_{1,3}$ lines chemical shift measurement high resolution spectrometers with Johansson and von Hamos geometry is used [4, 5]. This paper considers the investigation of SK$\alpha_{1,2}$ and SK$\beta_{1,3}$ lines chemical shift by conventional XRF spectrometer S8 Tiger (Bruker AXS, Germany) equipped with the Soller optical system.

To study the influence of sulfur speciation on the energy of XRF lines we applied the set of compounds representing basic chemical states of sulfur. To eliminate the cation influence we used only sodium compounds (sulphate, sulphite, thiosulphate and sulphide). Samples were prepared as pressed pellets on the boric acid substrate. The spectrometer's resolution is not enough to quantitative estimate shift value therefore to clearly recognize the differences in peak energy we applied the approach earlier successfully employed for manganese and iron spectra [7, 8]. The intensities of obtained spectra were normalized per intensity maximum of elemental sulphur spectrum, divided by the values of intensity measured in the position of elemental sulphur peak and then multiplied by the values of elemental sulphur intensity measured in peak position. This approach allows to find positions of spectrum, wherein intensity is proportional to SK$\alpha_{1,2}$ and SK$\beta_{1,3}$ lines chemical shift. Obtained data were applied for estimation of sulfur chemical state in Au-bearing ores. Comparison with gravimetric data showed that proposed XRF technique can be used to quantify the average sulfur chemical state.

The research was performed using equipment of the SB RAS Joint use centers (Geodynamics and Geochronology, Isotope-geochemical Research).

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WDXRF analysis of peat sediments

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Peat sediments are a potential archive for reconstructing the boreal zone environment with continuous permafrost. To estimate the climate control on weathering intensity, degree of sediment maturity the chemical and some other changes of environmental conditions it is advised to employ the geochemical modules based on quantification of major oxides. The X-ray fluorescence core scanner is mainly applied for the peat sediments wet cores analysis [1, 2]. However, it does not always provide sufficient accuracy in determination of rock-forming elements.

The authors made an effort to analyze peat sediments with wavelength-dispersive X-ray fluorescence (WDXRF) method using two sample preparation techniques. The method of homogenization by fusion has proved high accuracy of the rock-forming elements (Na, Mg, Al, Si, P, K, Ca, Ti, Mn and Fe) content determination in igneous rocks [3]. However wide variations of organic components can prevent full homogenization and affect results of peat sediments analysis. When analyzing the powder, the stages of grinding and pressing might contribute to the error in analytical results. Even stabilized conditions of peat sediment grinding may not provide consistency of granulometric composition. Using certified reference materials of silt, bottom and river sediments, the twenty one peat samples from the Sentsa River valley (Republic of Buryatia) were prepared by two techniques and analyzed by the WDXRF spectrometer S8 Tiger (Bruker AXS, Germany) equipped with 8 mm mask for small-sized sample analysis. For lack of reference materials of peat with certified content of rock-forming elements, obtained data were compared with the results of flame photometry, spectrophotometry and atomic absorption analysis. The WDXRF analysis errors reached 10 rel. % for fused and 25 rel. % for pressed samples.

The geochemical modules were assessed with acquired data. Together with the results of palynological analysis, it can become the basis for high-resolution paleoclimatic reconstructions of regional environment and climate changes.

The research was performed using equipment of the SB RAS Joint use centers (Geodynamics and Geochronology, Isotope-geochemical Research) and with Russian Science Foundation (Grants 16-17-10079, 17-77-10118) and Russian Foundation for Basic Research (Grants 15-05-01644, 16-35-00235) funding.

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WDXRF determination of the manganese valence state in Co-bearing ferromanganese crusts

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A complex study of the world ocean Co-bearing ferromanganese crusts is the necessary condition for further industrial development of this valuable ore. The important characteristic of the ferromanganese crusts is the data on the valence state and speciation of elements. The classical titration method usually applied to characterize the manganese oxidation state in nodules and crusts is laborious. The wavelength-dispersive X-ray fluorescence (WDXRF) method is widely used to analyze the elemental composition of geological objects [1]. A number of studies have shown that the parameters of XRF spectra are influenced by the manganese valence state and speciation. The most sensitive parameters for the average manganese valence state estimation are the relative intensities of the $MnK\beta_5$ line and the $MnK\beta'$ satellite [2-4]. In presented work we applied XRF method to determine the manganese valence state in Co-bearing ferromanganese crusts.

The measurements were carried out by a wavelength-dispersive X-ray fluorescence spectrometer S4 Pioneer (Bruker AXS). Certified reference materials of ferromanganese nodules, cobalt-manganese crusts, manganese and iron-manganese ores were dried at a temperature of 120 °C to remove hygroscopic moisture and pressed onto a substrate of boric acid. The total manganese and MnO_2 contents were certified, it allowed to calculate the average manganese valence state. The dependence of the manganese valence state on the relative intensities of the $MnK\beta_5$ line and the $MnK\beta'$ satellite was approximated by a polynomial equation which includes term proportional to the total iron content. Analysis by the titrimetric method showed that proposed XRF technique can be used to quantify the average manganese valence state. We analyzed 31 samples of Co-bearing ferromanganese crusts collected by Dr. Igor Peretyazhko on Govorov and Kotzebue guyots (Magellan seamounts). According to XRF data the average manganese valence state in analyzed samples varies from 3.62 to 4.00. Obtained analytical data has allowed to study the relationship between the layer concentrations of ore and impurity elements in Co-bearing ferromanganese crusts with oxidation-reduction conditions of their formation. The use of a single XRF method for elemental composition and speciation of elements determination allows expressly and with high productivity analyze samples of ferromanganese crusts.

The research was performed using equipment of the SB RAS Joint use centers (Geodynamics and Geochronology, Isotope-geochemical Research).

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Influence of Contamination Layer on Thickness Evaluation by X-ray Reflectometry

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Continued progress in characterization methods for nanomaterials is required in the field of production and R&D. One of the most fundamental structures of the nanomaterials is thin and multilayer films and then their thickness is an important parameter of their properties as well as their composition, density and surface/interface roughness of each layer. X-ray reflectometry (XRR) is a powerful tool for thickness evaluation of thin and multilayer films. We have studied in order to improve the thickness measurement technique with high accuracy and precision by using XRR. The main source of the uncertainty of thickness evaluation arises from the sample imperfection, not from the mechanical accuracy, precision and stability of the XRR apparatus. In the analysis process of the data, the model structure for the calculation is assumed and it is not necessarily good agreement with the actual structure. Furthermore, the surface changes caused by a surface contamination and a growing the surface oxide layer have to be paid attentions. In this study, we investigated the negative effect due to surface contamination for thickness evaluation with nanoscale accuracy. Technical guidelines for the thickness metrology by XRR will be established from this study.

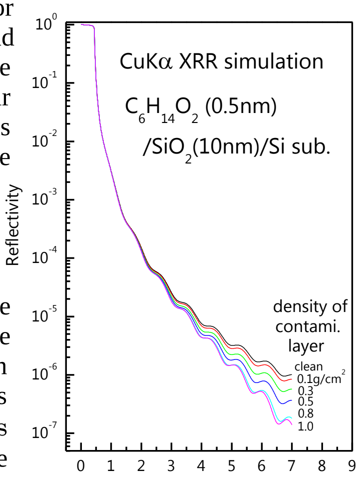

Fig. 1 XRR simulation results of contaminated SiO_2 film on Si sub.

