EXRS2012, June 18 - 22, Vienna, Austria

European Conference on X-ray Spectrometry

Organized by:
Atominstitut, Vienna University of Technology, Vienna, Austria

hosted by:
International Atomic Energy Agency, Vienna, Austria

under the patronage of
the Austrian Federal Ministry for Science and Research, Vienna, Austria

Program, General Information and Book of Abstracts
Impressum
Offenlegung gemäß § 25 Mediengesetz:
Atominstitut, Vienna University of Technology
1020 Wien
Radiation Physics Department
Ao. Univ.-Prof. DI Dr. Christina Streli
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Atominstitut
Stadionallee 2
A-1020 Wien
Tel.: +43 1 58801 141330

Druck: www.grafischeszentrum.com
Welcome
The Local Organizing Committee of the 15th European Conference on X-ray Spectrometry 2012 is pleased to welcome all participants of this conference. About 300 participants from 61 countries will share opportunity to exchange ideas and knowledge related to X-ray Spectrometry, including fundamental aspects, technological developments, traditional and novel areas of applications and interdisciplinary research.

We are grateful to our sponsors and all people that helped us during the organization of this event. We hope you will enjoy the conference in a stimulating and friendly atmosphere.

Christina Streli and Andrzej Markowicz
Chair and co-chair of the local organizing committee

Local Organizing committee
• Christina Streli - ATI, TU Wien - Chair
• Andrzej Markowicz - IAEA - Co-chair
• Martina Griesser - KHM, Vienna
• Andreas Karydas - IAEA
• Michael Mantler - Vienna
• János Osán - KFKI-AEKI, Budapest, Hungary
• Roman Padilla-Alvarez - IAEA
• Giancarlo Pepponi - FBK, Trento, Italy
• Manfred Schreiner - Academy of Fine Arts, Vienna
• Peter Wobrauschek - ATI, TU Wien

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• Marie-Christine Lepy, France
• Jorge Sanchez, Argentina
• Szabina Török, Hungary
• Peter Wobrauschek, Austria

Conference secretary:
EXRS-2012 Secretariat
Atominstitut TU Wien
Stadionallee 2
1020 Wien, Austria
e-mail: exrs2012@ati.ac.at
**Scientific program**
The 15th EXRS conference is devoted to the exchange of information and experience on the emerging and innovative techniques in the field of X-ray spectrometry and related areas. The conference will provide a framework in which scientists of various research areas will be able to convene and discuss X-ray techniques and their successful applications. A rich scientific and social program will allow experienced experts, young scientists, and industrial exhibitors to exchange views and start new collaborative projects. Contributions are divided into 22 invited lectures, 93 oral presentations and 210 poster presentations.

**Conference Sessions:**
1. Art & Cultural Heritage
2. Interactions of X-rays with matter and fundamental parameters
3. PIXE & electron induced XRS
4. Microbeam / Nanobeam
5. TXRF, GIXRF and related techniques
6. X-ray imaging and tomography
7. Mobile and portable XRF
8. Synchrotron XRS, XAFS, RIXS and XES
9. Recent developments by XRS manufactures
10. High resolution X-ray absorption and emission spectroscopy
11. Advanced materials and nanoscience
12. XRS Metrology, QC/QA
13. XRS - Instrumentation (X-ray sources, optics and detectors)
14. Quantification methodology
15. Sample preparation and sampling strategies
16. Industrial quality and process control
17. Earth and environment sciences
18. Education and data interpretation
19. Life sciences and forensics
**Conference Sponsors:**

![TU Wien](image1)

![EXSA](image2)

![City of Vienna](image3)

![Rigaku](image4)

### Social Program

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
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</thead>
<tbody>
<tr>
<td><strong>Sunday</strong></td>
<td></td>
</tr>
<tr>
<td>15:00-19:00</td>
<td><strong>Opening mixer</strong> (Arcotel-Kaiserwasser) collection of ground passes and conference registration at IAEA Gate 1</td>
</tr>
<tr>
<td><strong>Wednesday</strong></td>
<td></td>
</tr>
<tr>
<td>14:00-18:00</td>
<td>Conference excursion (<strong>Klosterneuburg</strong> /<strong>Kahlenberg</strong>)</td>
</tr>
<tr>
<td>18:00-20:00</td>
<td><strong>Guided tour Academy of Fine Arts Painting Gallery</strong> (free of charge)</td>
</tr>
<tr>
<td><strong>Thursday</strong></td>
<td></td>
</tr>
<tr>
<td>20:00</td>
<td><strong>Heuriger Fuhrgassthuber</strong> partially sponsored by the Lord Major of Vienna</td>
</tr>
<tr>
<td>Invited Speaker</td>
<td>Presentation</td>
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<td>----------------------------------------</td>
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</tr>
<tr>
<td>Joy Andrews</td>
<td>Nanoscale chemical imaging of energy materials with full-field transmission X-ray microscopy</td>
</tr>
<tr>
<td>Samuel Bamford</td>
<td>Challenges and Status in the Development of ICT-Based Learning and Training Modules on Nuclear Instrumentation and Spectrometry</td>
</tr>
<tr>
<td>Artur Braun</td>
<td>Application of x-ray and electron spectroscopy to energy materials</td>
</tr>
<tr>
<td>Björn De Samber</td>
<td>Synchrotron Radiation based Micro- and Nanoanalysis applied to Biological Systems</td>
</tr>
<tr>
<td>Shinjiro Hayakawa</td>
<td>Depth selective XAFS characterization using simultaneous detection of x-ray fluorescence and conversion electrons</td>
</tr>
<tr>
<td>Joanna Hoszowska</td>
<td>High-resolution x-ray emission spectroscopy for fundamental parameters determination</td>
</tr>
<tr>
<td>Yuying Huang</td>
<td>Synchrotron radiation X-ray micro/nanobeam XRF and XANES techniques: application in life science</td>
</tr>
<tr>
<td>Nikolaos Kallithrakas-Kontos</td>
<td>Selective membranes in X-Ray Analysis: A preconcentration step or a sensor?</td>
</tr>
<tr>
<td>Ioanna Mantouvalou</td>
<td>Laser-produced plasma sources for applied spectroscopy in the soft X-ray region</td>
</tr>
<tr>
<td>Eva Margui</td>
<td>Total reflection X-ray fluorescence spectrometry in the environmental field: A review of some recent investigations and applications</td>
</tr>
<tr>
<td>Florian Meirer</td>
<td>Application of grazing incidence x-ray spectroscopy to the analysis of Arsenic doped Silicon produced by plasma immersion ion implantation</td>
</tr>
<tr>
<td>Beatrix Pollakowski</td>
<td>Species depth profiling of deeply buried nanostructures</td>
</tr>
<tr>
<td>Phil Potts</td>
<td>Provenance, Process and Propriety - Portable XRF in cultural heritage</td>
</tr>
<tr>
<td>Martin Radtke</td>
<td>The colour X-ray camera: basics, applications and perspectives.</td>
</tr>
<tr>
<td>Miguel Reis</td>
<td>PIXE in the slow collisions regime</td>
</tr>
<tr>
<td>Stefano Ridolfi</td>
<td>EDXRF portable systems for Analysis of Works of Art</td>
</tr>
<tr>
<td>Volker Rößiger</td>
<td>Standard Reference Material and Standardless XRFA</td>
</tr>
<tr>
<td>Rafal Sitko</td>
<td>Influence coefficient algorithms in X-ray fluorescence analysis of thick and intermediate-thickness samples</td>
</tr>
<tr>
<td>Andrea Somogyi</td>
<td>Scanning hard X-ray nanobeam techniques at the Nanoscopium beamline of Synchrotron Soleil</td>
</tr>
<tr>
<td>João Veloso</td>
<td>EDXRF Imaging with 2D detectors</td>
</tr>
<tr>
<td>Charalambos Zarkadas</td>
<td>Quality improvements of EDXRF instruments with close coupled geometries by means of Monte Carlo simulations</td>
</tr>
<tr>
<td>Janina Zieba-Palus</td>
<td>Examination of forensic traces by the use of X-ray spectrometry</td>
</tr>
</tbody>
</table>
Instructions for conference proceedings

The conference proceedings will be available for downloading by the participants after the conference. The conference proceedings will contain the submitted manuscripts in pdf format. Contributions transmitted to the Conference Secretariat before July 1st, 2012 will be automatically included, without any reviewing procedure. Here there are no specific instructions about size and shape: the manuscript will be included such as the authors will have prepared it, under their own responsibility.

Authors of accepted contributions are invited to submit one manuscript for publication in a special issue of X-Ray Spectrometry (Wiley Interscience). Manuscripts should be prepared in a strict format of the XRS and will be reviewed by the program committee of the conference.

Manuscripts have to be submitted to the conference secretary before June 15th. Authors Instructions according to the rules of XRS.


Industrial exhibition:

Traditionally EXRS conferences include an Industrial Exhibition featuring companies producing X-ray related instruments.

The Industrial Exhibition stands will be located in the Rotunda, where also the coffee in the coffee breaks is served. It will take place during the whole conference.

Industrial exhibitors and sponsors:

http://www.amptek.com/

http://www.bruker-axs.com/x_ray_spectrometry.html

http://www.e2v.com/

http://www.excillum.com/

http://www.helmut-fischer.de

http://www.ifg-adlershof.de/

http://www.i-tech.si/

http://www.ketek.net/

http://www.moxtek.com/

http://www.pndetector.de/

http://www.pnsensor.de/

http://www.rigaku.com/

http://www.siintusa.com/

http://www.edax.com/

http://www.spectro.com
Conference site:
## Program overview

### Sunday  
16:00-19:00  Opening mixer (+ pickup of ground pass)

### Monday

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
</tr>
</thead>
<tbody>
<tr>
<td>08:00-12:00</td>
<td>Registration</td>
</tr>
<tr>
<td>09:30-10:00</td>
<td>Opening session</td>
</tr>
<tr>
<td>10:00-10:30</td>
<td>Plenary lecture - P. Potts</td>
</tr>
<tr>
<td>10:30-11:00</td>
<td>Coffee break</td>
</tr>
<tr>
<td>11:00-13:10</td>
<td>1 Art &amp; Cultural Heritage</td>
</tr>
<tr>
<td>14:30-15:30</td>
<td>1 Art &amp; Cultural Heritage</td>
</tr>
<tr>
<td>15:30-16:00</td>
<td>Coffee break</td>
</tr>
<tr>
<td>16:00-17:10</td>
<td>4 Microbeam/Nanobeam</td>
</tr>
<tr>
<td>17:10-18:30</td>
<td>Poster session PS1 (Topics 1-11)</td>
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### Tuesday

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
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<tbody>
<tr>
<td>08:00-12:00</td>
<td>Registration</td>
</tr>
<tr>
<td>09:00-10:50</td>
<td>5 TXRF, GIXRF and related techniques</td>
</tr>
<tr>
<td>11:00-11:30</td>
<td>Coffee break</td>
</tr>
<tr>
<td>11:30-13:10</td>
<td>8 Synchrotron XRS, XAFS, RIXS and XES</td>
</tr>
<tr>
<td>14:30-16:00</td>
<td>Lunch</td>
</tr>
<tr>
<td>16:00-16:30</td>
<td>Coffee break</td>
</tr>
<tr>
<td>16:30-17:30</td>
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</tr>
<tr>
<td>17:30-18:00</td>
<td>EXSA General assembly</td>
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### Wednesday

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
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<tbody>
<tr>
<td>09:00-10:50</td>
<td>10 High resolution X-ray absorption and emission spectroscopy</td>
</tr>
<tr>
<td>10:50-11:30</td>
<td>Coffee break</td>
</tr>
<tr>
<td>11:30-12:30</td>
<td>12 XRS Metrology, QC/YA</td>
</tr>
<tr>
<td>14:00-18:00</td>
<td>Conference excursion</td>
</tr>
<tr>
<td>18:00-20:00</td>
<td>Guided tour Academy of Fine Arts Painting Gallery</td>
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</table>

### Thursday

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
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</thead>
<tbody>
<tr>
<td>09:00-10:50</td>
<td>13 XRS - Instrumentation (X-ray sources, optics and detectors)</td>
</tr>
<tr>
<td>11:00-11:30</td>
<td>Coffee break</td>
</tr>
<tr>
<td>11:30-12:50</td>
<td>Lunch</td>
</tr>
<tr>
<td>14:30-16:00</td>
<td>15 Sample preparation and sampling strategies</td>
</tr>
<tr>
<td>16:00-16:30</td>
<td>Coffee break</td>
</tr>
<tr>
<td>Time</td>
<td>Event</td>
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</tr>
<tr>
<td>16:30-17:20</td>
<td>17 Earth and environment sciences</td>
</tr>
<tr>
<td>17:20-18:30</td>
<td>18 Education and data interpretation</td>
</tr>
<tr>
<td></td>
<td>Poster session PS2 (Topics 12-19)</td>
</tr>
<tr>
<td>20:00</td>
<td>Conference Dinner</td>
</tr>
<tr>
<td>9:00-10:50</td>
<td>17 Earth and environment sciences</td>
</tr>
<tr>
<td>9:00-10:50</td>
<td>19 Life sciences and forensics</td>
</tr>
<tr>
<td>10:50-11:20</td>
<td></td>
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<tr>
<td></td>
<td>coffee break</td>
</tr>
<tr>
<td>11:20-12:40</td>
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<tr>
<td>12:40</td>
<td>Closing session</td>
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# Final Program

<table>
<thead>
<tr>
<th>Time</th>
<th>Boardroom A</th>
<th>Room M3</th>
</tr>
</thead>
<tbody>
<tr>
<td>09:30-10:00</td>
<td>Opening Session</td>
<td></td>
</tr>
<tr>
<td>10:00-10:30</td>
<td>Plenary lecture: P. J. Potts: Provenance, process and propriety - portable XRF in cultural heritage</td>
<td></td>
</tr>
<tr>
<td>10:30-11:00</td>
<td>coffee break</td>
<td></td>
</tr>
<tr>
<td>11:00-11:20</td>
<td>1 Cultural Heritage</td>
<td>2 Interactions of X-rays with matter and fundamental parameters</td>
</tr>
<tr>
<td></td>
<td>Chair: M. Schreiner</td>
<td>Chair: M. Mantler</td>
</tr>
<tr>
<td></td>
<td>OS1-1 L. Lühl, S. Mahlkow, B. Hesse, E. Aloupisiotis, M. Wilke, B. Kannegießer: Fe K-XANES measurements on both Attic sherds and their modern reproductions</td>
<td>OS2-INV1 J. Hoszowska: High-resolution x-ray emission spectroscopy for fundamental parameters determination</td>
</tr>
<tr>
<td>11:20-11:40</td>
<td>OS1-3 V. Zvereva, V. Trunova, N. Polosmak: Investigation of organic findings (hair, bones, teeth) from the royal burials of Xiongnu (last years BC-early AD, Noin-Ula, Mongolia) by SRXRF</td>
<td>OS2-1 J. Fernandez, V. Scot, L. Verardi, F. Salvat: Electron contribution to photon transport in coupled photon-electron problems: inner-shell impact ionization correction</td>
</tr>
<tr>
<td></td>
<td>OS1-4 A. Galli, L. Bonizzoni: No simple answers to archeometrical questions: how to get the most of PXRF spectrometer on different materials</td>
<td>OS2-3 M.-C. Lépy, Y. Ménesguen: Measurements of the fluorescence yields of Germanium by two independent approaches</td>
</tr>
<tr>
<td>12:00-12:20</td>
<td>OS1-5 S. Scrivano, F.J. Ager, M.L. de La Bandera, B.G. Tubio, I.O. Felui, M.A. Respaldiza: Identification of welding processes in ancient gold jewelry by micro-XRF spectroscopy</td>
<td>OS2-4 P. Hönice, B. Beckhoff, M. Müller, M. Kolbe, M. Krämer, M. Mantler: Experimental verification of L-shell photo ionization cross sections of Pd and Mo</td>
</tr>
</tbody>
</table>

### Info FP Initiative

- **14:30-14:50** A. Le Gac, F. Gil, M. Manso, S. Longelin, S. Pessanha, A. Freitas, L. Carvalho: Characterization of two baroque sculptures of the Immaculate Conception: the art of combining innovation with tradition