Table 1 Evaluated thickness from contamination free model

density (g/cm^2)	evaluated thickness (nm)	Δd (nm)
0.1	10.02	0.02
0.3	10.05	0.05
0.5	10.09	0.10
0.8	10.16	0.17
1.0	10.23	0.24

Figure 1 shows XRR simulation results of a contaminated SiO_2 film (10 nm, 2.2 g/cm^3) on Si substrate (2.3 g/cm^3) with Cu Kα. $C_6H_{14}O_2$ (0.5 nm) film is assumed as the contamination layer and its density was varied from 0.1 to 1.0 g/cm^3. The XRR profile varies in accordance with the density value of the contamination layer. If an analysist does not notice the existence of the contaminants or ignore it, these data are analyzed by a contamination free structural model (SiO_2 film on Si sub.). Table 1 summarizes the analysis results for each data from the contamination free model. The evaluated thicknesses of the SiO_2 layer are slightly larger than the original thickness (10 nm). The difference of the thicknesses (Δd) is in proportion to the ratio of the density between the contamination and the SiO_2 layer. This result indicates that the influence of contamination layer on thickness evaluation is limited in the case for the low-density contamination layer. The actual measurement and the analysis results for contaminated samples will be presented and discussed at the conference.

Structural determination of LASSBio-1860: a new lead-compound candidate of the *N*-acylhydrazone class

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LASSBio-1860 is *N*-acylhydrazonic derivative inhibitor of phosphodiesterase type 4 (PDE4). This enzyme plays a major role in modulating the activity of virtually all cells involved in the inflammatory process acting in the control of cAMP levels [1]. This compound was planned and synthesized in Laboratory of Evaluation and Synthesis of Bioactive Substances – LASSBio® as part of a research program to develop a series of compounds with anti-inflammatory activities. As important as the planning and synthesis of new drugs is its structural characterization, since its structure may be related to a biological activity.

In this work we determined the crystal structure of LASSBio-1860 compound using X-ray powder diffraction (XRPD) that has been a very important tool in the structural determination of new synthesized compounds. XRPD data were used for indexing with the Topas Academic v.5 software program [2], a simulated annealing algorithm implemented in the DASH software program [3] were used to determine the crystal structure of LASSBio-1860, on the basis of previous procedures [4,5] and a Rietveld refinement of the final crystal structure was conducted using the Topas Academic v.5 software program [2].

Our preliminary results showed that LASSBio-1860 crystallized in a monoclinic system (*P21/c*) and the crystal structure consists of four formula units per unit cell ($Z = 4$), thus accommodating four molecules in the asymmetric unit ($Z' = 1$). Rietveld plot of LASSBio-1860 showed the good agreement between the experimental data and the calculated profile and the goodness-of-fit indicator as well as R-factors were $\chi^2 = 3.931$, $R_{\text{Bragg}} = 1.448\%$, $R_{\text{wp}} = 4.482\%$ and $R_{\text{exp}} = 1.140\%$.

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CRYSTAL STRUCTURE DETERMINATION OF A BIOACTIVE *N*-ACYLHYDRAZONE: LASSBIO-129

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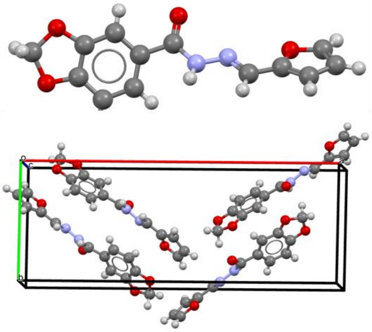
The complete knowledge of a crystal structure, including stereochemistry, is essential for lead optimization in drug discovery. The methodology of structure determination from X-ray diffraction data has been employed as a tool able to define the configurational and conformational aspects of new bioactive compounds, which are directly related to the biological activity. In this work, X-ray powder diffraction (XRPD) were used to carry out the crystal structure determination of LASSBio-129, which was initially obtained as part of a project of synthesis of novel anti-inflammatory and analgesic leads with a *N*-acylhydrazone scaffold. LASSio-129 presented a platelet anti-aggregant prototype, with significant activity. This compound, at 100 μM concentration, was able to significantly inhibit (72.1%) the arachidonic acid-induced platelet aggregation (200 μM) in rabbit citrate-rich platelet plasma [1,2]. This compound is an isoster of LASSBio-294 and they differ from each other only by a furanic ring in place of the thiophene ring. In order to evaluate the contribution of isosterism, for the conformational aspects and the activities of these compounds, powder XRPD data of LASSBio-129 were used to determine its crystal structure, according to a procedure described previously [3].

The measurement was performed at room temperature on a Stoe STADI-P powder diffractometer in transmission geometry by using a Cu$K\alpha_1$ (λ = 1.54056 Å) wavelength. LASSBio-129 crystallizes in an orthorhombic crystal system, space group $P2_12_12_1$, with unit-cell dimensions a = 24.5603(11) Å, b = 9.28285(27) Å, c = 5.06822(16) Å and V = 1155.502(70) Å^3. The crystal structure is comprised by four formula units per unit cell (Z = 4), accommodating one molecule in the asymmetric unit (Z´ = 1). The goodness-of-fit indicator and R-factors were, respectively: χ^2 = 1.848, R_{Bragg} = 1.381%, R_{wp} = 5.308% and R_{exp} = 2.872%. Additionally, other experimental techniques were employed in characterization of this compound.



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Chemical elements in soil, grapevine and wine in selected Croatian vineyard regions

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It has been found that grape of different grapevine varieties are better at a certain type of soil, respectively at a certain location. Such a relationship between soil and wine is the fundamental concept of "terroir" (a complete natural environment to which certain wine is produced, including factors such as soil, topography, climates, etc.). The purpose of this research was to establish the possibility of the authentication of the geographical origin of wine by knowing the concentration of chemical elements in soil and wine. Small and medium-sized vineyards with Croatian most known sorts Plavac mali (especially Dingac and Postup), Posip and Zlahtina have been sampled for research. Chemical elements K, Ca, Mn, Fe, Ni, Cu, Zn, Ga, As, Rb, Sr, Zr, Pb and Th in soil, pulverized grapevine and wine pre-concentrated by freeze drying will be analysed by EDXRF technique with the goal to determine: i) if the elemental composition of grapevine and wine can be linked to corresponding soil and therefore to its geographic origin; ii) which chemical elements are the best discriminators for determination of wine provenance; and iii) the extent of the anthropogenic influence on the elemental composition of grapevine and wine, predominantly by usage of various protective chemical agents. Determining the geographical origin of wine is of great importance to consumers and producers since this can be a decisive criterion that guarantees quality.

12 Friday program

	Marmorna Hall 1	Marmorna Hall 2
	Chair: W. Malzer	
9:00	Invited: **25 years of aerosol studies by PIXE and complementary techniques at LABEC** *F. Lucarelli* (p. 337)	
9:30	Invited: **Contribution of X-ray fluorescence spectrometry in graphical documents characterization** *M. Manso* (p. 338)	
	Session X: XRS APPLICATIONS IN ADVANCED MATERIALS AND NANOSCIENCE Chair: W. Malzer	Session XI: XRS APPLICATIONS IN EARTH AND ENVIRONMENT Chair: M. Žitnik
10:00	**Operando near sulfur K-edge X-ray absorption spectrometry of Li-S battery coin cells** *C. Zech* (p. 339)	**Elemental Characterization of $\mathrm{PM}_{2.5}$ in Nairobi, Kenya by PIXE Technique** *J. Boman* (p. 346)
10:15	**Operando SXM study of rechargeable Zn-air battery anodes in deep-eutectic solvent electrolyte** *M. Kazemian Abyaneh* (p. 340)	**Elemental composition of ambient particulate matter in two Asian megacities measured with a near real time XRF spectrometer** *R. Pragati* (p. 347)
10:30	**Application of Total Reflection X-Ray Fluorescence for the Investigation of Transition Metal Dissolution in the Field of Lithium Ion Batteries** *M. Evertz* (p. 341)	**Non-destructive characterization of airborne particulate matter by combination of cascade impactor sampling and total-reflection X-ray fluorescence related methods** *J. Osán* (p. 348)
10:45	**Coupling operando absorption tomography and X-ray diffraction computed tomography characterization for lithium/sulfur batteries** *G. Tonin* (p. 342)	**Characterization of ambient PM10 dust in industrial locations by continuous fence-line ED-XRF analysis** *H. Indresand* (p. 349)
11:00	Coffee Break	

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	Session XII: XRS applications in industrial quality and process control Chair: R. Van Grieken	Session XIII: XRS Instrumentation II.(X-ray sources, optics and detectors) Chair: T. Jach
11:30	**Applying X-ray spectroscopy to assess chemical elements and inorganic compounds in Eye Shadow Cosmetics** *I. Queralt* (p. 343)	**IAEA Nuclear Science and Spectrometry laboratory: Support to XRF laboratories and recent applications** *R. Padilla* (p. 350)
11:45	**Traceable characterisation of calibration samples for advanced thin film materials by reference-free X-ray spectrometry** *C. Streeck* (p. 344)	**HPC-detectors for X-ray spectroscopy** *D. Sisak Jung* (p. 351)
12:00	**Real-time Monitoring of Precious Metals in Slurries: Problems and Solutions** *Y. Van Haarlem* (p. 345)	**ARDESIA: a 4-Channels Fast SDD X-ray Spectrometer** *M. Carminati* (p. 352)
12:15	Closing	

25 years of aerosol studies by PIXE and complementary techniques at LABEC

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At the 3 MV Tandetron accelerator of the LABEC laboratory of INFN (Florence, Italy) an external beam facility is fully dedicated to PIXE-PIGE measurements of elemental composition of atmospheric aerosols. All the elements with Z > 10 are simultaneously detected by PIXE typically one minute. This setup allows us an easy automatic positioning, changing and scanning of samples collected by different kinds of devices: long series of daily PM_X samples can be analysed in short times, as well as size-segregated and high time-resolution aerosol samples.

Thanks to the capability of detecting all the crustal elements, PIXE-PIGE analyses are unrivalled in the study of mineral dust: as a consequence they are very effective in the study of natural aerosols, like, for example, Saharan dust intrusions.

Among detectable elements there are also important markers of anthropogenic sources, which allow effective source apportionment studies in polluted urban environments by the use of multivariate method like Positive Matrix Factorization (PMF).

Examples regarding monitoring campaigns, performed in urban and remote areas, both on a daily basis and with high time resolution (hourly samples), as well as with size selection, will be presented. The importance of the combined use of Particle Induced Gamma Ray emission technique (PIGE) and of other complementary (nuclear or not) techniques will be highlighted.

Contribution of X-ray fluorescence spectrometry in graphical documents characterization

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Paper and parchment have been for centuries the support of artistic and historical evidence. The analytical study of these supports and coloring materials gives historians and conservators the possibility of obtaining information on its material composition. This information not only helps in its safeguard but also in the comprehension of the artistic methodology of production, in the provenance and in the authentication issues and in the retrieval of hidden documents. X-ray fluorescence (XRF) is a suitable technique for the study of graphical documents due to its non-destructive character. It gives a quick highlight over the elements with a $Z>12$, allowing its identification and quantification in supports and coloring materials. The research group has been developing XRF setups with different characteristics according to the needs of each heritage object type [1, 2]. Triaxial geometry equipment present a great advantage in the analysis of trace elements in low-Z matrix objects such as paper and parchment documents. This geometry significantly reduces the background of the measured spectra by eliminating the Bremsstrahlung produced in the X-ray tube through crossed polarization in the secondary target and in the sample. In this way, a better peak-to-background ratio is obtained, improving the detection limits and leading to higher sensitivity. Portable XRF setups are mostly required for in-situ analysis of graphical documents that are not allowed to leave the museums or archives. In X-ray fluorescence spectrometry, the use of quantitative methods, independent of geometric and physical factors requires the use of standards of known composition, which should be as similar as possible to the unknown sample. The accuracy of this method depends on the number of standard samples used in the quantification and on the similarity of their composition with the unknown sample. A paper standards database consisting of well-known elemental composition paper samples is under construction enabling the elemental content determination of paper documents [3]. In this talk, the most relevant work developed by the research group, concerning XRF setups development and quantitative methodologies applied to the study of graphical documents, will be presented.

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Operando near sulfur K-edge X-ray absorption spectrometry of Li-S battery coin cells

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The complete understanding of the functionality of battery components requires the correlation with underlying physical and chemical properties which is the challenge for most analytical methods due to a lack of reference materials. Lithium Sulfur (Li-S) batteries are promising candidates for improved batteries offering up to 5 times higher capacity than conventional lithium ion batteries. The main degradation is caused by polysulfides formed during cycling which are soluble in the electrolyte solution. For a better understanding of this process in-situ and operando characterization techniques are required [1].

We use CR-2032 coin-cell formed Li-S batteries with DOL/DME (1:1 wt.%) 1 Mol TFSI electrolyte modified with thin cathode current collector and thin window enabling the transmission of excitation and fluorescence radiation. SI traceable X-ray spectrometric measurements were performed using radiometrically calibrated instrumentation in the PTB laboratory at BESSY II synchrotron radiation facility. By means of operando near sulfur K-edge X-ray absorption spectrometry (NEXAFS) recorded during galvanostatic cycling with potential limitation (GCPL) measurements we could determine the different sulfur species in the cell.

For 8 full charge/discharge cycles (0.1 C) operando sulphur K-edge NEXAFS could be registered. After spectral deconvolution the different sulfur species and their behavior over time were analyzed. While for the first cycles a reversible formation of polsulfides is visible further cycles show a steady increase of polysulfides due to the solubility in the electrolyte solution and, thus, the loss of cathode active material and capacity fading.

The investigation of polysulfides for different states of charges (SOC) and state of health (SOH) enables a deeper understanding of the main degradation process. This information helps to improve the battery system by modifying its materials e.g. with binder components or by choosing an optimal (dis-)charge current. The simple set-up enables also investigations from the anode side. In addition, the-set up can be adapted for different types of batteries with other active materials, e.g. NCM Li-Ion batteries.

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Operando SXM study of rechargeable Zn-air battery anodes in deep-eutectic solvent electrolyte

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The steady increase of electrical energy demand brings into the spotlight ethical, environmental, societal and political concerns related to the usage of fossil fuels. Renewable sources could replace hydrocarbons, but sustainability imposes the integration with reliable and efficient energy storage (EES) facilities. Electrochemistry is playing a key role in the quest for the definitive EES device and, among diverse electrochemical storage concepts, Zn–air batteries (ZAB) exhibit storage potentialities ranging from low-power portable consumer electronics, to automotion, home and grid applications. Aqueous chemistries have been extensively investigated and show high potentialities for primary devices, while serious drawbacks are delaying the full-scale development of secondary concepts. The use of non-aqueous solvents, such as deep eutectic solvents, is highly promising for electrically rechargeable systems.

The present research is the first operando SXM study of cathodic and anodic processes of Zn electrochemical phase formation from a choline-chloride/urea deep eutectic solvent (DES) electrolyte. High-resolution SXM images have been acquired in two modes: (i) dynamic mode at a fixed beam energy, allowing to follow morphology development under electrochemical control; (ii) acquisition of stacks of images by scanning the photon energy across the Zn L-edge, with static morphologies obtained after appropriate growth steps. Our operando measurements employed a novel wet cell, improving the design and filling protocol of earlier-generation cells developed by the same authors [1,2]. In order to calibrate the electrochemical conditions, we have performed classical cyclic voltammetry measurements in the wet cell, showing clear under- and overpotential Zn electrodeposition and stripping. The DES reactivity in the operating potential range is negligible.