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**Chair:** M. Griesser

**Chair:** A. Karydas

**3 PIXE & electron induced XRS**
<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:50</td>
<td>OS1-7</td>
<td>F. P. Romano, S. Garraffo, L. Pappalardo, F. Rizzo: Mercury-silvering evidence in late Roman coins by the combined use of the portable XRF and low energy micro-XRF techniques</td>
</tr>
<tr>
<td>15:00</td>
<td>OS3-1</td>
<td>M. Ren: Sub-100nm STIM imaging &amp; PIXE quantification of rare earth elements in Algae cells</td>
</tr>
<tr>
<td>15:10</td>
<td>OS1-8</td>
<td>A. Galli, L. Bonizzoni: Comparison between XRF, TXRF and PXRF analyses for provenance classification of archaeological bricks</td>
</tr>
<tr>
<td>15:10</td>
<td>coffee break</td>
<td></td>
</tr>
<tr>
<td>15:30</td>
<td>OS1-9</td>
<td>A. Galli, L. Bonizzoni: Comparison between XRF, TXRF and PXRF analyses for provenance classification of archaeological bricks</td>
</tr>
<tr>
<td>15:40</td>
<td>coffee break</td>
<td></td>
</tr>
<tr>
<td>16:00</td>
<td>OS4-INV1</td>
<td>A. Somogyi: Scanning hard X-ray nanobeam techniques at the Nanoscopium beamline of Synchrotron Soleil</td>
</tr>
<tr>
<td>16:10</td>
<td>OS3-3</td>
<td>S. Imashuku, S. Sakatoku, J. Kawai: SEM-EDX analysis of insulating samples using a diluted ionic liquid</td>
</tr>
<tr>
<td>16:30</td>
<td>OS3-4</td>
<td>M. Roumie, U. Wicenciak, C. Atallah, B. Nsouli: PIXE characterization of pottery production from the necropolis of Jiyeh archaeological site</td>
</tr>
<tr>
<td>16:50</td>
<td>OS4-2</td>
<td>T. Wolff, W. Malzer, C. Herzog, I. Mantouvalou, P. Zimmermann, B. Kannegießer: Quantitative 3D micro-XRF analysis with laboratory setup</td>
</tr>
<tr>
<td>16:50</td>
<td>OS3-5</td>
<td>S. R. Byreddy, F. Dessalegn, S.S. Abdul: Trace element analysis of some indigenous medicinal plants of Ethiopia by PIXE</td>
</tr>
<tr>
<td>17:10</td>
<td>Poster session PS1</td>
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**Chair:** K. Tsuji
<table>
<thead>
<tr>
<th>Tuesday</th>
<th>Boardroom A</th>
<th>Room M3</th>
</tr>
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<tbody>
<tr>
<td>TXRF, GIXRF and related techniques&lt;br&gt;Chair: N. L. Misra</td>
<td>6 X-ray imaging and tomography&lt;br&gt;Chair: D. Wegrzynek</td>
<td></td>
</tr>
</tbody>
</table>

| 09:00-09:30 | OS5-INV1 F. Meirer: Application of grazing incidence x-ray spectroscopy to the analysis of Arsenic doped Silicon produced by plasma immersion ion implantation | OS6-INV1 B. De Samber: Synchrotron radiation based micro- and nanoanalysis applied to biological systems |
| 09:30-09:50 | OS5-1 C. Vázquez, O.M. Palacios, M.C. Rodríguez Castro, L.M.M. Parra: Domestic dog hair samples as biomarkers of arsenic contamination |

| 10:00-10:20 | OS5-3 T. Cherkashina, S. Panteeva, A. Finkelshtein, V. Makagon: Determination of Rb, Sr, Cs, Ba, and Pb contents in K-feldspars in small sample amounts by total reflection X-ray fluorescence (TXRF) analysis |
| 10:20-10:40 | OS5-4 N. Novikovskii, V. Raznomazov, D. Sarichev: Series of highly sensitive X-ray fluorescence spectrometers TXRF and GIXRF |

| 11:00-11:30 | OS7-INV1 S. Ridolfi: EDXRF portable systems for analysis of works of art |

| 11:30-11:50 | OS5-5 P. Hönicke, Y. Kayser, B. Beckhoff: X-Ray induced characterization of ion implantation depth profiles |


| 10:00-10:20 | OS6-1 M. Haschke, U. Waldschläger, R. Tagle: New developments in μ-XRF |
| 11:00-11:30 | OS6-3 A. L. Silva, M.L. Carvalho, J. Veloso: Elemental imaging analysis with a full-field micropattern gaseous detector |

<p>| 12:20-12:40 | OS7-1 M. Alfeld, G. van der Snickt, K. Janssens, J. Dik, J. Blaas, M. Haschke, K. Erler: Scanning macro-XRF investigation of historical paintings: Recent progress in instrumentation |
| 12:20-12:40 | OS7-2 I. Nakai, Y. Abe, K. Tantrakarn: Development of a new portable X-ray fluorescence spectrometer suitable for analysis of Mg in archaeological glass objects in air equipped with polycapillary optics |</p>
<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Title</th>
<th>Speakers/Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>12:40-13:00</td>
<td>OS7-3</td>
<td>S. Piorek: Benefits of using handheld EDXRF analyzer for screening toys and children products for compliance with toy directive</td>
<td>S. Piorek</td>
</tr>
<tr>
<td>13:10-13:20</td>
<td>OS7-4</td>
<td>C. Vanhoof, K. Holschbach-Bussian, B. Bussian, R. Cleven: Applicability of hand-held EDXRF systems for waste characterization</td>
<td>C. Vanhoof, K. Holschbach-Bussian, B. Bussian, R. Cleven</td>
</tr>
<tr>
<td>13:00-15:00</td>
<td>8 Synchrotron XRS, XAFS, RIXS and XES</td>
<td>Chair: M. C. Lepy</td>
<td>9 Recent developments by XRS manufactures Chair: Y. Kawai</td>
</tr>
<tr>
<td>14:30-15:00</td>
<td>OS8-INV1</td>
<td>A. Braun: Application of x-ray and electron spectroscopy to energy materials</td>
<td>A. Braun</td>
</tr>
<tr>
<td>16:30-16:50</td>
<td>OS8-5</td>
<td>M. Müller, B. Beckhoff, S. Sioncke, C. Fleischmann, S. Choudhury: X-ray spectrometry for the characterization of novel materials for energy storage and nanoelectronics</td>
<td>M. Müller, B. Beckhoff, S. Sioncke, C. Fleischmann, S. Choudhury</td>
</tr>
</tbody>
</table>

*coffee break*
<table>
<thead>
<tr>
<th>Time</th>
<th>Presentation</th>
</tr>
</thead>
<tbody>
<tr>
<td>16:50-17:00</td>
<td>Spektro: D. Wissmann</td>
</tr>
<tr>
<td>17:00-17:10</td>
<td>XIA: P. Grudberg</td>
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<tr>
<td>17:10-17:20</td>
<td>Thermo: P. Lemberge</td>
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<tr>
<td>17:20-17:30</td>
<td>Bruker: M. Haschke</td>
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<tr>
<td>17:30-18:00</td>
<td>EXSA General assembly</td>
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<tr>
<td>Time</td>
<td>Session</td>
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<td>09:00-09:30</td>
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<td>OS11-2 Y. Kayser, W. Blachucki, J.-C. Dousse, J. Hoszowska, M. Neff, S. Nowak, V. Romano: High-resolution micro-XRF and GEXRF applied to the investigation of the distribution of dopants in optical fibres</td>
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| OS17-7 J. Osan, D. Breitner, R. Daehn, A. Keri, I.E. Sajo, M. Fabian, S. Torok: X-ray microspectroscopic investigation of the uptake of Cs(I), Ni(II), Nd(III) and U(VI) by argillaceous rocks of the Boda Siltstone Formation, Hungary | OS19-3 V. Zaichick: Energy-dispersive X-ray fluorescent analysis in human prostate gland studies |
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### 7 Mobile and portable XRF

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8 Synchrotron XRS, XAFS, RIXS and XES

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- Kenji Yoshii, Ignace Jarrige, Daiju Matsumura, Yasuo Nishihata, Chikashi Suzuki, Yoshiaki Ito, Takeshi Mukoyama, Tatsunori Tochio, Hiroshi Shinotsuka and Sei Fukushima. Probing the Ba 5d states in BaTiO3 and BaSO4: A resonant x-ray emission study at the Ba-L3 edge

- Masaharu Uemura, Takayuki Hasegawa, Takabumi Tsurui, Masayoshi Shimizu, Sinsei Yokoi, Toshiaki Ohta, Kenta Amemiya, Noboru Fukada, Muneyuki Motoyama, Kazuhiro Kanda and Sei Fukushima. L-edge for the 1st period transition elements


- Iztok Arcon, Mirjana Kuezma, Robert Dominko and Miran Gabrscek. In situ XANES and EXAFS analysis of Li2NiTiO4 cathode materials for Li-ion batteries

- Juan Leani, Héctor Sánchez and Carlos Pérez. Micro-Determination of Oxidation States by means of Confocal X-Ray Raman Spectroscopy

- Juan Leani, Héctor Sánchez and Carlos Pérez. Grazing-Incidence X-Ray Resonant Raman Scattering (GI-RRS)

- Sybelle Deloule, Johann Plagnard, Marc Denoziere and Isabelle Aubineau-Lanièce. HPGe and Si-PiN characterization for measurement of continuous photonic emission (E < 50 keV) of medical X-ray tubes

- Chanapa Kongmark, Wantana Klysubun, Natthapong Monarumit and Pornsawat Wathanakul. Titanium local structure in blue sapphires probed by X-ray absorption spectroscopy


- Andrew Neal, Kalotina Geraki and Frederick Mosselmans. Mineral localisation and complexation in ferritin-expressing wheat grain

- Wiwat Wongkokua, Tobias Häger, Wantana Klysubun, Monarumit Natthapong and Wathanakul Pornsawat. X-ray absorption near edge structure of Al2O3-Cr2O3 series

- Michael Hagelstein, Tao Liu, Rolf Simon, David Batchelor and Vladimir Nazmov. The application of mosaic prism lenses for wide band-pass X-ray monochromatisation

10 High resolution X-ray absorption and emission spectroscopy

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There has been a substantial growth in the application of XRF in the field of cultural heritage in recent years. Some of this expansion has been stimulated by the availability of new portable instrumentation coupled with the realisation that XRF can provide new types of information. The range of artefacts to which the XRF technique has been applied is astonishing and includes pottery and porcelain, building materials, stone implements, paintings, frescoes and inks, paper, coins and metallic objects. Despite this wide range of materials, there is more uniformity in the use to which XRF data is put. At the most basic level, elemental composition data can be used to identify the materials used to manufacture an artefact. However, these data are often of more value in elucidating the process of manufacture, the provenance of an artefact, or its authenticity. In a significant number of applications, a multi-technique approach is favoured, often because conventional XRF does not directly offer information on molecular species.

Hand held XRF is essentially a surface analysis technique. Although this can offer real advantages in some applications, in many, the objective is to determine the bulk composition of an artefact. It is then necessary to have some expert knowledge of the origin of the XRF signal in relation to the homogeneity of surface layers to ensure appropriate interpretation of the analytical results.

The aim of this presentation is to review developments in the application of portable XRF in the analysis of cultural heritage artefacts, using the speaker’s involvement in the characterisation of stone axes and other lithic artefacts, some of which are related to the Neolithic Stonehenge monument. This prompts the question of what is the difference between data and information, and to what extent can the XRF technique be developed in the future to provide a reliable interpretation of results.
Fe K-XANES measurements on both Attic sherds and their modern reproductions

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The well known Attic vases, dated between 620 and 330 BC, are decorated with red or black figures. A reddish clay paint (or slip), derived from a colloidal illitic clay suspension in water, is applied on the leather-hard dried body as decoration. In a three step firing process under oxidizing-reducing-oxidizing atmosphere the decoration layer vitrifies and turns to black, while the body becomes reddish-brown. The characteristic shiny decoration layer is called “black gloss” due to its appearance. In physicochemical terms the gloss itself can be described as a potash-aluminosilicate glass that contains nanocrystals of magnetite which are responsible for the black colour.

Though the manufacturing process concerning the clay–paint preparation and the firing cycle are well understood and replicated [1] there are still open physicochemical questions related to different technological practices in antiquity. An example is the understanding of the parameters that influence the exact colour of the gloss layer, the best quality of which is characterized by a bluish hue. Thus the exact oxidation state of iron is expected to be an indicator of the firing conditions, i.e. temperature and duration of each stage. Calculations of the ratio of Fe$^{3+}$ to the total amount of iron by means of investigations of the pre-edge of Fe K-XANES spectra [2,3] from modern replicas enable a better understanding of the creation of the black gloss.

For such in-situ measurements it has to be ensured that the detected signal originates exclusively from the black gloss. We performed 2D and 3D Micro-XANES simultaneously, while for 3D Micro-XANES the probing volume was placed inside the black gloss only. A comparison of both 2D and 3D Micro-XANES shows, that 2D Micro-XANES is applicable in most cases. Nevertheless self-absorption effects have to be taken into account due to high iron contents. A reliable inclusion of self-absorption effects was possible due to our newly developed reconstruction procedure for 3D Micro-XANES [4].

The study of the attic sherds in comparison with laboratory specimens enables us to discuss and describe different manufacturing processes in antiquity.

Applications of the PART II XRF-Spectrometer at the Kunsthistorisches Museum Vienna

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In the analysis of artworks x-ray fluorescence (XRF) spectroscopy has gained high significance because of the non-destructiveness of the method. The information achieved can lead to new insights into technologies and materials and support conservation and restoration efforts.

In cooperation with the International Atomic Energy Agency (IAEA) and the Atomic Institute (ATI), Vienna University of Technology, a portable energy-dispersive XRF spectrometer was designed and constructed [1] within a project funded by the Austrian Science Fund (FWF, Project No. L430-N19). The instrument was optimized to cope with the diverse analytical problems of a wide-spread museum’s collection as it is kept at the Kunsthistorisches Museum (KHM).

By now these spectrometer PART II (Portable Art Analyzer II) is in use for two years and was applied to a variety of different objects. A range of diverse applications will be presented with emphasis on the advantages of the new instrument, including positioning in front of three-dimensional objects and low-Z element determination. Within these examples a broad palette of materials, i.e. glass, ceramics, metals, pigments, manuscripts, and pesticides, will also be covered.

Investigation of organic findings (hair, bones, teeth) from the royal burials of Xiongnu (last years BC – early AD, Noin-Ula, Mongolia) by SRXRF

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Between the 3rd and 2nd cc. BC the Xiongnu state – the first nomadic empire of Central Asia – appeared. It united many nations of South Siberian, Far East and Central Asia. The main source of the information about Xiongnu is the ancient Chinese chronicles, which narrate mainly about the events, not about the humans. Archeological findings widen the knowledge about the Xiongnu culture. Despite the burials were totally robed and anthropological material was rare, the burials in Noin-Ula Mountains (Northern Mongolia) are one of the most informative cultural site of Xiongnu.

The burials of grand Xiongnu people are unique source of information due to the great number of utensils and other metallic things discovered. There is also variety of organic material (hairs, fragments of bones, teeth, textile, and lacquered things). Hair material is unique in itself. It can give the information about the culture of buried people, their origin and adaptation to the environment. Often, when there is a lack of anthropological material, the teeth and bones are the one source of data on the buried people – the leader and his people.

The SRXRF analysis of hair samples, different types of regional clay, fragment of radial human bone, and woolen cloth discovered in the burials of grand Xiongnu people was carried out. The anomalous high copper content in all investigated hair samples was observed – in the range of 0.1-1.6 % (by weight), whereas the levels of copper content in bone and clay was about μg/g and several tens of μg/g, respectively. New archeological findings, e.g. tooth enamle and bones from the burials of common people, were investigated for the last year. Nowadays, the main goal of our investigation is to determine the possible reason (and the source) of such a high copper content in some organic samples, including hairs.
No simple answers to archeometrical questions: how to get
the most of PXRF spectrometer on different materials

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Handheld XRF spectrometers lately became fast, accurate and cheaper, allowing to work in the field virtually on any kind of materials [1, 2, 3]. Archaeometric analyses had took great advantages from this class of spectrometers and some dedicated solutions are now available. Notwithstanding, working on unique and not standardized objects requires to pay attention on details and to know how to choose correct parameters and calculation algorithms to obtain reliable results. Indeed opportunities to deal with these objects are very limited and results have implication in other fields.

Starting from a case-study (workshops in a medieval Charterhouse), this work aims to expose various details, including the strengths and the weaknesses of typical XRF analysis, emphasizing preferable instrumental set up and limits or advantages over static XRF spectrometers. Examples reported concern in situ easel paintings and pigment characterization, copper alloys, bricks and stained glasses, comparing obtained results with laboratory measurements on analogous samples. Possibility of performing quantitative analysis on listed materials is considered, too.

Identification of welding processes in ancient gold jewelry

by Micro-XRF spectroscopy

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In science applied to cultural heritage, the study of the method of manufacture of ancient metal artifacts is of particular relevance. In fact, metal manufacturing is directly correlated with the development of the civilization.

The aim of this work is to reconstruct, by means of experimental archeology, the ancient welding processes, in order to identify them in real samples using a portable micro X-ray fluorescence (μXRF) system. This portable and non-destructive technique provides an essential method for characterizing the manufacturing of ancient gold jewelry.

Various gold alloys were produced with different Ag and Cu content to simulate real cases. Besides, based on archaeometallurgy techniques, replicas of decorations were fabricated following the ancient recipes such as those described in Naturalis Historia and Leiden papyrus X. The content of Au, Ag and Cu within the soldering areas was quantified with the μXRF technique.

The methodology described in this work was applied in the particular case of alloys with high gold concentrations to identify the different soldering techniques. Based on this interpretation, it will be possible to systematically study and characterize the manufacture of ancient gold jewelry, especially in very pure gold alloys such as Tarsetic jewelry (4\(^{th}\)-5\(^{th}\) BC).

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Characterization of two baroque sculptures of the **Immaculate Conception**: the art of combining innovation with tradition

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This research focuses on two baroque statues depicting the **Immaculate Conception**, intended for religious sanctuaries of Coimbra, Portugal. These two sculptures are very alike from a sculptural perspective but they are of different sizes. The first one was conceived as a monumental and immovable artwork, the back remaining deliberately unfinished. The second one, of medium size, was simultaneously used for regular devotion and carried in procession, as suggested by the fact of having been carved in the round and entirely polychrome. Much information is available concerning the largest one as regards the identity of the sculptor (Lay Brother Frei Cipriano da Cruz) and the painter (Manuel Ferreira), the dates of production (1685 for the wooden carving and 1691 for the polychromy) and the altarpiece to which it was intended in the Church of St. Benedict (Coimbra). Very little is known about the smallest one (conserved at the present in the Coimbra museum), whose authorship, dating and original location have been recently the subjects of an extensive research but whose attribution to Frei Cipriano da Cruz remains an open issue [1].

The polychrome coating of both sculptures offers important elements of comparison, especially since the treatment of the Virgin’s mantle gave rise to the creation of very different raised applications to imitate high-quality trimmings in a sumptuous blend of colors and textures. In the present work, a detailed characterization of these coatings was carried out by several methods of examination and analysis. The implemented methodology required the use of normal and raking light, of in situ digital microscopy (Dino-Lite) for optical imaging and in situ Energy Dispersive X-ray Fluorescence (EDXRF) in order to assess the elemental composition. Based on this information, several spots identified as being relevant for the research were selected for sampling and the application of complementary analytical techniques in laboratory. Further examination with optical microscopy (OM) was done aiming at comparing the different structured layers and techniques used by the painters-gilders. Complementary analyses by Raman spectroscopy and by X-ray Diffraction (XRD) were carried out to identify the coloring substances and binding media.