In this work we have proved for the first time the possibility of mapping the distribution of Zn in situ during electrodeposition and corrosion. Unstable growth features have been followed dynamically and the local cathodic current density distribution has been correlated with the development of SXM images. These results provide fundamental information for the control of dendrite development, a process not only of general interest in electrometallurgy, but also specifically exhibiting a notable impact on battery durability. Moreover, successful operation of our wet cells has provided useful information for the development of a fully microfluidic device.

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Application of Total Reflection X-Ray Fluorescence for the Investigation of Transition Metal Dissolution in the Field of Lithium Ion Batteries

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The state-of-the-art Lithium Ion Battery (LIB) negative electrodes consist of graphite with a decent capacity 372 mAh g^{-1} and lithium transition metal oxides ($LiMO_2$) as positive electrodes supplying capacities of around 150 mAh g^{-1} (M = Mn, Co, Ni). One common material is the class of layered transition metal oxides with different benefits and drawbacks, e.g. increased capacities in the charged state and high thermal stability.[1] On the other hand, these materials suffer from fading capacities during continuous cycling, especially at elevated charge cut-off voltages exceeding 4.4 V, which cause is still a matter of discussion in literature.[2,3]
One postulated cause is assigned to the dissolution of transition metals - originating from the positive electrode – which claims to have a negative influence on the surface of the solid electrolyte interphase (SEI) as it leads to cracking of this. This would result in a loss of available active lithium as well as loss of active cathode material, resulting in steady capacity decrease.[2,3]

In order to examine transition metal deposition on negative electrodes and other cell components, a versatile and robust tool for the detection of transition metals is desirable. Here, the x-ray fluorescence in the setup of total reflection (TXRF) is a powerful tool for the bulk detection of transition metals in carbonaceous anode materials as well as on lithium metal and in the electrolyte.[3]
In this work, several active layered transition metal oxides (NCM111, NCM532, NCM622, NCM811 and NCA) were cycled *vs.* Li/Li^+ and investigated based on their transition metal dissolution. Therefore, TXRF was applied to quantify deposited content of transition metals in cycled lithium metal half cells. Furthermore, all other cell components – separator and electrolyte – were quantified on their transition metals content using the TXRF. Additionally, a previously developed method for the quantification of TMD on carbonaceous anodes was successfully applied.

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Coupling *operando* absorption tomography and X-ray diffraction computed tomography characterization for lithium/sulfur batteries

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Lithium-sulfur (Li/S) batteries among the most promising candidates for replacing conventional Li-ion batteries for future energy storage systems, due to their higher theoretical specific capacity, and to the abundance and low cost of their constituent materials. Li/S cells transport energy via a series of complex electrochemical processes between solid and soluble sulphide species during charge and discharge. This causes serious morphological change in the positive electrode upon cycling and leads to a gradual decrease of the performances [1].

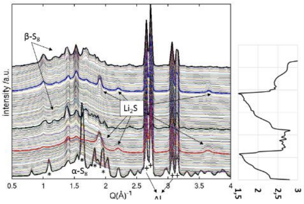
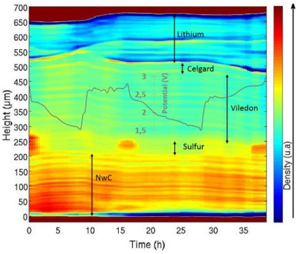


Figure 2 : XRD patterns evolution of sulfur positive electrode as a function of time and state of charge.

In situ and *operando* X-ray diffraction techniques have proven to be interesting characterization tools [2] to map sulfur based crystalline products on the positive electrode with temporal resolution. In addition, X-ray absorption tomography allows changes in the global morphology of the electrodes to be studied upon cycling [3].

Figure 1 : Temporal and spatial evolution of absorption tomography data during two first cycles.



Recently [4], we combined X-ray absorption tomography and spatially resolved X-ray diffraction to study the time evolution of working batteries. Here, we will report on an extension of that work, in which the combination with X-ray diffraction computed tomography (XRDCT) to produce time resolved 3-dimensional maps by both techniques and obtain information at different length scales and resolutions, allowing the extraction of important parameters of the dynamic processes.

The combination of electrochemistry, absorption tomography and XRDCT allows the correlation of macroscopic to microscopic phenomena in whole batteries under true operando conditions. We believe that such characterization tool could be applied by material scientists while designing and characterizing new solutions developed for Li/S cells.

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Applying X-ray spectroscopy to assess chemical elements and inorganic compounds in Eye Shadow Cosmetics

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Cosmetic materials are usual consumer products consisting of various organic and inorganic substances. Among these products, eye shadow is the typical example of a group of cosmetic products in which the significance of pigments is great. Heavy metals are usually found in eyeshadows as a part of pigmenting agents or as impurities of raw materials used in its formulation. Some potentially toxic elements and their compounds are water-soluble and moist skin can therefore promote the percutaneous absorption of elements added intentionally or occurring as impurities in the pigments used for manufacture. Excipients and inorganic fillers used can also affect the absorption through the skin. The skin of the eyelids is thin and eczemas of the eyelids have been reported for a long time in sensitive and allergic people [1].

Safety and quality are essential for the manufacture of personal care products and end consumers are increasingly demanding proof of quality, compliance and efficacy from raw materials to finished products. According the Cosmetics EU Directive [2], personal care products and their ingredients have to be safe under conditions of normal use and must be thoroughly evaluated for their safety prior to their marketing. A safety assessment should be performed on finished products taking into consideration the toxicological profile of the ingredients, their chemical structure, and their potential risk to human health. EU Directive reports more than 1000 chemical substances which may not be used in cosmetic products, due to their toxicological properties. According to this list, several metals as antimony (Sb), arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), mercury (Hg), nickel (Ni) and lead (Pb) are prohibited ingredients in cosmetics because they are considered unsafe.

In this work, we describe X-ray based methodologies for the identification and discrimination of components in eye shadow samples. The aim was to evaluate the analytical capabilities of low power EDXRF, TXRF for the determination of major and trace elements (Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Nb, Sn, Sb, Ba, Hg, Pb) and XRD for the identification of inorganic crystalline phases, mainly minerals, existing in eyeshadows. These techniques allow the analysis of solid samples directly on the packed cosmetic or with a minimum sample treatment, in very short time. Analyses of fifty different market eyeshadows of common use have been analysed. Up to ten mineral phases (carbonates, clay minerals and titanium oxide polymorphs) have been identified as main compounds. Among the metallic trace elements, the presence of tin is ubiquitous, and manganese, iron, copper, zinc, are common. Some samples also exhibit chromium and antimony in its composition.

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Traceable characterisation of calibration samples for advanced thin film materials by reference-free X-ray spectrometry

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The question of the certification of calibration samples for the characterisation of advanced thin film materials has to be addressed within the framework of reliable process control or quality management purposes. A reference measurement technique such as Reference-Free X-Ray Fluorescence analysis (RF-XRF) can be used in order to address the gap in appropriate Certified Reference Materials (CRMs) for thin film analyses both in industrial and scientific context [1].

RF-XRF is a physically traceable method enabling the quantitative analysis of the elemental mass deposition or composition of the samples of interest. The traceability of the method is based on well-known synchrotron radiation and radiometrically calibrated instrumentation as well as on good knowledge of the atomic fundamental parameters [2]. This allows for a SI traceable analysis without the need for any reference materials.