The whole data put in evidence the extreme richness of the polychrome coatings under study and, above all, the genius of artists who knew how to reproduce to perfection the tactile effect of the seventeenth-century brocade fabrics and passementarie. The unexpected use of beeswax and fine sand unveiled in this research showed that even materials not belonging to the painting trade could perfectly fit the search of realism and of deep visual contrasts that were matters of priority at the baroque time. The obtained results allow new comparisons with earlier and contemporary coatings already studied on other statues from Coimbra [2][3].

Mercury-silvering evidence in late Roman coins by the combined use of the portable XRF and low energy \(\mu\)XRF techniques

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Roman coinage underwent a severe debasement of silver during the time and the production of plated coins became a common practice for giving the impression of a high finesses of the alloy. In 294 AD, Diocletian introduced the nummus, manufactured with the same standard in all the mints by using an internal Cu-Sn-Pb-Ag core and presenting a thin silvered patina (about 2\(\mu\)m) on its surface. The silver plating of the nummi have been investigated in the past and different methods have been suggested for its manufacturing (e.g. segregation during casting, chemical treatments, mercury-silvering) [1,2]. However, previous analyses were focused on few samples and, consequently, this technological issue remained unresolved. In the present work, the BSC-XRF (Beam Stability Controlled –XRF) [3] and a LE-\(\mu\)XRF (Low Energy-\(\mu\)XRF) portable spectrometers developed at the LANDIS laboratory in Catania (Italy), have been applied for the in-situ analysis of the silvered nummi belonging to the Misurata Treasure (Museum of Leptis Magna, El-Khomes, Libya). The treasure is composed of 108 thousand coins manufactured in 19 Imperial mints operating in the period 294-333 AD. In order to establish if, and at what extent, the mercury-silvering was used to produce the thin Ag-patina of the nummi, the non-destructive investigation was extended to 1050 well preserved coins. Measurements allowed to explore the presence of Hg and the Hg-Ag correlation at the coin surface. The portable BSC-XRF and the LE-\(\mu\)XRF techniques are suited to approach this study. A new version of the BSC-XRF spectrometer, consisting of a compact high-intensity x-ray tube (50 kV; 4 mA) coupled to a 80 mm\(^2\) SDD detector (138 eV @ 5.9 keV), was developed for the fast determination of mercury traces in a large number of coins (measurement time is 15 seconds; MDL for Hg is 100 ppm). The investigation allowed to identify the Imperial mints and the periods where the mercury-silverying were probably used. However the BSC-XRF analysis is not limited to the surface and the Ag-Hg correlation cannot be evidenced in the patina layer. The integration of the results with the LE-\(\mu\)XRF measurements allowed to overcame this limit. Our LE-\(\mu\)XRF technique operates in a low energy domain; the system consists of a fine focus x-ray tube (8 kV; 1.5 mA) equipped with a 200 \(\mu\)m straight-shaped capillary, coupled to a 50 mm\(^2\) SDD detector (133 eV @ 5.9 keV). The system, applied to selected samples, excited efficiently the Hg-M and Ag-L lines, limiting the analytical depth to about 2 \(\mu\)m. Moreover the high lateral resolution allowed to perform the surface scansion of the coins, evidencing the searched correlation between Hg and Ag at the surface of the nummi. Results allowed to demonstrate that mercury-silvering was used in the late period (mainly after 318 AD) and only in some specific mints.

Comparison between XRF, TXRF and PXRF analyses for provenance classification of archaeological bricks

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Ceramics provenance studies based on minor and trace elements are widely used to help in gathering knowledge of local furnace presence and commercial trades. Most of the times, destructive analyses are allowed due to the high amount of material, but sometimes (integer vessels, architectural decorations…) a non destructive examination is required. In both cases, XRF analysis can be a useful tool \cite{1,2}.

In this work, we compare the classification results obtained on a set of bricks from the Po valley in Northern Italy exploiting XRF, portable XRF and TXRF spectrometers.

XRF non destructive analyses were performed both \textit{in situ} before sampling and in laboratory without preparing the shards. Grounded samples were instead used to obtain basic semi-quantitative TXRF analysis without dissolving the samples, but using a suspension in high purified water \cite{3}. Aim of the project was to verify if a correct classification was possible also avoiding quantitative determination of minor and trace elements, allowing a faster response if a large amount of data is concerned. So, weight concentration was determined only from laboratory XRF measurements, while semi-quantitative results and entire spectra \cite{4} were considered respectively for TXRF and \textit{in situ} campaign. Data were then submitted to different statistical data treatment to obtain provenance classification.

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High-resolution x-ray emission spectroscopy for fundamental parameters determination

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Investigation of photon-atom interactions and decay channels is equally important in fundamental research and for x-ray based applications in many fields of sciences and technology. The new brilliant x-ray sources as well as advances in photon-in photon-out experimental techniques and theory have opened new exploration routes for atomic x-ray physics. In this perspective, high-resolution x-ray emission spectroscopy represents a powerful method for studying x-ray interactions with matter and for atomic fundamental parameters (FPs) determination with reduced uncertainties. Improving FP databases is of prime importance for the fundamental parameter approach to x-ray fluorescence analysis which is employed in different fields such as material sciences, biology, medicine, mineralogy, or cultural heritage. In particular, the emerging novel nano-scale materials and electronic devices require highly sensitive analytical techniques and the state-of-the art methodologies to probe their electronic properties.

In my talk I will report on a number of projects that were undertaken by the Fribourg Atomic and X-ray Physics (AXP) group in the field of the metrology of x-ray transitions and fundamental parameters determination. Measurements of the fundamental parameters and the investigation of the related physical processes have been performed over the last two decades. The works focused on line energies, x-ray transition linewidths and level widths, x-ray transitions relative intensities, influence of chemical- and solid-state effects on x-ray line intensities and energies, shake satellites, the Radiative Auger Effect (RAE) transitions, Coster-Kronig (CK) transition probabilities, and the Resonant Raman Scattering (RRS) process. The measurements were carried out with two instruments developed in Fribourg, namely the Laue-type DuMond and the Bragg-type von Hamos crystal x-ray spectrometers, using both conventional x-ray sources and x-ray synchrotron radiation.

Future projects aiming on the methodology development for FPs determination with reduced uncertainties and improvement of the XRF databases in a collaborative effort between research institutes and industrial partners will be also outlined.
The most accurate description of the radiation field in x-ray spectrometry requires the modeling of coupled photon-electron transport, since Compton scattering and the photoelectric effect produce both photons and electrons as secondary particles. Up to now, in deterministic codes this complex problem has been simplified by neglecting the contributions of secondary electrons and, consequently, a pure photon transport equation is used. This approximation has a twofold effect on the solution: (a) the bremsstrahlung contribution (which produces a continuous photon energy spectrum) is missing; and (b) the inner-shell impact ionization (which modifies the intensity of the characteristic lines) is ignored.

It is possible to improve this approximation by keeping the advantages of a pure photon transport model. In this work a corrective term of the photon kernel is introduced to include the effect of inner-shell impact ionization. The code PENELope (coupled electron-photon Monte Carlo) is used to characterize this correction in terms of angular, spatial and energy distributions. It is demonstrated that the angular distribution of the characteristic photons due to inner-shell impact ionization can be safely considered as isotropic, and that the source of photons from electron interactions is well represented as a point source. The energy dependence of the correction is quantified in the energy range 1-150 keV, for all the emission lines (K, L1, L2 and L3) of the elements with atomic numbers Z=11-92. For each characteristic line, the energy dependence is represented by simple parametric expressions corresponding to the 5 energy regions delimited by the K, L1, L2 and L3 edges.

The formal representation of the new photon kernel comprising the correction for inner-shell impact ionization is given. It is suitable to be adopted in photon transport codes (deterministic or Monte Carlo) with a minimal increase in complexity.

The new kernel is studied for different elements and lines in order to establish a general behavior.
Reliable uncertainty budgets for the determination of atomic fundamental parameters of high Z elements

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Reliable quantification in XRF analysis depends on the knowledge of fundamental parameters of the elements in the sample. Using reference or calibration standard specimens the influence of the uncertainties of these fundamental parameters is relatively small. But if there is a lack of appropriate reference samples the quantification relies on the good knowledge of all experimental, instrumental and fundamental parameters involved. Their uncertainties affect the uncertainty of the quantification result directly. A reliable uncertainty budget of fundamental parameters published is often missing, as the uncertainties are mostly assumed or only based on fits over a compilation [1-3].

Employing a reference-free XRF approach [4] fundamental parameters of L-subshells of high Z elements, such as Coster-Kronig transition probabilities and fluorescence yields, have been experimentally determined. In addition, the transmittance of the same samples at the exciting photon energy as well as the fluorescence line energies has been determined to derive the self-absorption correction factors experimentally.

Together with the experimentally determined photoelectric cross sections from the transmission measurements Coster-Kronig transition probabilities and fluorescence yields for different high Z elements have been determined, whereas special attention has been paid on a reliable uncertainty budget for these fundamental parameters. The photon-in-photon-out experiments allow for the further reduction of the relative uncertainties in the quantification by reference-free XRF analysis.

Measurements of the fluorescence yields of Germanium by two independent approaches

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Germanium is a key element and is currently used as semiconductor detector in X- and gamma–ray spectrometry. Accurate Monte Carlo simulation of such detectors response requires improved knowledge of the atomic parameters of germanium such as fluorescence yields and attenuation coefficients.

In general, the knowledge of fluorescence yields is rather poor and based on old measurements. Nowadays, the use of tunable monochromatic X-ray sources allows performing optimized measurements.

In a first step, accurate values of the germanium attenuation coefficients are measured both at the Metrology beam line of the SOLEIL synchrotron and using the SOLEX source [1], using procedures such as optimized for similar measurements [2]. Special care is taken around the K and L binding energies of germanium, and on the energy of its characteristic X-rays.

In a second step, the K and L fluorescence yields are determined using two experimental approaches:

- In a traditional experimental configuration where a germanium target is installed at 45° both from the incident radiation and from the spectrometer;

- Without any target, using only the escape peaks of a high purity germanium (HPGe) detector, evaluating the escape-peak to parent-peak intensity ratio the intensity of which directly depends on the fluorescence yield [3]. The figure shows an example of the spectrum obtained with 17 keV parent peak (incidence energy) and the associated $K_{\alpha}$ and $K_{\beta}$ germanium escape peaks.

In both cases, several incident energies are used to get experimental spectra with energy-dispersive spectrometers. The peaks of interest are processed using the COLEGRAM software which allows detailed fitting of the peak shape. The required attenuation coefficients are taken from the first step of the experiment.

Experimental verification of L-shell photo ionization cross sections of Pd and Mo

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Keywords: sub-shell photo ionization cross sections, Coster-Kronig transition probabilities

An exact knowledge of the atomic fundamental parameters (FP) is required for reliable quantitative X-Ray fluorescence analysis. Amongst other issues, an accurate knowledge of the diverging energetic behavior of the three L-subshell photo ionization cross sections (PCS) leads to significant improvements in quantitative analysis as compared to using constant jump ratios. Theoretically calculated PCS, e.g. Scofield’s data [1] predict energy dependent ratios between the L₁, L₂ and L₃ subshells.

In this work, the energetic run of the PCS for Mo and Pd between their respective L- and K-edges have been experimentally determined using PTB’s reference-free XRF instrumentation [2]. Metal coated silicon nitride foils have been used as the sample material. The experiments were carried out at both the laboratory of the PTB at BESSY where monochromatized synchrotron radiation up to 10 keV is available and at the BAMline at BESSY where higher photon energies up to 50 keV are accessible. The PCS were derived from the energy dependent fluorescence intensities of each subshell. Relevant other FPs, e.g. Coster-Kronig transition probabilities have also been experimentally determined.

The determined results confirm the diverging behavior of the L₁ photo absorption cross section compared to L₃ and L₂. The data obtained is in good agreement with some of the available FP compilations.

Measurement of $^{241}$Am L X-ray Relative Emission Intensities with a High Energy Resolution Magnetic Calorimeter

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Americium-241 is one of the most frequently measured radionuclide, due to its 59.6 keV gamma emission useful for example for efficiency calibration of photon spectrometers. However the X-ray intensities are not well known because of the complexity of the L X-ray energy spectrum. Americium-241 decays by alpha emission to Neptunium-237 which emits more than twenty intense L X-ray lines lying between 1.87 and 22.40 keV [1]. Considering the modest energy resolution of semiconductors detectors and the energy proximity between the lines, the spectrum processing is delicate and can lead to large systematic errors. Because of their high energy resolution power, cryogenic detectors can provide decisive improvement of the knowledge of photon emission intensities.

Using a metallic magnetic calorimeter, a kind of cryogenic detector, optimized for X-ray spectrometry below 25 keV, we measured the L X-ray relative emission intensities of Neptunium by energy dispersive X-ray spectroscopy. This detector has a constant detection efficiency over the Neptunium L X-ray energy range and it provides an energy resolution of 37 eV close to the X-ray natural line width. The energy spectrum quality is significantly improved; the overlapping is minimized, therefore the systematic errors due to the spectrum processing are reduced.

The relative emission intensities are compared with previously published data determined with semiconductor detectors [2]. While the comparison of individual line intensities reveals discrepancies that will be discussed, the comparison of intensities of the L groups L$_l$, L$_{\alpha}$, L$_{\eta}$, L$_{\beta}$, and L$_{\gamma}$ is consistent.

PIXE in the slow collisions regime

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Traditionally, Particle Induced X-ray Emission work is carried out using proton beams of 2 to 4 MeV, still in many cases, other proton beam energies and other beam particles are needed. Having this in mind, roughly 10 years ago a working line started aimed initially at speciation methods using beam energy scans. First results were promising [1], but deeper analysis revealed a puzzling situation, namely the variation of relative intensities of lines corresponding to transitions to the same LS coupling scheme sub-shell [2]. Although the variation in this type of relative intensities was known to occur due to changes in the chemical environment of the emitter, no reason could be determined for a change associated to a simple modification in the ionization process. In fact, the invariance of relative intensities among transitions to the same LS coupling sub-shell being an ergodic condition for most of the work in X-rays, the result was indeed puzzling.

Relative intensities studies in Lisbon started long ago in the 1970s using photographic plates and wavelength dispersive spectrometers. Presently, using IST/ITN's X-ray microcalorimeter spectrometer (XMS) this work is much facilitated, even if a whole new insight into the problem emerges. Furthermore, the use of the XMS for low energy PIXE work, bring us to a completely new set of problems. It apparently provides plausible simple hypothesis for the solution of the line ratio variation problem, but in fact by producing much more data than we are used to handle, a great deal of practical problems must be faced. A significant amount of work at both experimental and theoretical levels is therefore still needed before stable conclusions can be reached.

In this talk we will present a fast overview on the evolution from the 1970s to the present day XMS capabilities. In the meantime, hidden problems low energy PIXE using both standard Si(Li) detectors and high-resolution EDS XMS, will be discussed. PIXE spectra of a silicon monocrystal will be used to show the level of detail reachable and problems faced using the first generation IST/ITN's XMS system. Finally, changes on W thick target PIXE spectra in face of beam energy changes of just 10% will clarify the present development stage of low energy PIXE work.

Sub-100nm STIM imaging & PIXE quantification of rare earth elements in Algae cells

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The uptake of rare earth elements (REEs) such as Nd$^{3+}$, Gd$^{3+}$ and Er$^{3+}$ by Euglena gracilis 848 algae cells has been studied using nuclear microprobe techniques at the Centre for Ion Beam Applications, National University of Singapore. A recent upgrade of the Scanning Transmission Ion Microscope (STIM) beamline allows sub-100nm morphological imaging of algae cells, revealing the intact structure of the whole cell. Nanometric strips on the cells were observed in the STIM density map. These show structural information, namely the helical coiling of the pellicle strips of such cells, similar to the information obtained from SEM images (see Figure below). High resolution RBS imaging, showing the distribution of Erbium in the cell, will be reported as well.

Subsequent quantification of the rare earth elements was carried out using a combination of nuclear techniques such as PIXE (Proton Induced X-ray Emission), Rutherford Backscattering Spectrometry (RBS) and STIM. Our results indicate significant variability in the uptake of REEs by algae cells, the amount of Erbium absorbed is nearly one order of magnitude higher than that of Neodymium by Euglena gracilis 848 cells. On the other hand, the Gadolinium uptake was below the detection limit of 200ppm.
Combined use of quantitative ED-EPMA, ATR-FT-IR imaging, and Raman microspectrometry for the characterization of individual particles of micrometer size

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Recently, the potential of the combined use of a quantitative energy-dispersive electron probe X-ray microanalysis (ED-EPMA), called low-Z particle EPMA, and attenuated total reflectance FT-IR (ATR-FT-IR) imaging techniques for the characterization of individual aerosol particles has been demonstrated in our group [1-4]. These single particle analytical techniques provide complementary information on the physicochemical characteristics of the same individual particles, such as low-Z particle EPMA technique on morphology and elemental concentrations and ATR-FT-IR imaging technique on molecular species, crystal structures, functional groups, and physical state. In addition, the feasibility of the combined use of low-Z particle EPMA and Raman microspectrometry (RMS) for the characterization of chemical species and internal mixing state of the same individual particles was investigated in our group [5]. Our previous works demonstrated that the characterization of individual particles including chemical speciation and mixing state analysis can be performed more in detail using either ED-EPMA and RMS or ED-EPMA and ATR-FT-IR imaging in combination than with the two single particle techniques alone. In this presentation, the combined use of the three single particle analytical techniques such as ATR-FT-IR imaging, RMS, and low-Z particle EPMA for the characterization of the same individual particles will be described with the discussion of the merit and practical considerations of this new methodology.

By dropping $10^{-2}$ to 1 wt. % of ionic liquid (1-ethyl-3-methylimidazolium acetate: EMI-CH$_3$COO) diluted with ethanol on insulating samples, we succeeded in obtaining clear SEM images in micrometer scale regions [1,2]. In the present study, we carried out SEM-EDX analysis of insulating samples containing transition metals, whose excitation efficiencies are low, using the diluted EMI-CH$_3$COO. Figure 1 shows EDX spectra of a slag sample with and without the diluted EMI-CH$_3$COO. K lines of Mg, Al, Si, Ca, Mn, and Fe, which were contained in the slag sample, were detected in the EDX spectrum of the slag sample with the diluted EMI-CH$_3$COO (Spectrum A). On the other hand, as for the slag sample without the diluted EMI-CH$_3$COO (Spectrum B), K lines of Mn and Fe were not detected. Zr L$\alpha$ and Cu K lines were additionally detected. We verified that electrical charging occurred on the surface of insulating samples and that the electrons from the electron gun were bent and bombarded on materials containing copper such as the sample stage and the wall of the SEM chamber. Also, zirconium of the collimator of the X-ray detector was excited by characteristic X-rays emitted from materials underneath the slag sample. By using the diluted EMI-CH$_3$COO, the electrical charging and detection of Cu and Zr can prevent.

PIXE characterization of pottery production from the necropolis of Jiyeh archaeological site

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Today the remains of the ancient Porphyreon lie within the territory of the modern day town of Jiyeh, located on the Mediterranean coast, about 28 km due south of Beirut and 8 km north of Saida (ancient Sidon). In 2004, the work concentrated on the area occupied by the Romano-Byzantine necropolis. These excavations revealed the remains of some pottery production features beneath a level of graves. The discovered material enabled the identification of two different phases of pottery production, dated to the Late Hellenistic and Early Roman periods. The pottery recovered from the production area has been compared with that obtained from some test pits excavated in the area of the ancient village, located about 200m south of the necropolis.

Particle induced X-ray emission technique PIXE was used to determine the elemental composition of the studied excavated shreds and cluster analysis. A proton beam of 3 MeV and a funny filter of aluminium, used as X-ray absorber, allowed the detection of almost 20 elements in one spectrum (Na, Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Ba and Pb). However, only 12 elements were used in a multivariate statistical program to identify and classify into groups the studied objects, where two different groups were identified.
Trace element analysis of some indigenous medicinal plants of Ethiopia by PIXE

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Medicinal plants contain both organic and inorganic constituents. Research work has been carried out extensively on the organic constituents of the medicinal plants, while the role of inorganic elements in the medicinal plants has received relatively less attention. The chemical constituents present in the plants responsible for their medicinal properties include bases comprising alkaloids, amines, glycosides, etc. Trace elements play an important role in the formation of these compounds. They are intimately involved in the physiological functions and are important co-factors in the production of enzymes. They are also necessary for the maintenance and regulation of cell, gene and membrane functions. The data obtained on concentrations of different elements of the medicinal plants will be useful in deciding the dosage of traditional drugs prepared using these plant materials. Such analysis is also necessary to ensure that they do not contain heavy metals in toxic proportions.

Trace elemental analysis of three indigenous medicinal plants of Ethiopia, bearing botanical names *Croton macrostachyus* (leaves), *Salvia nilotica* (leaves) and *Solanum incum* (bark) is carried out by PIXE using 3MV pelletron facility at the institute of Physics, Bhubaneswar. These samples were collected around the Dilla region of Ethiopia. Each plant sample was cleaned, dried, ground and then homogenized in an agate mortar. A quantity of 120mg of each powder sample was mixed with high-purity graphite powder (9.999%) to monitor the beam current. This mixture was compressed using a 10-ton hydraulic press into pellets to be used as targets for the PIXE experiment. In a similar method, thick targets of certified reference material of NIST apple leaves (1515) were prepared and irradiated for quantification and verification of the results. A proton beam of 3MeV energy was employed to excite the samples. The beam current was kept at about 20 nA. An Si(Li) detector was used for the detection of X-rays produced. Data analysis was carried out by using Gupix software [1] and trace element concentrations were determined.

Various elements ranging from sulphur to strontium were detected in different concentrations. In Ethiopia, *Croton macrostachyus* has folk medicinal uses as purgative and vermifuge, and for treatment of various skin problems, helminths and venerealdiseases[2]. Similarly *Solanum incum* has many medicinal uses based on its analgesic properties. Through out tropical Africa ailmens like sore throat, angina, stomach ache, rheumatic pains etc. are treated by *Solanum incum*. We made an attempt to find a correlation between the presence of the trace elements detected in these plants and their curative properties. Apart from this the present study provides useful data for researchers working in related fields like ethnopharmacology.

(2) Getachew Belay et al, Phytopharmacology 1(5), 2011, 133
Scanning hard X-ray nanobeam techniques at the Nanoscopium beamline of Synchrotron Soleil

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Numerous technological and methodological advances have recently fostered the development of innovative scanning hard X-ray nanobeam techniques. State-of-the-art focusing optics provides the possibility of achieving $\leq 50$ nm spatial resolution in real-space microscopy. On the other hand, coherent diffractive imaging techniques yield spatial resolution well below the lateral size of the probing nanobeam via the inversion of far-field intensity measurements. Advanced fast and sensitive detectors permit high-resolution imaging of extended objects and three-dimensional (3D) X-ray imaging. The simultaneous implementation of complementary techniques using contrast mechanisms such as absorption and phase contrast, dark field (or small-angle scattering) contrast, and X-ray fluorescence spectrometry (XRF), provides multimodal information about the sample structure and composition.

The Nanoscopium scanning hard X-ray nanoprobe beamline of Soleil is dedicated to implementing these imaging techniques, exploiting the 155 meter distance between the source and the experiment stations to reach some tens of nm spatial resolution in the 5-20 keV energy range. High sensitivity 2D/3D quantitative structural, elemental, and chemical analysis will be available by coherent scatter imaging and X-ray spectro-microscopy. Efficient and high throughput multimodal imaging will be implemented through a combination of pre-screening and mapping of samples, online vetoing and pre-processing of scan data, and post-processing of the experimental results. This will enable new possibilities in the scientific areas targeted by the beamline, e.g., biological, health, earth and environmental sciences. In this presentation, the key features and the future scientific possibilities of Nanoscopium will be presented.
Evaluation of analytical performance of confocal micro-XRF spectrometers

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Micro-X-ray fluorescence (micro-XRF) analysis is a promising method for observing elemental distributions of inhomogeneous samples. In particular, the micro-XRF analysis has a great advantage of nondestructive elemental analysis at an atmospheric pressure. Moreover, the recent trend in micro-XRF is 3D elemental analysis under confocal arrangement. Osaka City University (OCU) has developed a confocal micro-XRF instrument by using polycapillary x-ray lenses with a spatial resolution (depth resolution) of 13.7 micro-meters at an energy of 11.4 keV (Au Lb) [1-2]. This instrument has a high spatial resolution, however, analytical sensitivity for low Z elements was not in the satisfied level. On the other hand, the Vienna University of Technology Atominstitut (ATI) has developed a confocal micro-XRF with a vacuum chamber. A great advantage for detection of low-Z elements was expected with ATI spectrometer.

A joint research project on confocal micro-XRF analysis of low Z elements especially for forensic samples has started between JSPS in Japan and FWF in Austria. Under this program, analytical performance of OCU and ATI confocal micro-XRF spectrometers was compared. We prepared several standard thin metallic layers on Si wafers for evaluating the analytical performance of the confocal micro-XRF instruments as well as standard reference materials (SRM) and identical paint samples. The depth profiles and lower limit of detections were evaluated by measuring layered structure sample and SRM, respectively. A comparison of the results obtained by two spectrometers will provide a useful information for development of confocal micro-XRF instrument in the laboratory.

References
Quantitative 3D micro-XRF analysis with laboratory setup

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3D micro-XRF has become a well established tool in non destructive analysis [1]. Confocal setups have been realized at synchrotron radiation facilities for qualitative and quantitative analysis. Furthermore several 3D micro-XRF spectrometers with tube excitation have been developed during the last years. Up to now only qualitative results are reported from these laboratory setups.

This confocal geometry influences an important aspect of XRF, making this technique to an interesting tool: the possibility of quantitative analysis without reference samples, based on the fundamental parameter (FP) method. A new analytical description was developed [2] and successfully tested with 3D micro XRF measurements with synchrotron radiation on standard reference samples and on archaeometric objects in the last years. The procedure is based on fitting routines of the analytical model to the measurement data, for both quantitative analysis of unknown samples and determination of calibration parameters with measurements of reference material [3].

The procedure was now extended to setups with polychromatic tube excitation. Both calibration parameters, the integral sensitivity of the setup and the size of the probing volume, depend on excitation- and fluorescence energy. Since only integral excitation information can be obtained, the procedure had to be modified in order to extend it for polychromatic radiation. The procedure was validated based on measurements on multielement glass references and stratified polymer samples.

Application of grazing incidence x-ray spectroscopy to the analysis of Arsenic doped Silicon produced by plasma immersion ion implantation


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Grazing incidence (GI) geometry exhibits an exotic geometry in x-ray fluorescence (XRF) spectroscopy and is mainly used to restrict the information depth of the analysis to the sample surface. For samples with sufficiently small surface roughness variation of the angle of incidence within the range of the critical angle of total reflection allows to obtain information about the depth distribution of elements within the sample’s surface. When using Synchrotron radiation as x-ray source the method can be combined with x-ray absorption spectroscopy (XAS) analyzing the local coordinate structure of an element of interest in the sample.

In this presentation I will outline the application of GI-XRF and GI-XAS spectroscopy to the analysis of ultra shallow arsenic implants in silicon. Focus of this study is to characterize implants produced by Plasma Immersion Ion Implantation (PIII) and subsequent laser annealing, by analyzing the sample surface, the As implantation profile and the local structure of the dopant for a range of implantation energies and (laser) annealing power. Results from x-ray methods will be complemented with data from other analytical methods including secondary ion mass spectrometry (SIMS), instrumental neutron activation analysis (INAA), scanning electron microscopy (SEM), and atomic force microscopy (AFM).

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Domestic dog hair samples as biomarkers of arsenic contamination

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Hair arsenic concentrations were measured in 25 dogs living at Barrio Los Alamos, Gran Buenos Aires, Argentina. This study was performed in order to evaluate the contamination risk in humans living in an area with arsenic levels higher than maximum allowed limit of 10 µgL-1. This region belongs to the zone in Argentina with Chronic Endemic Hydroarsenicism (HACRE). Quantification of the samples was done using total reflection X ray fluorescence technique after a sample preparation procedure. Independently of genre, age and breed, hair dogs from Los Alamos had significantly higher arsenic concentrations than a set of 10 dogs used as blank coming from a free arsenic area. These found levels in hair indicated a chronic contamination in dogs and suggest similar presumption in humans. Results of this study encourage the potential of using pets as biomarkers of environmental metal contamination.
Determinations of low atomic number elements in real uranium oxide samples using Vacuum Chamber TXRF

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Determination of low atomic number (Z) elements by XRF is a difficult task. Recently, we have explored the possibility of determination of low Z elements using synthetic samples [1]. However, analyzing real uranium samples for low Z elements using TXRF has its own problems. Some studies to assess the feasibility of vacuum chamber TXRF in real analysis of uranium oxide for low Z elements were initiated. For sample measurements the ATI low Z TXRF vacuum chamber spectrometer having Cr Tube was used [2]. Cr Kα monochromatic X-rays obtained using a W-C multilayer was used for sample excitation.

Known amounts of Certified Reference Materials (CRMs) for trace element: CRM-1 and CRM-2 of uranium oxide developed by Department of Atomic Energy, Government of India, containing certified amounts of low Z elements: Mg and Al along with other elements [3] were dissolved in small amount of suprapure concentrated nitric acid. These solutions were later diluted in such a way as the HNO₃ present attains a molarity of 3M. Uranium was selectively extracted from these solutions using 30% solution of tri-n-butyl-phosphate (TBP) in dodecane as extracting agent. The TXRF spectra of the aqueous phases, obtained after three equilibration of the analyte solutions with TBP extractant, were measured by depositing 2 μL of the solution on quartz sample supports. These spectra did not show presence of Mg Kα whereas strong U-M lines giving escape peak at Al Kα position were observed. In addition dead time of the detector was approximately 90%. Mg and Al Kα peak of appreciable intensity could be seen in aqueous phases after equilibration with TBP-dodecane solution for six times and with dodecane (to remove any dissolved TBP in aqueous phase) one time. These aqueous phases were mixed with internal standard solution (Sc) and four microlitre aliquots of the solution mixture thus obtained were deposited on quartz sample supports and TXRF spectra were measured for a live time of 1000 s. The low Z elements Mg and Al were determined after processing the spectra with computer program AXIL and using the area of X-ray peaks and corresponding sensitivity values. The TXRF determined Mg in CRM-1 and -2 were in good agreement with the certified values. However, the TXRF determined Al values were higher with respect to certified values. The higher amount of aluminum obtained by TXRF may be due to interference of escape peak of U Mα with Al Kα. This study suggests that due to very strong absorption of low Z elements K-X-ray lines by uranium, almost complete separation of uranium either by phase separation or precipitation shall be required for routine analysis of low Z elements in uranium matrix by Vacuum chamber TXRF. In addition, excitation sources efficient to excite low Z K X-ray lines but not capable to excite U M lines shall be advantageous.

References:
Determination of Rb, Sr, Cs, Ba, and Pb contents in K-feldspars in small sample amounts by total reflection X-ray fluorescence (TXRF) analysis

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The information about rare element contents in K-feldspars is used for obtaining granitoid geochemical characteristics. The contents of Rb, Sr, Cs, Ba, and Pb are significant for the geochemical investigations of the K-feldspars. Rb/Cs and Ba/Rb relations in the K-feldspars are important in exploration works for the typification and the ore content estimation of pegmatites [1]. The separation of a K-feldspar monomineralic fraction is a time-consuming process demanding special skills. The determination of the rare elements in small sample amounts (50 mg) can be carried out by TXRF [2].

The investigations were conducted using TXRF-spectrometer S2 PICOFOX (Bruker Nano GmbH). Certified Reference Materials (CRMs) of granitoid rocks and K-feldspar samples were prepared in a suspension form, dried, and pipetted on quartz sample carriers as shown in [2]. The contents of the rare elements were determined using the internal standard method. As internal standards Se solution with 200 mg/l concentration and Rb contents preliminary determined by the flame photometry method were used. The accuracy of the determination was estimated by comparison of the element contents in the CRMs and the K-feldspar samples. The variation coefficient characterizing the total error of Rb, Sr, Cs, Ba, and Pb determination in the range from a few tens of ppm up to 1500 ppm was the value of less than 20%.

Series of highly sensitive X-ray fluorescence spectrometers

TXRF and GIXRF

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We have designed and developed a series of novel portable X-ray spectrometers XFS for TXRF and GIXRF. An arrangement of the spectrometer is shown in Figure. Primary X-rays from microfocus X-ray tube (1) (power ~ 7W, anode: Ag, Rh or Mo) cause excitation of the secondary fluorescence radiation from the flat target (2). We use the targets with large concentration of elements whose K shells can be excited by characteristic part of the primary X-rays. The secondary beam from the target (2) passes through mirror collimator (3) and suffers total reflection from the amorphous quartz plate (4) with a flat surface and thin exploring specimen applied on it. X-ray fluorescence radiation emitted from the specimen is analyzed by a semiconductor detector (5) with energy resolution of about 160 eV, which is disposed close to the specimen to increase a counting rate.

Since cross-sections of absorption processes for the primary X-rays noticeably exceed those of scattering ones, bremsstrahlung intensity in the secondary X-ray beam is essentially less than in the primary beam thus causing decrease of radiation background in the fluorescence spectra from the specimens and making an advantage of the scheme proposed.

XFS spectrometers provide opportunity for performing express qualitative and quantitative X-ray fluorescence analysis of the specimens with low amount of the analyzed elements[1].

We show an experimental total X-ray reflection fluorescence (TXRF) spectrum of a dry specimen containing 0.1 ng of Cr, Fe, Co, Ni, and Cu. For measuring this spectrum, we used the X-ray tube with Mo anode and the SrCO₃ target to emit secondary X-rays. Spectra of biological, medical and nanotechnology samples are also presented.

Figure. Arrangement of the XFS-002 spectrometer: 1) X-ray tube with Ag, Rh, or Mo anode. 2) The target providing secondary X-rays. 3) Mirror collimator of the secondary X-rays. 4) Amorphous quartz plate (X-ray mirror with surface roughness < 500 Å). 5) Semiconductor detector.

X-Ray induced characterization of ion implantation depth profiles

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An X-ray induced characterization method using Grazing Incidence X-Ray Fluorescence (GIXRF) analysis has been applied to the characterization of various ion implantations into silicon and other substrates. Multiple implanted species with nominal fluences between $1 \times 10^{14} \text{cm}^{-2}$ and $1 \times 10^{16} \text{cm}^{-2}$ over a wide range of implantation energies from down to 0.5 keV up to several hundred keV have been characterized using this methodology.

The depth profiling with GIXRF analysis is based on the induced changes of the X-ray Standing Wave (XSW) field intensity. The XSW field arises between the primary and the reflected beam and is dependent on the incident angle [1]. The implantation depth profile is convolved with this intensity distribution and creates a specific angular fluorescence curve during a GIXRF measurement.

The experiments have been carried out at the laboratory of the PTB at BESSY using monochromatized synchrotron radiation of well-known radiant power and spectral purity [2]. The results obtained with this method show good agreement with secondary ion mass spectrometry and medium energy ion scattering [1] as well as grazing exit X-ray fluorescence [3] investigations.

Novel approach to simultaneous analysis of grazing incidence X-ray reflectivity and X-ray standing wave data.