Most of analytical techniques rely on reference materials or well-known calibration standards. However, there are only a few adequate CRMs available for the steadily increasing number of sample systems on the micro- and nanoscale. For a reliable analysis and complete understanding of these new materials, the correlation of the materials' chemical and physical properties with its functionality is mandatory. Ideally, a calibration sample has a similar matrix and layer structure to avoid calibration errors due to matrix or other non-linear effects. Thus, qualifying an out-of-production samples originating from an operating production line as calibration sample by using a reference measurement method like RF-XRF would solve the problem where no appropriate CRMs are available.

Many of novel thin film materials are alloys that are, in general, associated with secondary enhancement processes in X-ray fluorescence analysis. Out of an industrial project interesting examples are e.g. Ni-V nanolayers or Ni-P microlayers with secondary fluorescence contributions up to 20% to the primary intensities.

For the RF-XRF analysis of these sample systems several measurements were performed at different photon energies. This allows for a dedicated switching off and on of the secondary fluorescence effect. This data set including parallel transmission measurements was employeded for a more reliable XRF quantification analysis showing more stable fitting results.

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Real-time Monitoring of Precious Metals in Slurries: Problems and Solutions

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Australia

Real-time, on-stream analysis of the metal content of mineral process slurries is an essential prerequisite for process monitoring and advanced control of mineral processing circuits. There are several on-stream X-Ray Fluorescence (XRF) analysers for base metal applications available commercially. Typically they form the basis of many beneficiation plants control strategies. These commercial technologies have been insufficiently sensitive to measure precious metals such as gold and platinum group elements, typically present at part-per-million (ppm) and sub ppm levels.

In this paper, we will discuss problems encountered in slurry analysis: X-ray spectral fitting, line shape analysis, matrix and particle size variations in the slurry solids and how these issues can be addressed. We will introduce the development of CSIRO's UltraGold technology as a case study to tackle these problems. Additionally, this technology incorporates the use of Highly Ordered Pyrolytic Graphite crystals in a geometry that was optimised using extensive Monte Carlo simulations.

OLGA (On-Line Gold Analyser), shown in figure 1, is the analyser that incorporates the UltraGold technology and is being commercialised by Gekko Systems. We present the latest proof of principle with real plant slurries that showed a precision for gold in tailings (i.e. mineral processing waste streams) better than 30 parts-per-billion.

As projected grades in (gold) mining around the world fall and several large-scale mines approach the limits of their economic reserves, this method can enable significantly reduced operating costs by rapid analysis to improve circuit efficiency and hence vastly improve recovery.

Figure 1: Picture of OLGA.

Elemental Characterization of $PM_{2.5}$ in Nairobi, Kenya by PIXE Technique

Boman, J.[1], Gaita, S.M.[1], Erythriadou, S.[1] and Gatari, M. J.[2]

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Particle Induced X-ray Emission (PIXE) spectroscopy is a useful tool in elemental analysis of airborne particulate matter as it has low detection limits and covers a wide range of elements. In this study, particulate matter less than 2.5 µm ($PM_{2.5}$) were collected in Nairobi, Kenya, from September 2015 to January 2016. To understand the particulate air pollution situation in Nairobi (the source to impact relationships) the $PM_{2.5}$ were analysed for elements using PIXE spectroscopy and black carbon (BC) was analysed using reflectometry. The $PM_{2.5}$ mass was determined gravimetrically, and the mass concentration varied between 1.0 and 99 µg m^{-3} with an average of 17 µg m^{-3}. Though the average was below World Health Organization 24 h limit of 25 µg m^{-3}, this limit was exceeded during 15% of all the sampling days. By applying the local air quality standard, the $PM_{2.5}$ concentrations exceeded the limit (75 µg m^{-3} which is currently set for the industrial areas only) on only one day. The measured fifteen elements and BC accounted for 30% of the total $PM_{2.5}$ mass. Statistical analysis of the data using Principal Component Analysis and Positive Matrix Factorization produced four possible sources of the ambient $PM_{2.5}$ in Nairobi; mineral dust, combustion processes, traffic and industrial activities, in agreement with an earlier study [1] conducted from 2008 to 2010. This study reported on Al and Si, which accounted for 17% of the total detected elements, thus lowering the uncertainty of the unidentified component of $PM_{2.5}$ from the previous studies in Nairobi city.

[1] S. M. Gaita, J. Boman, M. J. Gatari, J. B. C. Pettersson and S. Janhäll, Atmospheric Chemistry and Physics 14(18), 2014, 9977-9991.

Elemental composition of ambient particulate matter in two Asian megacities measured with a near real time XRF spectrometer

Pragati Rai[1], Markus Furger[1], Jay G. Slowik[1], Francesco Canonaco[1], Ru-Jin Huang[2], Sachchida N. Tripathi [3], Dilip Ganguly[4], Urs Baltensperger[1] and André S. H. Prévôt[1]

[1] *Paul Scherrer Institute, Laboratory of Atmospheric Chemistry, 5232 Villigen PSI, Switzerland*
[2] *Institute of Earth Environment, Chinese Academy of Sciences (CAS), Xian, China*
[3] Department of Civil Engineering and Centre for Environmental Science and Engineering, Indian Institute of Technology Kanpur, Uttar Pradesh, India
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Pragati.rai@psi.ch

The deterioration of air quality is becoming a major concern in Asian megacities due to rapid development. Heavily urbanized areas typically have high particulate matter (PM) mass loading from different emission sources, which must be quantified for the formulation of efficient pollution mitigation strategies. Size-resolved measurements of trace elemental composition are a powerful tool for the identification of aerosol sources. The utility of such measurements is enhanced by doing sampling with high time resolution.

Measurements were performed in two Asian megacities Beijing, China (November/December 2017) and New Delhi, India (January/March 2018) at urban sites. Sampling and analysis was performed by an Xact® 625i ambient metals monitor with PM_{10} and $PM_{2.5}$ inlet switching system alternatively with one hour time resolution. Xact® 625i can measure up to 67 elements with an atomic number between Aluminum (Al) and Uranium (U). Source apportionment is performed using the multilinear engine (ME-2) implementation of positive matrix factorization (PMF) (Paatero 1999; Canonaco et al., 2013).

The results show that Cl, S and K are mostly contributing in fine mode in Beijing, indicating regional background sources for e.g. coal combustion and industrial activities, while Si, Ca, Fe and Al are dominating in coarse mode suggesting their concentrations are driven by resuspension due to anthropogenic activities. In New Delhi, Cl is the most prominent element in both size ranges followed by S, Si, K, Ca, Fe and Al. Cl concertation is higher during night time indicates burning of municipal solid waste which is relatively higher in winter than in summer. Traffic-related elements (e.g. Cu, Sb, Cr, Ba, Fe, Sn, Mn) in both size ranges show the morning and evening rush hours peaks at both locations.

[1] F. Canonaco, M. Crippa, J. G. Slowik, U. Baltensperger, A. S. H. Prévôt, Atmospheric Measurement Techniques, **6**, 2013, 3649-3661.

[2] P. Paatero, P, Journal of Computational and Graphical Statistics, **8**, 1999, 854-888.

Non-destructive characterization of airborne particulate matter by combination of cascade impactor sampling and total-reflection X-ray fluorescence related methods

János Osán[1,2], Árpád Farkas[1], Endre Börcsök[1] and Szabina Török[1]

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Friedensstrasse 1, A-2444 Seibersdorf, Austria

The health and climate effects of airborne particulate matter are strongly size dependent therefore an analytical technique capable of determining elemental concentrations and speciation of metals in size fractionated aerosol could contribute significantly to explore this environmental issue. The most difficult part of this analytical task is the sampling from submicron particles that are the most harmful to human health and the determination of trace concentrations from sample amounts of less than a microgram. Combination of non-destructive elemental analysis by means of total-reflection X-ray fluorescence (TXRF) and harmonized cascade impactor sampling was developed covering a diameter range of the collected particles below 100 nm.

Test aerosols composed of $CuSO_4$ and $KMnO_4$ were generated in order to gain information on the collection efficiency at different stages of the cascade impactor. The size distribution was monitored by an optical aerosol spectrometer (200 nm – 10 μm range) and a scanning mobility particle sizer (SMPS, 10–500 nm range) in parallel to cascade impactor sampling on Si wafers. In addition to measurements, Computational Fluid Dynamics (CFD) methods have been applied to characterize the airflow field within the impactor and to compute the collection efficiencies of the plates. The aerosol-loaded Si wafers were measured using TXRF, calibrated with two types of standards imitating deposited microparticles, (i) Cr pads prepared using photolithography and (ii) series of droplet residues prepared using a nanoliter injector. The mass size distribution of test aerosols calculated from the combined dataset of optical aerosol spectrometer and SMPS results was compared to size distribution of elemental masses of Cu, S, K and Mn obtained by TXRF, yielding a good agreement. The CFD calculation of the collection efficiency model resulted in values close to the expected ones.

The combination of TXRF and cascade impactor sampling on Si wafers was applied to study the size distribution of elemental concentrations in ambient aerosol samples in Hungary close to industrial, traffic and combustion related sources. The maximum concentration of elements related to high-temperature processes (e.g. K – biomass combustion, Zn – traffic) was observed in the 180–300 nm fraction. X-ray absorption near-edge structure spectrometry was applied in the TXRF detection mode on the same samples, in order to obtain information on the size variation of chemical states of Cu and Zn. Characteristic difference of Zn speciation was observed between submicrometer and coarse particles from combustion and traffic related sources. In contrast, no significant size variation of the Zn chemical state was observed for aerosols sampled close to an iron smelter with galvanization unit.

Characterization of ambient PM10 dust in industrial locations by continuous fence-line ED-XRF analysis

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[2] *Eramet Norway AS Kvinesdal, Øyesletta 61, 4484 Øyestranda, Norway*

On-line chemical analysis of ambient particulate matter (PM) is gaining popularity as a useful tool in industrial emissions monitoring and research.

Norms for PM concentrations and criteria pollutants found in airborne dust are becoming stricter. Industries need better monitoring tools to assess the air quality around the factories due to a demand for documentation with less uncertainties, i.e. models and estimations. In addition, many industries today have goals of achieving zero-emissions processes and need measurements that can aid in understanding their emissions sources better with the end goal of forming sound prevention and control measures.

A continuous (semi-online) ED-XRF system was used in a 3-month study at three silico and ferro manganese plants in Norway to speciate elements in PM10. Measurements were set up in fence line distances of 100-500 m in the predominant wind direction. In addition to the XRF system (CES Xact 625i), a continuous PM monitor (Palas Fidas 200s) and two meteorology stations were placed at the same locations for two of the plants (2 months).

The on-line XRF analysis was able to capture elements temporal variations and dust composition that can be very useful information for industrial objectives. The results are focused around Mn concentrations and variations correlated with plant activities and meteorology. Other elements and natural sources of PM are also discussed.

IAEA Nuclear Science and Spectrometry laboratory:

Support to XRF laboratories and recent applications.

R. Padilla-Alvarez, A. Migliori, I. Darby

Nuclear Science and Instrumentation Laboratory, International Atomic Energy Agency (IAEA) Laboratories, A-2444 Seibersdorf, Austria
R.Padilla-Alvarez@iaea.org

Through the Nuclear Science Programme the IAEA carries out activities to assist and advise its Member States (MSs) in assessing their needs for capacity building, research and development in the nuclear sciences, as well as in supporting the MSs' activities for deriving benefits in specific fields.

Over the last 20 years, the IAEA Nuclear Science and Instrumentation Laboratory (NSIL) has contributed to capacity building (knowledge and expertise) in the effective utilization of X-ray spectrometry techniques using a variety of laboratory and portable instrumentation, including the development of instruments and validation of analytical methodologies.

NSIL also operates dedicated measurement chambers at beam lines of the Elettra Sincrotrone (Trieste, Italy) and Ruder Boskovic Institute (Zagreb, Croatia). The access to such facilities is facilitated through the organization of Coordinated Research Programs.

More than 100 fellows have been trained in XRF analysis as part of IAEA Technical Cooperation Program, and different techniques have been applied to a wide range of topics, including environmental problems, plant breeding, soil erosion, food traceability and safety studies and for the characterization of advanced materials and cultural heritage objects in cooperation with scientists from other institutions. Some recent activities and developments are presented.

NSIL also supports XRF laboratories worldwide in addressing recommendations for Quality Management, Method validation and Quality control. Since 2002 Proficiency test exercises are organized in support of the needs for external verification faced by laboratories pursuing improve the quality of obtained results.

HPC-detectors for X-ray spectroscopy

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In the last decade, Hybrid Photon Counting (HPC) technology has transformed almost all X-ray based analytical methods. Among them, X-ray diffraction was the technique that benefited the most from the advantages of HPC-detectors. Noise-free detection, energy discrimination, a single-pixel point spread function, high frame rates and a high dynamic range have set new standards for the data quality.

Although equally promising, HPC-technology has made slower headway in X-ray spectroscopy. Several early papers report on the successful utilization of HPC-detectors for time-resolved X-ray absorption Fine Structure (XAFS) studies [1, 2], dynamic X-ray Photon Correlation Spectroscopy (XPCS) [3], high-resolution X-Ray Fluorescence (XRF) and X-ray absorption (XAS) [4]. Since then, HPC-detectors were used for many other applications at synchrotron sources, but also in laboratory spectrometers. In this work, we present how MYTHEN, PILATUS and EIGER detectors advance XAFS, Scanning X-ray Microscopy (STXM), and XRF-CT studies under challenging conditions: extremely short exposure times, sample heterogeneity, high background signal , limited absorbed dose and single-shot data collection.

Two recently developed laboratory spectrometers, equipped with the MYTHEN detector, will be used to illustrate the advances in XRF and XAS analysis.

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[3] Westermeier, F. et al. J. Phys., 2013, 425, 202005.

[4] Kleimenov, E. Et al. J. Phys., 2009, 190, 012035.

ARDESIA: a 4-Channels Fast SDD X-ray Spectrometer

I.Hafizh [1,2], G.Bellotti[1,2], M.Carminati[1,2], C.Fiorini[1,2], A.Balerna[3], V.Tullio[3],
G.Borghi[4], A.Gola[4], N.Zorzi[4], A.Capsoni[2], S.Coelli[2], L.Bombelli[5]

[1] *Politecnico di Milano, Dipartimento di Elettronica, Informazione e Bioingegneria, Milan, Italy (carlo.fiorini@polimi.it)*
[2] *INFN, Sezione di Milano, Milan, Italy*
[3] *INFN, Laboratori Nazionali di Frascati, Frascati, Italy*
[4] *Fondazione Bruno Kessler - FBK, Trento, Italy*
[5] *XGLAB srl, Milano, Italy*

This work presents the ARDESIA X-ray spectrometer, supported by the Italian INFN. ARDESIA is a SDD-based, multichannel X-ray spectrometer, optimized for synchrotron applications that require a high-count rate (> 1Mcps/channel) and high-resolution (below 150 eV FWHM at peaking time faster than 200 ns) for X-ray fluorescence detection. The main applications of the ARDESIA detector are X-ray fluorescence (XRF) and X-ray absorption fine structure (XAFS) techniques. The detector is based on a monolithic array of 4 SDD of 25mm^2 area each, which optimizes detector solid angle. After the optimization of the 4-channels detection module [1], the mechanical structure grants cooling, with a double Peltier strategy, vacuum, insulation from the harsh surrounding environment and possibility to place side-by-side several SDD modules to realize larger number of channels. The detector signals are amplified by a new monolithic four-channels CUBE preamplifier chip and processed by digital pulse processors (e.g. XGLab-DANTE, 4 channel XIA DXP-XMAP) to achieve good performances of the module at high count rates (Fig.1). At the DAΦNE DXRI soft X-ray beamline, XRF tests on low atomic number elements, down to C-K$_\alpha$ line at 270eV, have been performed and also near absorption edge XANES spectra of silicon in a Pyrex glass sample (Fig.2) have been measured.