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Structural analysis of periodic multilayers with small period thickness (~4 nm) is a challenging task, especially when thicknesses of intermixed interfaces become comparable to individual layer thicknesses. In general, angular dependent X-ray fluorescence measurements, excited by the X-ray standing wave (XSW) that is formed in the Bragg reflection conditions, can provide information about the in-depth distribution of atoms in a multilayer. The atomic depth profiles in periodic multilayer structures can be obtained with high resolution by simultaneously analyzing the fluorescence data from XSW experiments, together with the analysis of grazing incidence X-ray reflectivity (GI-XRR) experiments. As a first step, the electron density distribution in the multilayer period is obtained by fitting of GI-XRR data. Next, the electromagnetic wave distribution in the multilayer is calculated based on the reconstructed electron density profile which is then used to calculate fluorescence yield from specific materials in x-ray standing wave experiments. The traditional data analysis approach is the simultaneous fit of these two sets of data and it depends on two distributions: the atomic distribution and the electron density distribution. In case of unknown atomic intermixture, there may not be a clear connection between these two distributions leading to fit of non physical parameters.

Our new approach is that the atomic profile can be directly calculated by combining measured fluorescence yields from specific atoms with the averaged electromagnetic field distribution in a multilayer period. Calculations involve solving the system of linear analytical equations using the technique of ill-posed problems. The averaged electromagnetic wave distribution in a period is calculated based on the summation of field distributions in each period of the multilayer, as obtained from GI-XRR analysis. Obtained atomic distribution automatically describes accurately measured XSW data. Additional advantage of this approach is that fitting only GI-XRR data is significantly faster than the traditional simultaneous fit of GI-XRR and XSW data. Uniqueness of obtained results can be checked by comparing of obtained atomic distribution profiles to electron density profiles.

The atomic profile reconstruction method described here has been applied to the analysis of short period (d = 3.4nm) La/B₄C and LaN/B₄C multilayers considered for application in 6.x nm projection lithography. Optimization of multilayer optical performance requires accurate determination of the multilayer structure. Reconstructed electron density profiles of both multilayers were comparable and didn’t explain increased at-wavelength reflectivity of LaN-based mirror with respect to La-based. However, when the GI-XRR analysis was combined with XSW analysis according to our new approach, the distribution of La showed that La atoms are more localised in LaN-based multilayer, while in La-based multilayer La atoms are even present in the position of B₄C layer, hinting at significant intermixture. This clearly shows that nitridation of La prevent its diffusion into B₄C layer, increasing multilayer optical contrast and as the result increasing at-wavelength reflectivity.
Investigation of elemental composition and surface structure of solid thin films by TXRF

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It is known that dielectric thin films may be used as an alternative of traditional silicon dioxide in the nanoelectronic and in several in the manufacturing of microdevices [1]. The main problem of dielectric thin films synthesis using HF-sputtering of ceramic target in plasma is the film’s elemental determination control [2]. The physical properties of the thin film BST (Ba_{x}Sr_{1-x}TiO_{3}), for example, depend on value of the stoichiometric parameter x [3,4]. It is known that the elemental composition of the deposited thin films is determined at first 60 seconds of the HF-sputtering process. However, the value of thickness and the chemical elements concentration of the sputtering films during the first seconds of sputtering are very low.

The results of TXRF investigation of BST solid thin films on LaAlO_{3} substrate are presented. By fluorescence lines dynamic on TXRF spectra depending on time of sputtering and azimuth orientation from first x-rays we obtained data about elemental composition and surface structure of solid thin film. The data were obtained on the TXRF spectrometer XFS-002 [5,6], which was developed in the Institute of Physics of Southern Federal University. In this work not only intensity time dependence of chemical elements lines was investigated but intensity of scattered line of anode MoK\alpha was investigated also. Results of these investigations are shown.

Decrease of intensity of MoK\alpha line represents interest. It is clear that such decreasing as scattering MoK\alpha line and lines of chemical elements (SrK\alpha) of a film and also substrate line LaK\alpha can be connected only with change of structure of a surface of a film. Therefore we have begun search of dependences between intensity of MoK\alpha scattering and structural properties of surfaces of films. For this purpose we had been used an atomic-forces microscope. Dependence of scattering MoK\alpha intensity on size of the roughness received on AFM is presented. It seems for us that one of the more reasonable dependencies can be approximated by the simple linear one.

Obtained results show that the first 180 seconds are characterized by alignment of film surfaces. After that the film starts to grow in regular intervals.

In work the theoretical substantiation of interaction of x-ray radiation with a rough surface which is based on standing waves is given. The conclusion becomes what to conduct the TXRF on a detection limit it is possible only considering features of structural properties of surfaces.

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[3] V. B. Shirokov at. al.// PRB. V. 73. 2006.-P.104-116
Reference-free X-ray fluorescence analysis of Cu(In,Ga)Se$_2$ thin films for elemental depth profiling

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Thin layers of Cu(In,Ga)Se$_2$ of about 2 µm thickness are used as absorber materials of thin film solar cells with efficiencies of up to 20%. The efficiency of the solar cells depends on the variation of the band gap due to an In/Ga gradient with depth in the absorber layer. Hence, for a versatile band gap engineering in laboratory research and industry quality control a reliable measurement method is required. Combining angle resolved X-ray fluorescence analysis with an absolutely calibrated experimental arrangement enables a non-destructive access to the elemental in-depth gradients.

The measurement of fluorescence photons with known efficiency in combination with well-known excitation radiation allows for a reference-free quantitative analysis that does not even require any reference standards for pre-calibration. This configuration is based on x-ray metrology and radiometry activities in the laboratory of the Physikalisch-Technische Bundesanstalt (PTB) at the synchrotron radiation facility BESSY II.

In order to develop appropriate quantification algorithms and to check the reliability of the related fundamental parameters an elaborate set of layers and layer stacks of the corresponding elements of different compositions and a set of differently graded Cu(In,Ga)Se$_2$ samples with steep and low gradient of Ga and In through the layer was selected. Measurements were carried out at the four-crystal monochromator beam line in the PTB lab with photon energies of 11 keV, using a set of incidence angles from gracing incidence conditions (0° to 4°) up to 45°. By means of this set-up and strategy, the penetration depth of the exciting photons was tuned to give access to various information depths of the samples.

The aim of these investigations is to demonstrate the capability of angle resolved X-ray fluorescence analysis for the non-destructive, reference-free determination of various elemental depth gradients. Furthermore, we investigate the resolution limits of the method and the impact of the experimental parameters such as solid angle of detection and beam width on the obtained depth profiles.
Grazing Incidence X-ray Fluorescence analysis in confocal measuring geometry

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Grazing Incidence X-ray Fluorescence (GIXRF) analysis is a powerful analytical tool for the characterization of thin films in terms of layer thickness and elemental composition [1, 2, 3]. In our work we have combined GIXRF analysis with a confocal measuring geometry with the aim to develop methodology suitable for local characterization of thin film samples. In standard GIXRF measuring geometry a large area of sample, with the size of few square millimeters, is irradiated at varying incidence angle. The XRF signal induced in the irradiated area is collected by a detector positioned at fixed angle. By analyzing the data collected in such measuring geometry the average thickness and average elemental composition of layers can be obtained. In order to characterize thin layers locally, with lateral resolution at the order of a few tens of micrometers, GIXRF analysis was performed in confocal geometry by using a laboratory X-ray tube source. The confocal volume was established by overlapping the foci of the primary beam polycapillary X-ray lens, fixed at the exit of Mo-anode X-ray tube and of the polycapillary conical collimator positioned in front of silicon drift detector entrance window. The effective diameter of the confocal volume was about 25 micrometers (at about 8.4 keV). Single element thin films (prepared by Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany) of Cu/Au, In/Au, Se/Au, and Au on glass surface and a photovoltaic absorber layer for thin film solar cells (CIGSe/Mo on glass [4]) were measured using a range of incident angles from 0 to 45 degrees. At each incident angle a confocal scan was performed by varying the position of the sample surface versus the fixed position of the confocal probing volume. The existing quantitative analytical model of confocal micro-beam XRF analysis of layered materials [5, 6], has been adapted to the measuring conditions and approximated for the case of semi-thin film samples. The obtained results were compared with results of combined analysis by Particle Induced X-ray Emission (PIXE) and Rutherford Backscattering Spectrometry (RBS).

Synchrotron Radiation based Micro- and Nanoanalysis applied to Biological Systems

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Owing to its high sensitivity and non-destructive nature, synchrotron radiation (SR) induced scanning X-ray fluorescence (XRF) imaging provides three-dimensional (3D), quantitative information on the elemental distribution in a probed sample volume with trace-level detection limits on the (sub)micron scale. In a first part we will therefore highlight the tremendous potential of X-ray fluorescence imaging in a few case studies such as (1) Pharmacokinetic analysis of a bromine containing drug in rat thin sections (2) Zn aquatic toxicology studies on the water flea ‘Daphnia magna’ (3) Uranium and plutonium exposure in occupationally exposed former nuclear workers (4) Nanochemical imaging of Zn in human neutrophil extracellular traps (NETs).

In a second part, we compare a new variant of X-ray fluorescence micro-imaging, namely full field X-ray fluorescence (FF-XRF), with scanning micro-XRF methods with respect to 2D/3D trace-level analysis. Scanning XRF techniques are based on the use of single detectors and X-ray micro/nanobeams for scanning the sample under investigation. A considerable disadvantage of these scanning techniques, however, is the long measuring time required (typically several hours per scan), which is not only impractical in case of synchrotron radiation experiments due to the limited beam time available, but also poses a significant risk of sample-damage in case of radiation sensitive (e.g. biological) samples as a result of prolonged exposure to highly focused X-ray beams.

In a third part, we will highlight some of the first experimental results performed at PETRA III at DESY (Hamburg, Germany), which is a new 3rd generation synchrotron radiation facility currently under commissioning. Due to its large circumference (2300 m) and special positron optics (80 m of damping-wiggler) it has a particularly small horizontal emittance of 1nmrad, making it the most brilliant 3rd generation synchrotron radiation source in the hard X-ray regime in the world and therefore also ideally suited for micro- and nanofocussing. The “Hard X-ray Micro/Nano-Probe” beamline P06 is currently under construction at PETRA III and will provide a unique platform for non-destructive micro/nano-analysis using different X-ray techniques, including X-ray fluorescence (XRF), X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD), microradiography (absorption, phase contrast) and various tomodographies.

Nanoscale chemical imaging of energy materials with full-field transmission X-ray microscopy

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Correlation of chemistry and morphology in hierarchical functional materials such as battery electrodes, fuel cells and catalysts can drive design of more efficient materials. Full-field nanoscale chemical imaging has been used to collect single-pixel XANES ($\sim$1E6 spectra per energy stack; acquired in minutes) at down to 30 nm resolution. The full-field transmission X-ray microscope (TXM) on beam line 6-2 at the Stanford Synchrotron Radiation Lightsource combines large field of view (tens to hundreds of microns) with high resolution imaging from $\sim$4.5 to 14 keV ($\Delta E/E < 1E^{-4}$), for XANES chemical speciation. Custom software (TXM Wizard; available free for public use) is used to produce chemical and morphological maps of various composite systems in 2D and 3D. \textit{In situ} and \textit{ex situ} results from full-field XANES microscopy of Li-ion battery electrodes and other catalytic materials, rendering insight into performance and structure, will be presented.
New developments in µ-XRF

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µ-XRF is introduced in between as a powerful method for elemental analysis with spatial resolution. Despite this technique is known for a longer time there are still improvements for their analytical performance and functionality possible.

One of the main requests is the improvement of spatial resolution which depends mainly on the spot size of the analyzed sample area but also on measurement conditions like step size and accumulated intensity. It will be demonstrated that due to an optimization of all these parameters but in particular by a reduction of the spot size the spatial can be improved.

The common method to concentrate the excitation radiation and generate small spots is the use of poly-capillary optics. The reduction of spot size of these optics is possible by shorter working distances due to less divergence of the total reflected X-ray in the single capillaries and the influence by the shape of the lens. In this way spot sizes down into the range of slightly larger than 10 µm are possible.

Further it is also important to have effective possibilities for data evaluation. In particular for high throughput chemistry which works with small sample amounts µ-XRF can be a powerful tool for element analysis. But if in this case a high number of single measurements are performed corresponding evaluation methods are required. In particular chemometric methods can be very interesting for a data compression. Few of these techniques will be demonstrated for the evaluation of large data amounts.
X-ray tomography of large wooden artworks: the case study of “Doppio corpo” by Pietro Piffetti

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X-ray computed tomography (CT) is now widely used in the Cultural Heritage field thanks to its non-invasivity and for the high number of information which can be obtained on the inner structure of the object. Until recently only medical devices have been used, permitting the analysis of only some particular artworks with small size (to fit the acceptance of medical CT scanners) and materials (similar to human tissue). To overcome these limitations a custom instrumentation has been designed and built to perform analysis on artworks, of very different sizes, shapes and materials.

In the frame of the neu_ART project, aiming to develop state of the art transmission imaging and computed tomography, a facility for the X-ray tomography of large size artefacts has recently been installed in a dedicated area of the Centro Conservazione e Restauro “La Venaria Reale”. This instrument is based on a X-ray source (up to 200 kV), a linear X-ray detector (50 cm long) and a high precision mechanics (both for the movement of the source and the detector, and for the revolution of the object). With this device one can obtain information both on materials, constructive technique and state of conservation of an artwork before the restoration process.

In this contribution the results obtained with this instrument on the first large object are presented. It is the “Doppio corpo”, a piece of furniture masterfully inlaid by Pietro Piffetti, the most famous cabinet-maker in Piedmont in the XVIII century and now housed in the Quirinale, the official house of the Italian President in Rome. This analysis permitted to obtain fundamental information about the state of conservation, previous restorations and the distribution of various materials (different kind of woods and metals, ivory, etc.). Moreover the dimensions and arrangement of several wooden pieces used by the author have been evaluated, allowing interesting hypotheses about the constructive technique of this masterpiece.
Elemental imaging analysis with a full-field Micropattern Gaseous Detector

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In this study a full-field energy dispersive X-ray fluorescence imaging system is used [1,2]. The entire sample is excited by a broad X-ray beam and the fluorescence radiation is detected by a Micropattern Gaseous Detector, named 2D-MHSP (Micro-Hole and Strip Plate) detector. The photon counting detector presents an active area of \(28 \times 28 \text{ mm}^2\) and enables energy resolved X-ray imaging (14\% FWHM for 5.9 keV X-rays) with a spatial resolution of about 125 \(\mu\text{m}\), and a counting rate capability of up to 0.5 MHz [3] limited by the present electronic readout configuration.

The 2D-MHSP detector (using Xe@1atm as the detection medium), the X-ray tube, and a pinhole camera compose the experimental setup of the EDXRF imaging system which remains in fixed position during acquisitions. Different types of samples have been analyzed exploring the capabilities of the system.

Results will be presented and discussed for the analyzed samples.

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\textbf{References}
EDXRF portable systems for Analysis of Works of Art

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EDXRF is, currently, the most widely used technique for in situ analysis of Cultural Heritage. The reasons for this is the multielemental, non-destructive characteristics and the extreme simplicity of the technique. The continuous development of specific analytical procedures in which the XRF plays a primary role, as in the case of first and fast approach to the characterization of the materials or in the case of characterization of pigments in a painted surface or metals in the alloys, keeps the technique up-to-date with the arising of new diagnostic problems.

In literature always more articles report the use of portable EDXRF as standalone analytical technique or as part of a more complex experiment [1].

EDXRF used with portable instruments is a simple technique but not an easy technique. Parameters that must be kept in mind to make a meaningful measurement are many, among which can be emphasized the critical penetration depth, the detection limits and the total uncertainty of the measurement.

This paper reviews the present status of the development and application of EDXRF portable systems to Cultural Heritage. Case studies are reported such as the EDXRF analyses of the painting of Peter Paul Rubens "Saint Gregory the Great surrounded by the Saints Papianus, Maurus, Flavia Domitilla, Nereus, and Achilleus" in the Museum of the city of Grenoble, the EDXRF analyses of the Scrovegni Chapel in Padua, and the bronze equestrian statue of Vittorio Emanuele II in Naples.

[1] P J Potts and M West (Editors), Portable X-ray Fluorescence Spectrometry: Capabilities for In Situ Analysis. The Royale Society of Chemistry 2008
Scanning macro-XRF investigation of historical paintings:

Recent progress in instrumentation

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Scanning macro-XRF (MA-XRF) investigations for the acquisition of surface or subsurface elemental distribution images is a technique rapidly establishing in the analysis of historical paintings, as it allows to obtain unique insight in the creation of the paintings investigated by revealing pigment use and restorations as well as visualizing changes in the composition made during the creation of the painting. Sometimes even discarded and over painted older masterworks are rediscovered under the surface of later paintings.

While in the past such investigations were limited to synchrotron sources \([1]\), the development of mobile X-ray tube based instruments allowed for \textit{in-situ} investigations, considerably lowering the effort necessary to investigate a painting.

While the first instruments presented \([2]\) required several seconds of dwell time per pixel, continuous improvement of instruments and control software allowed to reduce dwell times to fractions of a second, while still being able to visualize the main elements present in the paint in noise free images. We will present two of these instruments in our contribution.

The current in-house built instrument of the University of Antwerp consist of two 60 cm motor stages with a measurement head consisting of a 10 W Rh transmission X-ray tube with a Pb pinhole collimator defining a 1 mm beam and four 50 mm\(^2\) SD-detectors mounted tightly around it. This scanner has proven capable of scanning the complete surface of paintings of several square meter size by stitching several image segments together.

Based on the experiences obtained with in-house build scanners at the University of Antwerp our institutions cooperated in the development of the commercially available M6 Jetstream, a dedicated XRF scanner for large objects, based on the M4 Tornado from Bruker. The scanner features a 30 W Rh anode X-ray tube with a polycapillary optic and a single 30 mm\(^2\) SD-detector mounted on a 80x60 cm\(^2\) motor stage. Two microscopes mounted on the measurement head allow to acquire an optical mosaic image of the investigated object and to select the investigated area and the distance to the sample. The beam size can be varied between 150 and 750 \(\mu\)m (FWHM of a 25 \(\mu\)m Au wire’s Au-L\(_\alpha\) gauss profile).

Both instruments will be presented and compared in terms of sensitivity and LODs. Their capabilities and the value of the data acquired to art-historians will be demonstrated with selected application examples from the workshops of painters such as Rembrandt van Rijn and Caravaggio.


Development of a new portable X-ray fluorescence spectrometer suitable for analysis of Mg in archaeological glass objects in air equipped with polycapillary optics

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So far, various kinds of portable and handy type XRF spectrometers have been developed and widely used in analyses of cultural heritage. However, most of the spectrometers sacrificed sensitivity for portability. We have tried to develop a portable XRF spectrometer with sensitivity better than desktop type instruments, yet is suitable for on-site analysis of cultural heritage since 2001[1]. We have introduced a bent toroidal monochromator of graphite (0002) to obtain monochromatic Pd-K X-ray source, which allows highly sensitive analysis of medium to heavy elements. We have also introduced SDD with Moxtek AP 3.3 polymer window into the system and a sample vacuum chamber suitable for quantitative analysis of Na and Mg in glass objects[2]. The present model is the 5th version of our development, which allows analysis of micro area and that of Na and Mg in air, aiming for analysis of small spot of a large object which cannot be measured inside the vacuum chamber.

The new portable XRF spectrometer, OURSTEX 100FA-V, was jointly developed by OURSTEX Co. and our laboratory. A schematic illustration of the spectrometer head is shown in Fig.1. The detector of our spectrometer is KETEK SDD with Moxtek AP3.3 window suitable for analysis of Na and Mg. The spectrometer head consists of an X-ray tube with Pd target excited at 6 to 40 kV with tube current available for 0.1 to 1.0 mA. A polycapillary lens is placed in front of Pd X-ray tube. This yields an irradiated beam spot approximately 200 μm diameter at the position of the sample. This spectrometer head can replace the conventional spectrometer head of OURSTEK 100FA-IV. So we can take 1 set of high-voltage power supply and a controller unit to the analysis site. Figure 2 shows a photo of the head successfully measuring a Sasanian glass bowl.

Low energy region of XRF spectrum of NIST SRM1831 standard sample measured at 6kV in air (400s) and in vacuum (200s) are compared in Fig. 3. Clear peaks of the Na and K lines can be observed even at the measurement in air. Calibration curves for quantitative analysis of Na and Mg in air are given in Fig.4 showing a good linear correlation. The MDL for Na and Mg is 2.44 and 0.46% in air and 0.36 and 0.14 % in vacuum, respectively. This MDL is good enough to distinguish plant ash glass from natron glass. The microbeam revealed the complex compositions (Fig.5(b)) of the core formed glass vessel with a complex design (Fig.5(a)).

Benefits of Using Handheld EDXRF Analyzer for Screening Toys and Children Products for Compliance with Toy Directive

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Recently updated European Union Toy Directive mandates that toys and children articles may not contain certain 18 elements at concentrations higher than those specified in European Norm EN 71-3. Specifically, the EN 71-3 document list limits of leachable rather than total concentrations of those elements. Numerous tests as well as recent study performed under the auspices of Prosafe[1] illustrate inadequacy of leachability concept and show advantages of using XRF instead.

In this paper we comment the results obtained in that study and discuss advantages of using XRF method for measurement of total concentrations of elements rather than leachable ones. Finally, we suggest the use of mass per unit area approach for XRF measurement of elements (such as lead...) in applied paint as more accurate and more reliable than mass fraction.

Applicability of hand-held EDXRF systems for waste characterization

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In consequence of several EU Directives (e.g. EU directive 1999/31/EC on the landfill of waste; EU Directive 2000/76/EC on the incineration of waste; RoHS Directive 2002/95/EC), there is an increasing need for rapid and easy-to-handle screening tools to identify hazardous substances or to verify the absence of those substances.

A field trial was executed to evaluate the capability of handheld XRF systems for screening waste loads on hazardous substances as incoming inspection at waste handling plants in order to identify the waste material or to classify it by its key variables (critical parameters). For the field trial 6 different waste materials have been prepared: construction waste, shredder material, contaminated soil, waste wood, Pb granulate, and slag from a municipal incineration waste. All together 5 handheld XRF instrument manufacturers participated to the workshop. Since some of the manufacturers used several handheld XRF instruments, in total 8 different handheld XRF instruments were available for the workshop. Both the performance of the XRF systems itself as the influence of sample pretreatment on the analytical results was considered. The obtained results will be presented during the lecture.

These results indicated that for screening analysis (with fivefold repeated measurements) the pre-treatment of the sample is of lower relevance. The homogeneity/heterogeneity of the material could be deduced immediately from the results of the repeated measurements. The major influence on the analytical results was driven by the correct matrix calibration. This means that for specific samples an appropriate adjustment of the matrix calibration is required to improve the accuracy of the results. In spite of strong scattering around the true value no false negative results were measured (false negative for this purpose is defined as: element not detected although within the accuracy of measurement the element should be detectable), whereas false positive results have been reported in single cases.

In the overall assessment, this analytical method can be recommended as a qualitative screening method for the analysis of waste. It should be noted that for the final quantitative determination of the elements other analytical methods combined with a more extended sample pretreatment e.g. EDXRF or ICP-OES, are required. The easiness of operation of the handheld XRF instruments and the low cost of the sample preparation are the major advantages compared to alternative analysis methods. Handheld XRF analysers are the detection method of choice for the initial analysis of elements in waste, as this method is fast, reliable, handy and cost-effective.

Application of x-ray spectroscopy to energy materials

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This is an overview of past and ongoing work on (energy) materials for batteries, ceramic fuel cells (SOFC) and photo-electrochemical cells (PEC). The functionality of electrodes and electrolytes depends on their electronic structure, the determination of which is a task for x-ray spectroscopy. For Li ion battery cathode studies I show a versatile transmission spectro-electrochemical operando cell with hard X-ray XANES studies [1,2], and combinations of soft- and hard x-ray emission and absorption studies [3,4,5], plus some Li X-ray Raman and NEXAFS spectra. For high temperature SOFC, I will show some sulfur K-edge spectra of anodes with unexpected traces of sulfate and thiophene [6] and a number of oxygen and Fe L-edge spectra of cathode iron perovskites [7]. We found an interesting quantitative correlation between conductivity and spectral weight of hole transitions in the oxygen pre-edges of such cathodes [8,9]. Further correlations between polaron conductivity and spectral weight near the Fermi energy was found in the high T valence band photo-emission data recorded for 300 K < T < 1000 K [10,11,12]. Maybe I show the resonant VB PES data of LaSrFe-Ni oxides [13]. Our fresh unpublished work includes operando high temperature – ambient pressure resonant photoemission spectroscopy on proton conducting ceramic electrolytes (BaCe/Zr-Y-oxides), which we performed parallel to electrochemical impedance studies; we did similar studies for metal oxide gas sensors with a novel AP PES-/XPS end station. Our success with the correlation of performance or functionality of perovskites with the spectral weight of hole doping peaks in the oxygen pre-edges was transferred to the field of photo catalysis. Here we found a new transition in the t2g-eg doublet depending on the N doping of TiO2 which scales with the nicotine degradation of TiON [14]. Another material of interest is hematite α-Fe2O3, which can be used for solar photo-electrochemical water splitting with O2 and H2 generation. The electronic structure of bulk and surface facing the electrolyte is important for functionality; electrical bias creates a new transition in the upper Hubbard band [15]. For microstructure characterization we use small angle scattering. Here I show examples for batteries and SOFC. I have a highlight to present: We succeeded to probe the valence band with hybridized Fe3d-O2p states in α-Fe2O3 with liquid electrolyte in-situ and operando with soft X-rays during electrochemical bias, and this in dark and in light condition, and we found something very exciting! And I have another highlight to present: The first in-situ and operando soft x-ray manganese L-edge spectrum from a working battery.

XANES and EXAFS studies of cadmium accumulation in hyperaccumulating plants on organ and sub-cellular level

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Hyperaccumulation of Cd (concentrations above 100 µg g⁻¹ of Cd in the aboveground dry biomass) is a rare phenomenon that has been reported in only few plant species [1]. The mechanisms that enable plants to cope with these extremely high Cd concentrations in photosynthetically active organs are still not well understood.

The reliable and detailed information on the spatial element distribution and ligand environment [2] within plant tissues provides basic knowledge for understanding the metal tolerance mechanisms. Therefore in this study we used μ-XRF imaging and Cd L₃ edge micro-XANES and Cd K-edge EXAFS analysis to obtain direct information on localization and chemical state of Cd in different organs and tissues of Cd hyperaccumulator Thlaspi praecox on cellular and sub-cellular level. The study of localization and chemical state of Cd in leaves and roots of plants grown in nutrient solution supplied with 300 and 100 µM Cd as CdSO₄ or CdCl₂ were aimed to resolve the mechanisms of accumulation and tolerance of Cd at tissue, cellular and sub-cellular level with the possible involvement of sulphur metabolism.

Micro-XRF quantitative imaging and Cd L₃ micro-XANES measurements with lateral resolution of 0.2 microns were performed at ID21 beamline of ESRF Grenoble (project EC-719). Cd L₃ XANES spectra of plant organs were collected at XAFS beamline of ELETTRA, Trieste (project 20110086), and at A1 beamline of HASYLAB, while Cd K-edge XANES and EXAFS spectra were measured at C beamline of HASYLAB (project I-20110082 EC).

In Cd L₃-edge XANES analysis the bonding of Cd are identified, using a high precision linear combination fit (LCF) method with XANES spectra of relevant reference compounds [3,4] to provide information on the ratios between Cd-O and Cd-S ligands. Limitations of analogous Cd K-edge XANES analysis for the same purpose are illustrated. The sources of possible systematic errors in LCF analysis due to self-absorption effects in fluorescence detection mode are discussed. In Cadmium K-edge EXAFS analysis, simultaneous multiple-edge EXAFS fit [2,5] is exploited to provide the information on average local structure around Cd atoms (number of neighbours, distances, and disorder) and identify dominant Cd binding compounds in different plant organs. The results elucidate the relations between sulphur metabolism and Cd uptake and transport processes and give insight in detoxification mechanism and/or antioxidant-based defence at the molecular level that contributes efficiently to Cd tolerance in hyper accumulating species [1,2].

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The role of lead in polychrome glazed ceramics from Portugal investigated by XANES.

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Following an ongoing investigation, polychrome glazed ceramic fragments (tiles and faïences) produced in Portugal (Coimbra and Lisbon) have been object of study. With the aim of tracing manufacturing techniques employed by these two main production centres, it is herby presented a part of this research. Previous investigations revealed that we are dealing with majolica pieces, i.e., lead-tin-based glazes with polychromatic surface decorative motifs [1]. This work shows information about lead structural properties, such as oxidation state or nature of the surrounding atoms. Such results are very important for the specific case of lead in order to clarify about its role in the pieces, whether it is hosted just in the glassy matrix or in yellow pigments as well, or even if it is associated to ageing mechanisms [2]. For this purpose XAFS (X-ray Absorption Fine Structure) measurements at the Pb L3-edge were performed at the µSpot beamline [3] at BESSY II (Berlin).

Comparing the Pb XANES spectra between standards and original pieces, one can already establish some differences. Identical edge positions and post-edge oscillations in all analysed glazes are indicatives for similar lead valences and atomic coordination environment, which sustains the hypothesis that lead is hosted in the glassy matrix as a network modifier. Conversely, comparing the Pb XANES spectra of the yellow decoration and respective glaze, differences in the edge position as well as in the post-edge oscillations are observed. A different lead compound is hosted in the yellow decorations. Moreover, differences in the Pb XANES spectra within the yellows from Coimbra and Lisbon tiles are noticed, which suggest differences in the manufacturing between these two centers.

Investigation of copper uptake of soil-inhabiting nematodes by means of synchrotron radiation

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Four of every five multicellular animals on Earth belong to phylum Nematoda. From the 28,000 known species, more than 16,000 are parasitic, however they are ubiquitous in freshwater as well as in marine and terrestrial environments. Soil-inhabiting nematodes may be used as bioindicators, because the composition of nematofauna (the ratio of different species) correlates closely with environmental parameters. Consequently, nematodes provide us a good tool to investigate the effect of heavy metal pollution in soil. Furthermore, due to their small size (the soil-inhabiting species are a few millimeters long, and their body diameter is about 50 µm) and simple anatomy but quite complex life processes, nematodes may be applied for investigation of several biological and biochemical processes. Copper is a common contaminant of agricultural soils, due to its application as pesticide. A former study [1] investigated the effect of some soil contaminating elements on nematodes, and copper was found to be one of the elements, which had the most drastic effects. The aim of our study was to investigate the elemental distribution in nematodes and the chemical microenvironment of copper in untreated („essential” copper), and in copper treated ones.

Synchrotron induced X-ray fluorescence- and XANES measurements were carried out at BAMline (Helmholtz-Zentrum Berlin, Germany). Nematodes were extracted from soil, starved for five days in tap water, and quickly rinsed with high purity water before further sample preparation. Three sets of worms were prepared: untreated, treated with 1 mmol/dm³ Cu(NO₃)₂ or CuSO₄ solutions for 24 hours. In order to retain the original structure of the samples (in case of elemental distribution measurements this is inevitable), a special freeze-drying method (lyophilization) was applied. After treatment and rinse, worms were put onto Kapton tape mounted on a plastic holder. In order to avoid the absorbance effects caused by fixing materials, no further fixation was carried out. Samples were plunged into liquid nitrogen in closed plastic vessels and frozen for two minutes, following this step a 72 hours long lyophilization were taken place. The samples were stored in the plastic vessels until the measurements. The elemental distribution was investigated at low (about 10 µm, with compound refractive lense and Bruker SDD detector) and at high resolution (about 1 µm, with double multilayer monochromator and colour X-ray camera) at 16 keV. The XANES measurements were carried out at 9 keV with bent-focusing double crystal monochromator and Bruker SDD detector, beamsize was 200 µm*1000 µm.

The copper distribution was found to be quite homogenous, however at higher resolution smaller hotspots were detected, but it can be established that no biomineralization takes place, unlike in case of lead in the nematode Caenorhabditis elegans [2]. From XANES measurements it can be concluded, that „essential” and the contaminant copper are in different chemical environment. It was also observed that the anions of the copper compounds had not any influence on the structure of the XANES spectra.

The techniques based on synchrotron radiation in the investigation of pathological processes occurring in the epileptic brain

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Although epilepsy has been a serious problem of clinical neurology for many years, the mechanisms of its pathogenesis are still not fully understood. The studies on epileptogenesis and testing new antiepileptic drugs require the use of adequate animal models of epileptic seizures and an ideal model should have a behavioral pattern most closely resembling clinical symptoms in humans [1,2]. The most frequently occurring type of epilepsy in adults is temporal lobe epilepsy (TLE) and the most often used and highly isomorphic with human cases of TLE animal model is one with seizures induced with pilocarpine.

In frame of the following studies X-ray fluorescence microscopy and Fourier transform infrared microspectroscopy were applied to follow the processes involved in the pathogenesis and progress of epilepsy in case of pilocarpine model. The measurements were carried at HASYLAB beamline L, ANKA beamline FLUO and SOLEIL beamline SMIS. The used experimental setups and measurement conditions allowed us to analyze the distributions of selected elements (S, K, Ca, Fe, Cu, Zn) and biomolecules (proteins, lipids and compounds containing phosphate bands) as well as anomalies in protein secondary structure and saturation level of phospholipids in specific brain regions with the spatial resolution from 10 to 20 micrometers.

The obtained results showed that seizure induced excitotoxicity, mossy fiber sprouting and iron induced increased production of reactive oxygen species are the mechanisms involved in the neurodegenerative processes which may finally lead to spontaneous seizures in the chronic period of pilocarpine model.

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X-ray Spectrometry for the Characterization of novel Materials for Energy Storage and Nanoelectronics

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The further development of advanced nano- and micro-structured materials requires reliable analytical methodologies for correlating chemical and physical properties with electrical material properties. In particular, systematic studies of the functionality require the characterization of the material properties such as elemental composition, chemical species and structure on the nano-scale. The analytical methods applied are preferably non-destructive and not relying on the need for a comparison to standards or reference materials. The non-destructiveness allows for the application of complementary methods and ensures that the material properties will not be changed before the investigation of the functionality. In the case of novel materials the use of standards and reference materials for the calibration of the analytical instruments suffers frequently from a lack of appropriate reference materials on the nanoscale which have to be similar to the materials of interest with respect to their spatial structure and elemental composition.

The paper will present synchrotron radiation based X-Ray Spectrometry (XRS) methodologies employed for the characterization of thin films for improved LiS batteries and nanoelectronic devices [1]. The sample properties that can be assessed by XRS are the elemental composition, the elemental depth profile at the nanometer scale and the chemical speciation of the thin films and their interfaces. XRS is a non-destructive technique and allows for a complete reference-free quantification of the sample composition when radiometrically calibrated instrumentation is used [2]. The information depth can be selected by adapting the beam geometry in the grazing incidence regime. Furthermore, the same experimental setup can be used to perform Near Edge X-ray Absorption Fine Structure (NEXAFS) spectrometry allowing for chemical speciation with a tunable information depth.