[1] G. Bellotti, at al., “The Detection Module of ARDESIA: a New, Versatile Array of SDDs for X-Ray Spectroscopy Synchrotron Applications”, 2016 IEEE NSS/MIC Conference Record.

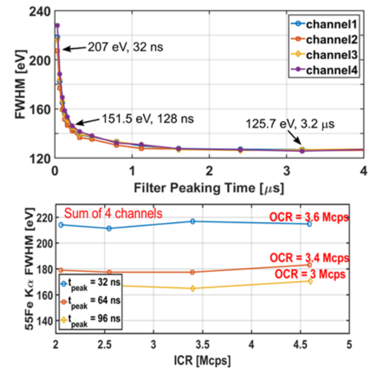

Fig.1. ARDESIA energy resolution vs. peaking time (top) and output count rate (bottom) vs. input count rate using the DPP Dante from XGLab.

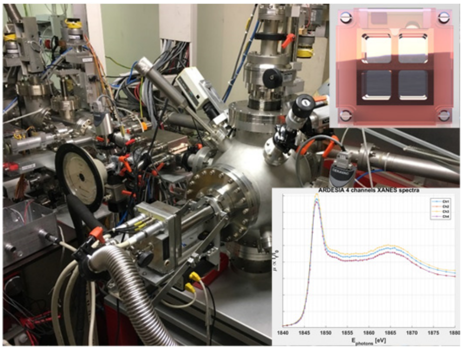

Fig.2. ARDESIA detector (upper inset) installed on the DAΦNE DXRI soft X-ray beamline in Frascati. In the inset the XANES measurements in fluorescence mode of a Pyrex glass sample are reported.

List of Authors

Space for notes

366

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0.5	80	135
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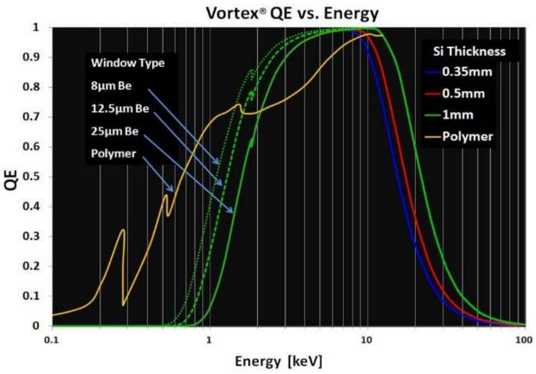
1.0	70	140



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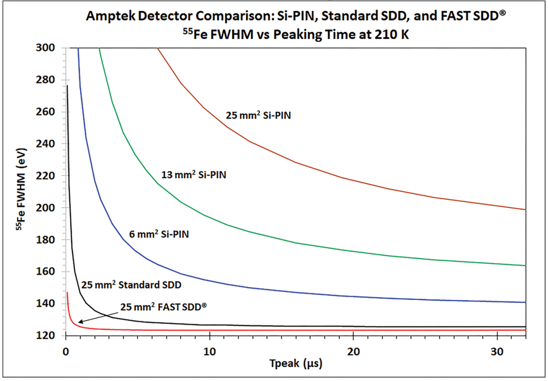

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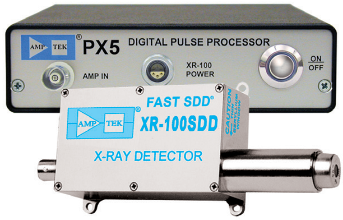

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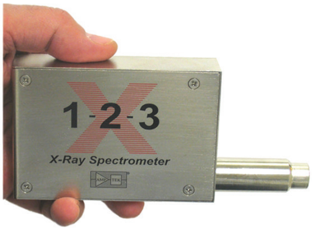

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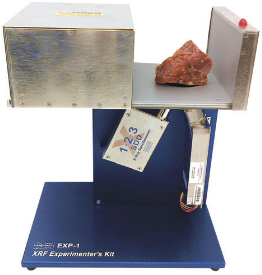

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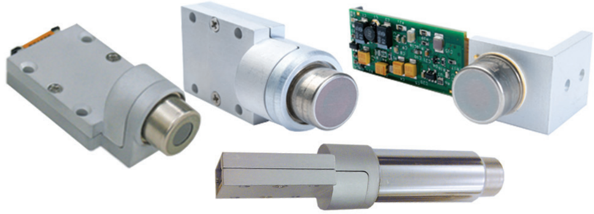
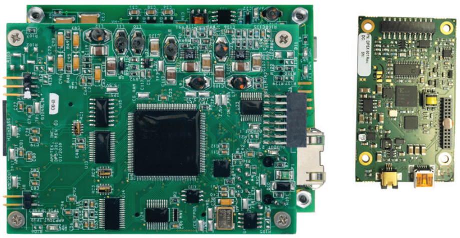


A sample of detectors with preamplifiers and heat sinks



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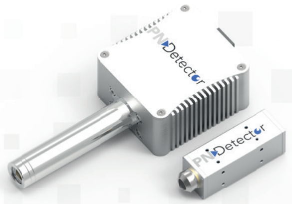

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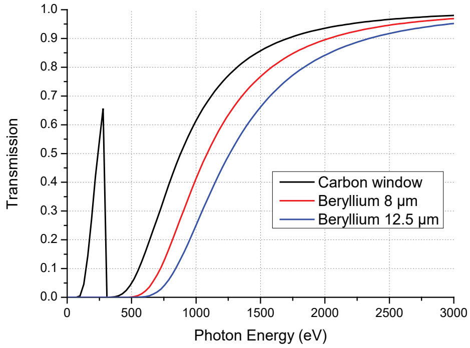

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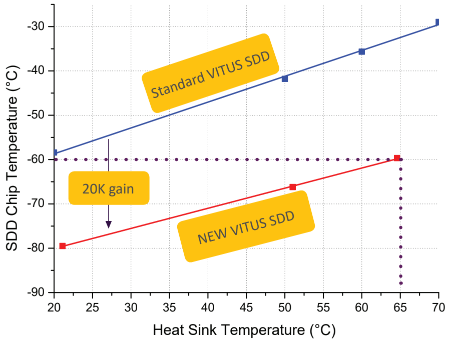

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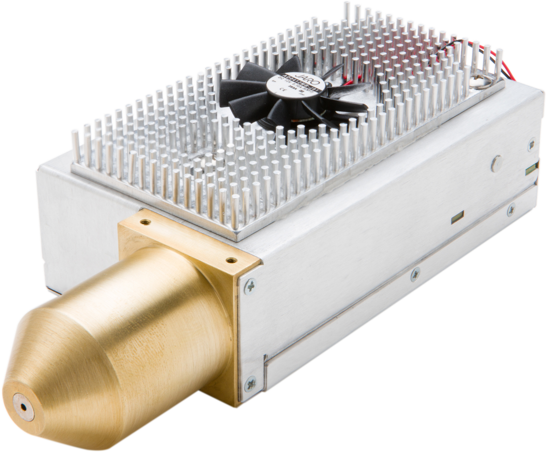