Experimental observation of quantum confinement in the conduction band of PbS quantum dots

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The search for new sources of clean energy is rapidly becoming one of the most pressing technological challenges that we are facing today. Development of inexpensive methods for synthesized materials that demonstrate both visible light activity and high solar energy utilization along with stability is still a challenge. The presented investigations address this important challenge by focusing, mainly, on electronic local structure studies with supporting optical, X-ray diffraction and transmission electron microscopic analysis of colloidal galena nano-particles (NPs) and quantum dots (QDs) synthesized using wet chemistry under microwave irradiation \(^{[1]}\). To develop a comprehensive understanding of the electronic properties of PbS NPs/QDs, the resonant inelastic X-ray scattering (RIXS) and X-ray absorption near-edge structure (XANES) measurements around sulphur K-edge were performed and their results will be presented. It was found that depending on synthesis parameters the bandgap of galena varies from \(\sim 0.4\) eV (bulk) to \(\sim 1\) eV (NPs/QDs). To interpret XANES spectra the \textit{ab-initio} code FEFF8.4 within the real-space full multiple-scattering approach was used \(^{[2]}\). Additionally, the experimental RIXS and XANES spectra were compared to the density of states and band structure calculated by first-principles within both the local-density and generalized gradient approximations incorporated in ESPRESSO code \(^{[3]}\).

\(^{[1]}\) X. He, I.N. Demchenko, W. Stolte, A. van Buuren, H. Liang, 2012, in review
\(^{[3]}\) \url{http://www.pwscf.org}
Depth selective XAFS characterization using simultaneous
detection of x-ray fluorescence and conversion electrons

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Simultaneous detection of x-ray fluorescence yield (XFY) and conversion electron yield (CEY) enabled depth selective x-ray absorption fine structure (XAFS) measurements. Experiments were carried out on the BL-11 of Hiroshima Synchrotron Research Center (HSRC) for X-ray fluorescence analysis and XAFS spectroscopy in the soft x-ray region [1-3]. The storage ring was operated at 700MeV, and the synchrotron radiation from a bending magnet was monochromatized with a Si (111) double crystal monochromator. A sample chamber was filled with He, and the energetic Auger electrons from a sample ionized surrounding He molecules. The created conversion electrons were collected with an electrode made of copper film of 100 nm deposited onto a polypropylene film of 6 mm thickness, and the electrode was placed 8 mm from the sample surface and biased at 100V. A commercial SDD (Amptek, super SDD) was placed normal to the beam in the plane of the orbit, and the XFY could be monitored through the transparent electrode.

The analyzing depth with the CEY was generally less than 10 nm in the soft x-ray region, and the net increase of the CEY around the absorption edge was sensitive to the surface area of the element of interest. The method was applied to the silver thin films deposited onto the silicon substrate, and the L3-edge XAFS spectra were measured both with XFY and CEY. The abundance of the silver could be derived from the XFY, and the relative surface area of the silver was evaluated from the CEY. The morphology of the silver films was modified into the island form with the annealing, and the decrease of the CEY was measured as the results of the smaller surface area.

The method was also applied to the supported Rh catalysis onto the Al2O3, and Rh occupied several sites such as outer surface, inner surface and the dissolved state. Rh L3-edge XAFS spectra measured with XFY and CEY were different each other owing to the difference of the analyzing depth, and the site specific XAFS spectra of Rh were evaluated numerically.

In this presentation the outline of the beamline and the results of the simultaneous detection of XFY and CEY will be presented.

Set up of an etched multilayer as a dispersive element in a Johan-type spectrometer

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Generally, to work in the soft x-ray range, *i.e.* for photon energies between 100 and 1000 eV, wavelength dispersive spectrometers are equipped with periodic multilayers instead of crystals as dispersive elements. However, owing to the large absorption occurring in this range, the number of diffracting bi-layers contributing to the Bragg diffraction is small resulting in a wide diffraction pattern and a poor spectral resolution. Thus, in this photon energy range only grating spectrometers can be used to obtain high-resolution x-ray emission spectra.

It has been shown from the theoretical and experimental points of views [1,2] that it is possible to decrease the width of the diffraction pattern by etching a laminar grating pattern within interferential multilayer mirrors. In such a structure, due to the introduction of voids, the radiation penetrates deeply within the stack and a large number of bi-layers participates to the diffraction process. Consequently, the diffraction pattern is decreased and the spectral resolution improved. Typically, an etched multilayer will have a grating period of 1 µm or smaller and a multilayer period of 5 to 15 nm with at least 200 periods (or bilayers). The etched multilayers are fragile because of their large aspect ratio, ratio of the multilayer bar height to its width, of 10 or larger. Thus, they have never been implemented in curved-crystal spectrometers for fear of a delamination of the mirror from its substrate upon the stress induced by the curvature.

We present the fabrication process of such an etched multilayer as a dispersive element, its characterization and implementation in a high-resolution Johann-type spectrometer [3]. The designed patterning of a Mo/B₄C multilayer is fruitful in the range of the C K emission (280 eV) as the diffraction pattern narrows by a factor 4 with respect to the non-etched structure. This dispersive element with an improved spectral resolution is successfully implemented for electronic structure study with an improved spectral resolution by x-ray emission spectroscopy. As a result, we show the difference between the chemical state of carbon atoms in various compounds, graphite, SiC and B₄C, by the different shape of their C K emission band.

High-resolution Al and Mg Kα emissions of some minerals

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The quantitative analysis based upon wavelength dispersive spectra obtained through electron microprobes relies on intensity measurements. For this purpose, most models determine the height of the emission at its photon energy maximum and compare this value for the unknown sample and a standard, considering the same position in both cases. However, a peak shift can exist between the maxima of the studied and standard samples [1,2], leading to potential errors of a few per cent of the intensity. This is particularly true in this case of relatively high-resolution spectrometers and when using used quick automated peaking without some verification.

In this communication, we present the energy variation of the maximum of Al and Mg Kα emissions for minerals, silicates and oxides, 21 containing Al atoms (alumina, spinel, chromite, …) and 10 containing Mg atoms (periclase, spinel, olivine, …). These materials are of significance in mineralogical and petrologic studies. The results are compared to those obtained with metallic Al and Mg. We utilize a high resolution Johann-type spectrometer, with crystals bent in a 500 mm diameter Rowland cylinder configuration. For the Al and Mg ranges, the crystals are respectively (10$ar{1}$0) quartz and (10$ar{1}$0) beryl and work at the first diffraction order.

Under our experimental conditions, depending on the sample, the line width is 0.85—1.0 eV for the Al Kα emission and 1.1—1.2 eV for the Mg Kα emission. These width variations indicate that more than one environment of the emitting atom exist in some of the studied minerals. With respect to the metals, a maximum shift of +0.5 eV is observed for the Al Kα emission of grossular garnet and +0.4 eV for the Mg Kα emission of a solid solution garnet (47% almandine, 41% pyrope, 11% grossular). In these extreme cases, due to the narrowness of the lines, this would lead to 40% intensity error for Al and 30% error for Mg, if the intensity maxima would be measured at the position of the metals. In practice, a not so large error would be introduced in the quantification process by the peak shift, as the chosen standard would be some oxide and not the metal. If sapphire (Al$_2$O$_3$) and periclase (MgO) are chosen as standards for Al and Mg Kα emissions, then the error on the peak height decreases to 15 and 10% respectively.

The observed emission shifts reflect the difference between minerals in the specific neighboring of the emitting element. We try to correlate these shifts to the nature, number and distance of nearest neighbours of the Al and Mg atoms.

Electron-phonon coupling triggered by Be inner-shell excitation of BeO

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The coupling between the electronic and atomic degrees of freedom may significantly influence the properties of one or both sub-systems of condensed matter. It may freeze electron propagation via self-trapping of excitons. Contrary, this interaction may give rise to conventional superconductivity and it is responsible for the colossal magneto-resistance in manganites. All of these cases correspond to dressed states close to the ground state.

Here, we focus on the other extreme, namely on electron-phonon coupling in BeO (bromellite) far away from the electronic or atomic ground state. BeO is a diatomic ionic compound with a large band-gap and it reveals very strong phonon excitations. In this work, electron-phonon coupling is triggered by Be K-shell excitation/ionization, induced either by the passage of \textit{fast heavy ions} or alternatively by monochromatic \textit{synchrotron radiation}. We have used the technique of resonant inelastic x-ray scattering (RIXS) at the Be K-edge, using photons around 120 eV delivered by the UE112 undulator of the BESSY synchrotron facility. In addition to the typical spectral structures, we find energy loss side-bands in BeO, present only around the core-hole resonance. In accordance with previous experiments \cite{1,2} and simulations \cite{2} for this system, these side bands are related to the theoretically well-understood core-hole exciton of BeO \cite{3}. For the first time, we present a lattice-temperature dependence of the Be-core-hole excitonic yield. All-over temperature variations of a few 100 degree K, give rise to significant changes of the exciton related structures. Heavy-ion induced Auger-electron spectra from BeO demonstrate also a very strong coupling between the electronic structure and the crystal lattice \cite{4}. In this case, electron temperatures beyond 50000 K in the vicinity of the Be-K vacancy site seem to trigger an ultra-fast local atomic rearrangement process (the so-called cold melting), as will be discussed at the conference.

\begin{thebibliography}{99}
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New frontiers of high rate X-Ray spectroscopy with Silicon Drift Detectors coupled with “CUBE” frontend electronics

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The development of radiation detectors for high-resolution X-ray spectroscopy is a research field of continuously growing interest, for its application either in scientific research or in industrial applications like X-ray fluorescence, X-ray diffraction and microanalysis with SEM. In most of the applications, especially when a mapping analysis is required, the general trend is to increase the count-rate. This reduces the measurement time or increases the accuracy thanks to the higher statistics. As alternative to Si(Li) detectors and silicon PIN diode, high-resolution and high-rate silicon drift detectors (SDDs) have become a valuable solution in an increasing numbers of spectroscopy apparatus. The figure-of-merit in terms of energy resolution and counting-rates is strictly dependent on the front-end electronics [1]. Very recently, a new monolithic CMOS charge preamplifier (named “CUBE”) has been proposed as alternative to the more commonly used JFET solution [2].

In this work, we compare the performances of our CUBE circuit with respect to the typical performances of the JFET transistor. We will show that CUBE enables to get superior energy resolution at short shaping time. As an example, Fig 1 shows the energy resolution with the two considered front-end. With CUBE, a FWHM resolution of 148 eV at the ultra-short peaking time of 100 ns is possible. As shown in Fig 2, the energy resolution remains quite constant up to 800 kcps (input), and an output count rate up to 490 kcps has been recorded thanks to the shortness of the peaking time. Different examples will be presented, like XRF measurements at very high count-rate in low-concentration, or EXAFS measurements with count-rate up to 1M cps.

Moreover, as known, the use of short peaking times reduces the impact of the detector leakage current on the total noise. Measurements using a 25 mm² SDD show a 310 eV FWHM resolution at room temperature (25 °C) and with peaking time of 100 ns. By moderate cooling the SDD, the measured resolution was instead as good as 165 eV for a temperature of 0 °C (at 300 ns peaking time). More examples of such performances will be shown as well.

Fig.1. Energy resolution at the Mn-Ka line 55Fe calibration source measured with a SDD, at a temperature of -50° C.

Fig.2. Measured energy resolution (at the Mn-Ka line) as a function of the input count-rate for 2 different peaking-times.

Resonant Raman Radiative Auger effect

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Due to energy conservation, spectral features in a scattering experiment are recorded with experimental energy resolution as soon as uncertainties of the projectile energy and of energies of all emitted particles are under control. When an inner-shell electron is ejected into continuum, coincidence detection of energy selected (threshold) photoelectron and Auger electron or emitted photon is required to sharpen the spectrum [1]. When projectile is an electron, coincidence detection of inelastically scattered electron and Auger electron is required to map the corresponding resonant Auger spectrum [2]. However, the resonant Raman concept is put at work most usefully for processes that involve photoexcited states below the threshold. When inner-shell electrons are resonantly excited by a brilliant monochromatic photon beam, a “simple” detection of emitted photons (RIXS) or Auger electrons (RA) with high energy resolution may significantly improve spectral resolution. This is important since sharper absorption spectra reconstructed from RIXS maps by HERFD slicing may obviously have larger analytical value in terms of XANES fingerprinting, and energy shifts of emission lines allow for the separation of multi-electron excitation features that may obstruct EXAFS analysis [3].

All these processes deal with a single reaction step, i.e. an electron or a photon is emitted in the direct decay of the photo-excited state. Here we report on the first observation of the resonant Raman effect in a two-step decay (in terms of the perturbation series expansion). It is known that in the radiative Auger decay an emitted photon shares available energy with another electron that may be promoted to an unoccupied bound state (bound RAE) or ejected into the continuum. In the former case a single photon detection still guarantees control over energy uncertainty if RAE decay proceeds from photoexcited bound state. We have observed linear dispersion of the bound K-MM RAE signal on the tail of the Kβ₁,₃ emission line upon resonant 1s → 4p excitation of argon. Resonant amplification and sharpening of the spectrum facilitate extraction of the bound RAE amplitude leading to doubly excited valence states of the 3p²4pn type selected by the primary resonant excitation. This is to be compared to the direct decay of inner-shell doubly excited states (1s3p)ˡnln’l’ that are (non-selectively) populated by (shake-up) photoabsorption, and with the non-resonant K-MM RAE that leads to singly excited valence states and exhibits a completely different spectral shape.

The resonant RAE represents a new possibility for selective study of subtle doubly excited valence states deep in the material by means of a high resolution x-ray spectroscopy. Although it is more difficult to interpret RAE spectra than single step absorption-emission spectra, the RAE energy shift with respect to the diagram x-ray line is substantially larger than spectral shift of the line emitted in decay of inner-shell doubly excited states – this fact facilitates separation of spectral contribution pertaining to final doubly excited states.

High-resolution investigation of the radiative decay channels of hollow K-shell atoms produced by single photon impact

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We report on the radiative decay of K-shell hollow atoms produced by single photon absorption. The double 1s vacancy states were produced by irradiating the samples with intense monochromatic synchrotron radiation beams at the European Synchrotron Radiation Facility (ESRF), in Grenoble, France. The sample x-ray emission was measured by means of high-resolution spectrometry, using a von Hamos curved crystal spectrometer [1] and a flat crystal wavelength dispersive spectrometer [2].

The knock-out and shake processes leading to the creation of double 1s vacancy states as a result of single photon impact will be discussed. The corresponding double K-shell ionization cross sections will be presented for several elements with \(12 \leq Z \leq 23\) [3]. The energies, natural widths and relative intensities of the hypersatellite x-ray lines emitted during the radiative decay of the double 1s vacancy states will be reported [4]. The two-electron-two-photon (TEOP) transitions which represent an alternative mode of radiative decay for hollow K-shell atoms will be also addressed. In particular the TEOP-to-hypersatellite branching ratios obtained for Mg, Al and Si [5] will be discussed and compared to existing theoretical predictions.

Lifetime-broadening-suppressed $L_3$ x-ray absorption spectrum of Xe

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One of the intrinsic problems of the standard x-ray absorption spectroscopy (XAS) is the natural linewidth broadening originating from the finite core-hole lifetime that ultimately limits the resolution of XAS spectra. This limitation can be circumvented by employing a high energy-resolution analysis of the emitted fluorescence in addition to the accurate control of the incident photon energy. When the experimental resolution is pushed below the natural linewidth, spectral features in such high energy resolution fluorescence detected (HERFD) absorption spectrum become significantly sharper than the core-hole lifetime broadening as demonstrated for the first time in the pioneering work of Hämäläinen et al. [1]. An alternative method to obtain lifetime-broadening suppressed absorption spectrum is to use a high-resolution resonant inelastic x-ray scattering (RIXS) spectrum taken at fixed excitation energy tuned below the corresponding absorption edge [2,3]. A third generation synchrotron light source combined with modern focusing type crystal spectrometer fulfills the experimental conditions in terms of efficiency and energy-resolution, which are both mandatory to record a high quality HERFD spectra at the selected absorption edge as well as RIXS spectra at excitation energies well below the absorption edge.

In our work Xe was chosen as a case study to demonstrate the capabilities of resonant x-ray spectroscopy to produce lifetime-broadening-suppressed x-ray absorption spectra. The $L_3$ absorption spectrum was measured using both approaches described above. A Johansson type crystal spectrometer for high-resolution spectroscopy in the tender x-ray range (~2-6 keV) was coupled to the ID26 beamline of the ESRF synchrotron. A full $L_3$-$M_{4,5}$ RIXS spectral map was recorded across the $L_3$ absorption edge as well as a single $L_3$-$M_{4,5}$ RIXS spectrum with low statistical uncertainty at 4760 eV excitation energy, which is almost 30 eV below the absorption edge. The overall energy resolution was ~ 0.75 eV well below the Xe $L_3$ core-hole lifetime broadening (2.82 eV). Excellent experimental resolution enabled successful decomposition of the measured spectra into the continuum and resonant contributions. Relative emission strengths and energies of the lowest resonant states converging to the $L_3$ edge were determined and compared to the theoretical calculations. The presented example demonstrates that a lifetime-broadening-suppressed x-ray absorption spectrum can be obtained even without the tunable light source using a high resolution RIXS spectrum at fixed incident photon energy below the absorption edge. This could be exploited in experiments using laboratory x-ray sources or even chaotic x-ray source such as FEL.

Species depth profiling of deeply buried nanostructures

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The characterization of deeply buried structures such as interfaces or thin films demands a non-destructive and non-preparative methodology to reliably reveal information on the material properties in view of a better understanding of the material functionalities. To derive information on these material properties, a characterization methodology that allow for a non-preparative and non-destructive analysis in a certain depth is needed.

The combined method X-ray fluorescence spectrometry under grazing incidence conditions with of X-ray absorption spectroscopy (GIXRF-NEXAFS) has demonstrated that a non-destructive analysis with respect to the chemical bonds of deeply buried single layers is feasible [1]. The penetration depth can be tuned to a buried nanostructure of interest by utilizing the nano-scaled spatial intensity distribution of the X-ray Standing Wave (XSW) field, which is directly related to the grazing incidence conditions. The information depth follows the penetration depth which can be adapted by changing the angle of incidence or the photon energy.