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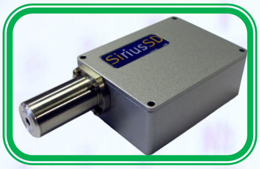

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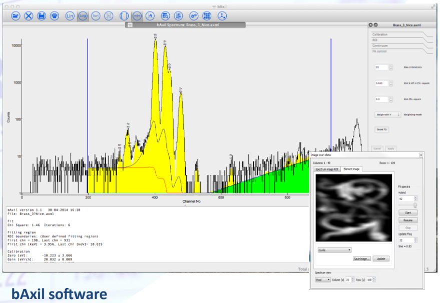

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File: Brass_3?Nice.axml

Fit
Chi Square: 1.46  Iterations: 6

Fitting region
ROI boundaries: (User defined fitting region)
First chn = 198, Last chn = 931
First chn [keV] = 3.956, Last chn [keV]= 18.639

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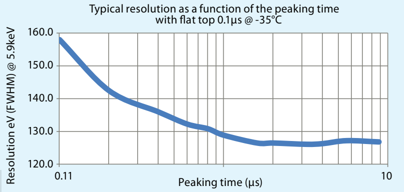
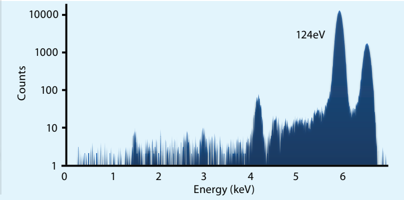
MIRION TECHNOLOGIES





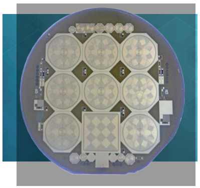
X-PIPS Series (Based on Drift Technology)

Features:

- Preamplifier included
- Temperature-controlled Peltier cooler included
- Size: 15 mm², 30 mm² and 80 mm²
- Thickness: 500 µm

Advantages:

- Excellent resolution < 135 eV
- Peak/Background > 15000
- Good stability
- Good performance with fast shaping time (< 1 µs rise time)



Single and Multi-Anode Drift Detectors

Features:

- Available as silicon chip
- Size: from 10 to 500 mm²
- Thickness: 300 and 500 µm
- Low leakage current, typically < 200pA/cm²
- Entrance window < 50 nm

7-element detector

Features:

- Array of 7 individual SDD's of 100 or 70 mm² (collimated to 80 or 50mm²) and 500 µm thickness in a close-packed geometry.
- CMOS preamplifier (CUBE based)
- 1 mil Be window
- Detector system includes preamplifiers, HV power supply and temp. controller
- Electrical cooling – Peltier or cryo-cooled

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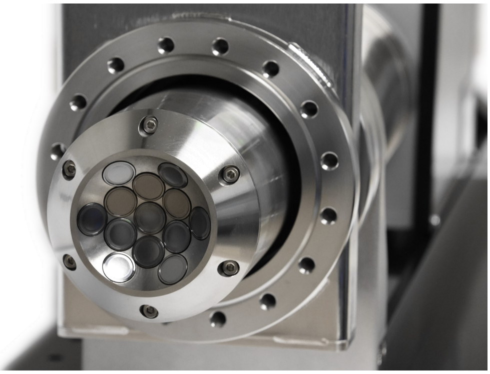
XIA
FalconX8
DIGITAL X-RAY SPECTROMETER
STATUS
I/O
RUN
RATE
1
2
3
4
5
6
7
8
SITORO

excillum


READY TO MAKE ITS IMPACT
Value beyond analysis
NEW



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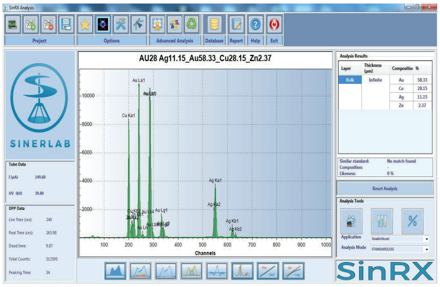

Tube Data
I (μA) 149.60
HV (kV) 39.80

DPP Data
Live Time (sec): 240
Real Time (sec): 265.98
Dead time: 9.87
Total Counts: 312595
Peaking Time: 34

Analysis Results

Layer	Thickness (μm)	Compositio	%
Bulk	Infinite	Au	58.33
		Cu	28.15
		Ag	11.15
		Zn	2.37

Similar standard: No match found
Composition: -
Likeness: 0 %

Application DeafultAczet
Analysis Mode STANDARDLESS

SINRX

Software for qualitative and quantitative analysis of energy dispersive X-ray Fluorescence (ED-XRF) spectra acquired on bulk and layered samples.

SPECTRA ACQUISITION

from different models of DPP's and by using different X-ray sources

QUALITATIVE ANALYSIS:

- calibration of the energy scale
- smoothing and background subtraction
- fitting of the spectrum
- automatic identification of elements through peak analysis:

QUANTITATIVE ANALYSIS:

- standardless - fundamental parameters
- empirical calibration with or without interelement corrections
- smart analysis and matching analysis for the rapid identification of the material
- report and databases

DPP2570-OEM

DESCRIPTION

Digital Pulse Processor (DPP) with integrated 16k-Multichannel Analyzer ready to use for laboratory and OEM integration

APPLICATIONS

- XRF (Xray flourescence)
- X and Gamma Spectroscopy
- Scientific Research
- Industrial Process Control
- Homeland security
- Nuclear Monitor

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Advanced XRF equipment and solutions

MICROMATTER Technologies Inc.

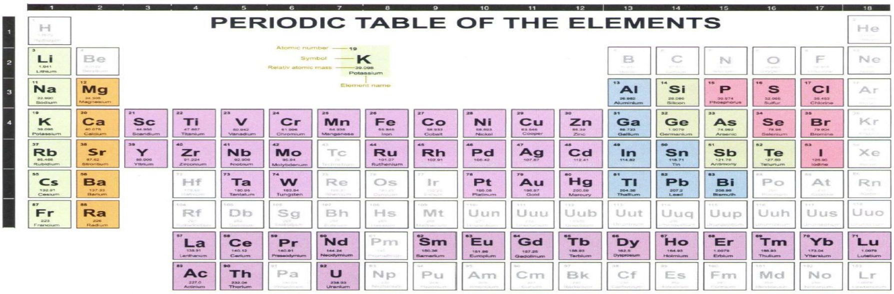
XRF Calibration Standards

MICROMATTER™ has produced highest quality XRF calibration materials for more than 50 years. Today, institutions in over 50 countries use MICROMATTER™ standards to calibrate their XRF spectrometers.

MICROMATTER™ standards are ideally suited for instrument calibration for trace analysis and thin film measurements. They are widely used in the pharmaceutical and petrochemical industries, for environmental compliance (e.g. lead and mercury emission, contamination) and in solar cell and semiconductor manufacturing. MICROMATTER™ standards are also useful as a source of pure element spectra in background subtraction routines as well as samples for routine checks of detector resolution and overall system performance.

All MICROMATTER™ standards are produced by vacuum deposition methods. All materials (metals and compounds) used to produce MICROMATTER™ standards are of 99.9% or higher chemical purity. Our standards are characterized by precision weighing, and certification is provided with each standard and all standards are certified as +-5%.

We also provide multi-element samples for rapid energy calibration. Our calibration materials are available in several thickness ranges starting as low as 0.5-1.5 $\mu g/cm^2$. We manufacture thin film and coating thickness standards for the elements highlighted below.



PERIODIC TABLE OF THE ELEMENTS

Atomic number — 19
Symbol — K
Relativ atomic mass — 39.098
Potassium
Element name

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo
				La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
				Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

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