The basic strategy for the investigations is illustrated by means of a nanolayered system, which consist of titanium oxide and metallic titanium layers, separated from each other by a 2 nm C layer. The combined procedure GIXRF-NEXAFS has been further developed to allow for an interface speciation. The methodology was validated by means of layered system consisting of the substrate Si(100) physically vapor deposited with Ni having a layer thickness of about 5 nm, and chemically vapor deposited with $B_xC_yN_z$. Different systems were prepared using varying temperatures during the deposition of the $B_xC_yN_z$ layers.

The species depth profiling as well as the interface speciation was derived by means of a differential approach. Two GIXRF-NEXAFS measurements at different mean penetration depths are necessary to characterize the whole system. The results demonstrate the high potential of the approach for analyzing advanced materials.

Improvements in X-ray analysis with the help of nanometer range coatings and multilayers

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Multilayers are increasingly used as monochromators in many fields of X-ray analysis, similar to crystals but also in wavelength regions where no crystals are available. However, being artificial structures with tunable parameters such as composition, period thickness and period number, multilayers can be applied in numerous other applications [1].

With the proceeding improvement and new development of laboratory X-ray sources such as micro-focus fixed anode tubes, rotating anode or liquid metal jet sources, measurements previously only feasible at synchrotrons have become possible in the lab. However, focusing or collimating of the radiation that is generally emitted with high divergence in laboratory sources is necessary for that purpose. Capillary optics are often used here but bended multilayers are a powerful solution, too, as they combine the beam shaping properties with the possibility to select a certain photon energy bandwidth.

For this purpose, the required multilayer period thickness on each position on the mirror surface has to be adjusted to the corresponding grazing incidence angle. This is achieved by varying the period thickness laterally (so-called laterally graded multilayers) creating highly efficient monochromating and focusing or collimating optics. This task is much more difficult to achieve with bended crystals e.g. in Johann or Johansson geometry [2].

On the other hand, by varying the layer thickness in depth, in the so-called depth graded multilayers, the monochromating properties of the multilayers can be adjusted to countless variations [3]. Broadband mirrors with bandwidths larger than 20% for energies from EUV to hard X-rays in the range of several tens of keV are prominent examples that have been simulated, fabricated and tested. Finally, very small period thickness polarizers (below 1 nm) working near the Brewster angle have been manufactured and tested for energies up to ~1250 eV.

The sub-nanometer precision technology applied in multilayer production can also be used to manufacture extremely thin and laterally homogeneous well defined one or multi element layers usable as reference samples for standard XRF, micro-XRF and TXRF [4].

An overview of the multiple possible applications of single and multilayer films is given in this talk together with a presentation of the newest results and developments in the field.

High-resolution micro-XRF and GEXRF applied to the investigation of the distribution of dopants in optical fibres

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The Institute of Applied Physics (IAP) of the University of Bern has recently presented a new approach for doping optical fibers for laser applications by filling quartz preforms with a mix of granulated silica and rare earth dopants and drawing afterwards the filled tubes to fibers in a standard drawing tower [1,2]. The advantages with respect to the conventional manufacturing process called MCDV (modified chemical vapor deposition) are a greater flexibility as well as a cost and time gain in the production process. In addition, alternative geometries for the final fibers can easily be adopted, something which is not feasible with MCVD. The drawback, however, is a less homogeneous distribution of the dopants, affecting directly the quality and possible performances of the optical fibers. In order to improve the quality of the optical fibers a systematic study of the dopant distribution and the production process is called for to optimize the latter.

The dopant distributions can be determined at the Physics Department of the University of Fribourg by means of micro-focused XRF (x-ray fluorescence) and GEXRF (grazing emission XRF) measurements of fiber sections produced by the IAP. The micro-focused XRF studies allow to perform a lateral mapping of the concentration levels of the different elements included in the optical fiber. To perform this 2D scans, the studied fiber sections are moved through a focused primary x-ray beam. The concentration distribution in the depth direction is realized by means of GEXRF. Indeed by studying the intensity dependence of a XRF line of a given element on the grazing emission angle, defined relatively to the target surface, it is possible to retrieve the concentration distribution of the studied element [3,4]. Due to the refraction of the fluorescence x-rays at the sample-vacuum interface and the long emission paths within the sample, the accessed depth region depends pronouncedly on the shallow observation angle.

To realize these measurements in optimal conditions, a low-power micro-spot x-ray tube with a collimating optics was installed in the von Hamos spectrometer of the University of Fribourg [5]. By inserting in the collimated beam a focusing polycapillary optics, micro-focused measurements can be performed. The implementation of these new devices in the existing high-resolution GEXRF setup as well as preliminary results of measurements performed with an Al-Er-P doped SiO₂ fiber will be presented.

Capabilities and limitations of X-Ray Reflectometry for in-line metrology of High-k Metal Gates

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X-ray reflectometry (XRR) is a well-established and non-destructive technique used for estimation of density, thickness and roughness of single layer and multilayered thin film structures. XRR fully automated tools are now installed in semiconductor R&D laboratories and manufacturing lines so as to accelerate the development of materials with fine-tuned physical properties and support the monitoring of well-established processes. Despite the worldwide recognition of the advantages of XRR as a reliable metrology technique, the further utilization of XRR for quality control and in the optimization of industrial process still suffers from the lack of reference samples and standardization of the modeling software. What is the possible impact of different hardware platforms and various measurement and modeling protocols on the information derived from XRR automated tools?

In order to address this point, a round robin XRR characterization study has been undertaken involving a series of blanket thin films consisting of materials currently of interest to the development of advanced High-k Metal Gates. Blanket SiON and TiN films along with SiON/HfSiON and SiON/HfSiON/LaO/TiN multilayered thin film structures were evaluated on four different hardware platforms and the experimental data modelled and refined using three different vendor software packages. We report on the influence of both the hardware (dynamic range, angular range, off-specular contribution, wafer chuck-induced variability) and the software (software package, fitting algorithms, goodness of fit indicators) contribution to the discrepancy of XRR-deduced thickness (Fig.1) and density amid our challenging dataset. In addition, complementary characterizations were run on the sample set so as to evaluate the trueness of the XRR-deduced thickness (TEM, GIXRF) and density profile (Angle-resolved XPS).

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{Fig1.png}
\caption{Discrepancy of the TiN thicknesses deduced from XRR data collected on four hardware platforms and modeled with three different software packages, using various algorithms.}
\end{figure}
Thermoelectric materials have the unique property to convert heat into electrical power and therefore they are used for waste heat recovery. Fields of application are amongst others the automotive industry or energy self-sustaining sensors. Estimations of the automotive industry come to the anticipation of a potential fuel saving of 5 – 7% by the use of thermoelectric generators. The development of chalcogenide p-type and n-type semiconductors for thermoelectric applications is of high interest. Because of their peak performance at room temperature, Bi₂Te₃, Sb₂Te₃ and Bi₂-xSbxTe₃ and Bi₂TeySe₃-y are the materials of choice. A most simple and not cost intensive method for the preparation of a system for gaining thermoelectric power may make use of electrochemical deposition from an aqueous electrolyte on Au or Pt substrates. Thermoelectric properties such as electrical conductivity ($\sigma$), thermal conductivity ($\kappa$) and the Seebeck coefficient ($S = \Delta U/\Delta T$, the generated voltage for an applied temperature difference) critically depend on the composition and the homogeneity of the materials. The electrochemical deposition indeed depends on many parameters, which can affect the composition. Especially for non-stoichiometric synthesis products a non-homogeneous deposition has been reported. This necessitates a determination of the homogeneity of the layers as it is possible with $\mu$-X-ray fluorescence ($\mu$-XRF) measurements. Also a structural control is desired, which makes the use of a combined $\mu$-XRF and $\mu$-powder diffraction ($\mu$-XRD) measurement setup favorable.

Previous results indicate small deviations of Seebeck-coefficients over the sample surface, which might be caused by variations of the elemental concentrations or structural variations. To investigate the lateral homogeneity of electrochemically deposited samples synchrotron $\mu$-XRF in combination with synchrotron $\mu$-XRD analysis is performed. The spot size in the experiments is 15 $\mu$m and the surface area is scanned with step width of approximately 300$\mu$m. The results show good homogeneity of the samples for both $\mu$-XRF and $\mu$-XRD and indicate the successful development of synthesis conditions. Nevertheless a potential explanation for the variation of Seebeck-coefficients deduced from the $\mu$-XRF results will be presented.
Standard reference material (SRM) is needed to secure traceable and comparable measuring results.

An XRFA technique which is based on a complete computer simulation of the measuring process has been developed to characterize layer systems (single layers and multi-layers) and homogeneous bulk material. Wide range validations have confirmed the reliability of this method which does not need any standards except from pure element samples of “infinite” thickness.

The combination of this standardless XRF technique with well-proved gravimetric and other analytical measuring procedures such as RBS and ICP-OES is applied to quantify SRM with optimal measuring uncertainties. Also SRM of accredited labs and state metrology labs (NIST, BAM …) can be included if available.
Application of Maximum Entropy Spectrum Unfolding to X-Ray Spectrometry

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It is well known that any spectrum measurement is changed by the detection system. The whole influence of the detector is quite complex to characterize and is usually expressed as the overlapping of different effects like the radiation transport inside the detector, the energy resolution and all the aspects related to the signal formation and processing. The direct reconstruction of these contributions gives an estimation of the detector response function (DRF), which allows the construction of the measured signal starting from the original spectrum distribution. However, due to the loss of information associated to the convolution in the DRF, the recovering of the original spectrum from the measured one (inverse process) is much more difficult. In addition, to be solved, the inverse problem must be discretized, resulting in an algebraic system represented by an ill-conditioned matrix equation. Therefore, it is necessary to recur to a regularization technique, which should be chosen according to its capability to take advantage of some physical features of the solution. In particular, the positivity of the x-ray spectrum is preserved by the maximum entropy unfolding technique, which has already been successfully used in other fields. This method is implemented in the code MAXED [1], which represents the state-of-art for unfolding of neutron spectra. MAXED needs as input parameters the measured spectrum with its variance, the computed DRF, an estimate of the solution called “default spectrum” (which contains a priori information) and the desired precision of the solution, expressed through the use of the chi-square per degree of freedom. It is worth noting that incorrect values of the default spectrum and the chi-square lead to meaningless results (or no result at all). To prevent this problem, the code GRAVEL [2] (a modified SAND-II algorithm) can be used together with MAXED.

In this article, it is presented a new strategy which allows the solution of the unfolding problem in x-ray spectrometry by using a suitable combination of the above mentioned codes. The program UMESTRAT (Unfolding Maximum Entropy STRATegy) has been developed to apply this strategy in a semi-automatic mode. In the first step, GRAVEL is used to obtain an initial value of the chi-square which ensures the convergence of the MAXED algorithm. In the second stage, the optimal default spectrum is computed with MAXED (using the chi-square just found) and a selective smoothing procedure is applied. In the final stage, the unfolded spectrum is obtained with MAXED using as input the chi-square computed with GRAVEL (in the first stage) and the previously found optimal default spectrum. At each step, the code UMESTRAT produces a graphical representation of the intermediate spectrum results. The presented methodology preserves the known property of the maximum entropy code MAXED of finding a solution only when the DRF is compatible with the variance of the measurement, thus evaluating the ambiguity of the DRF used in the unfolding process.

Reference Materials for the Performance Check and Specification of Energy Dispersive X-Ray Spectrometers in Electron Probe Microanalysis

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Apart from the various available reference materials provided with a certificate of the corresponding elemental concentration for almost all representative classes of solid materials there are some well selected materials which shall be consequently used to check periodically or even to specify the performances of an energy dispersive X-ray spectrometer (EDS).

In the first ISO standard of the ISO technical committee ISO/TC 202 Microbeam Analysis released in 2002 such specimens are recommended [1]. Meanwhile all major EDS instrument manufacturers specify rigorously the performances of their spectrometers in compliance with the procedures and specimens in this standard. In turn, the ED-EPMA (energy dispersive - electron probe microanalysis) operators - many of them working in accredited labs – employ also the same specimens. Hence, for the specification and periodical control of the energy resolution, an encapsulated $^{55}\text{Fe}$ source to measure the manganese K$\alpha$ line and a polytetrafluoroethylene (PTFE, Teflon®) piece or foil for the carbon and fluorine K lines is recommended to be used. In order to check periodically the FWHMs at high count rates as well as in the user laboratory, a polished manganese specimen can be used if $^{55}\text{Fe}$ is not available or may not be used in the laboratory due to safety regulations. Alternatives to PTFE to measure the carbon and fluorine K lines are respectively glassy carbon and a fluorine-containing mineral such as CaF$_2$. New approaches of alternative test materials to be employed for the periodical check of the energy resolution of an EDS will be presented. The survey is especially worthy for the energy range below 1 keV.

As far as the EDS spectrometer efficiency is concerned the ISO 15632 standard recommends flat, polished and sufficiently cleaned nickel or copper specimens to be used; as a measure for the energy dependence of the instrumental detection efficiency the L/K line intensity ratios shall be used. An alternative new approach of a multielement test specimen [2] for the same purpose and the resulting advantages will be presented in detail.

Reference to other reference/test materials employed by various spectrometer manufacturers or operators known by the authors as being used for the evaluation of the EDS performance will be also given.

Laser-produced plasma sources for applied spectroscopy in the soft X-ray region

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When a pulsed, high average power laser is focused onto matter a hot, localized plasma is formed and heated. This plasma can act as a source for tailored X-ray pulse emission depending on temperature, size, duration and target material. The tunability of the characteristics of the emitted X-ray pulse opens many new application fields, especially due to recent improvements in high power, high repetition rate solid state lasers.

Soft X-ray spectroscopy, imaging as well as metrology have up until now been primarily performed at synchrotron radiation facilities as other sources for microanalysis are not readily available. Laser-produced plasma (LPP) sources are promising alternative laboratory sources with spot sizes smaller than 30 µm and brilliance values comparable to 2\(^{nd}\) generation synchrotron sources.

This talk aims to give insights into the possibilities and challenges of LPP sources especially for applied spectroscopy in the soft X-ray region. With characterization examples from two different LPP sources both located at the BLiX (Berlin Laboratory for innovative X-ray technologies – http://www.blix.tu-berlin.de/) source parameters are discussed and first application experiments are demonstrated.
THE COLOUR X-RAY CAMERA: BASICS, APPLICATIONS AND PERSPECTIVES

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A new energy-resolving X-ray camera capable of energy- and space-resolved measurements has been developed. This device consists of a high-speed CCD detector coupled to Poly-capillary optics that conduct the X-ray photons from the probe to distinct pixels onto the detector.

The pnCCD has an active area of 12.7 x 12.7 mm², 264 x 264 pixels with 48 µm square pixel size. The column-parallel and split-frame readout enable frame rates exceeding 400 Hz (equivalent to 28 Mpixel/s) and a maximum count rate of 620 kcps. The spectroscopic performance at this speed is around 156 eV (FWHM) for Mn-Kα. The full depletion of detector volume enables quantum efficiencies approaching 100 % in the 1 keV-10 keV energy range and is still amounting to 22 % for 24 keV photons.

The camera is capable of fast acquisition of spatially and energy-resolved fluorescence images. A dedicated software enables the acquisition and the online processing of the spectral data for all 69696 pixels, leading to a real-time visualization of the elements distribution in a sample.

We present measurements with synchrotron radiation and laboratory sources showing the camera capability of performing full-field X-ray Fluorescence (FF-XRF), full-field total-reflection XRF (TXRF), X-ray Diffraction (XRD) and X-ray fluorescence Tomography. Examples from applications from various areas are given.
EDXRF Imaging with 2D detectors

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Energy dispersive x-ray fluorescence (EDXRF) technique allows elemental composition studies of samples and is distinguished by its universality and ability to perform non-destructive analysis of the studied samples. When this method is combined with imaging capability – EDXRF imaging – the elemental mapping distribution of a sample can be assessed. Nowadays, this combined technique, allows important applications in areas such as biology and bio-medicine, art history, industry, among others. Different, commonly used, x-ray fluorescence imaging systems are based on scanning or on "full field of view" systems. Recent developments, in solid state detectors as well as in MicroPatterned Gaseous Detectors (MPGDs), have shown excellent properties for single photon counting imaging in EDXRF applications when combined with pinhole lenses[1]. MPGDs are large-area gaseous detectors with 2D position capability, position resolution below 100µm, and fair energy resolution of about 850 eV for 5.9 keV x-rays. The different types of MPGDs are commonly produced with active areas higher than 100cm², allowing the analysis of large areas of interest.

Present status, and future prospects for these "full field of view" detectors in EDXRF applications will be discussed.

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Liquid-metal-jet x-ray source technology

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We have previously demonstrated prototype performance of a metal-jet anode x-ray source concept [1,2] with unprecedented brightness in the range of one order of magnitude above current state-of-the art sources. This type of source is suitable for a wide range of x-ray analytic and imaging applications. As many high-end x-ray applications today are limited by the x-ray source brightness, they would greatly benefit from such an increase in brightness, both in terms of resolution and exposure time.

In this talk we will present the metal-jet technology in detail covering both its benefits and potential limitations. We will review the current status of the technology in terms of spot size, stability, lifetime, flux and brightness. We will furthermore present recent data from applications within x-ray diffraction and phase contrast imaging [3].

SOLEX: a versatile monochromatic X-ray source for energy-dispersive detectors characterization

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Today, available experimental facilities, like monochromatic radiation (tunable X-ray source or synchrotron), should offer new perspectives of experimental measurements and give new possibilities to improve detector characterization.

The SOLEX facility [1] developed at the French national metrology Institute for ionizing radiation (LNHB) produces a tunable monochromatic X-ray beam in the 0.5-28 keV range. It is basically an X-ray tube used with a dispersive crystal to produce a monochromatic beam. The tube is windowless and is placed in a vacuum chamber together with the crystal. It runs in Johann geometry: the exit slit of the tube, the crystal and the exit slit are placed on a Rowland circle of 20 cm of radius. Different crystals are available and the setup can be run in the Cauchois (transmission) or the Johann (reflection) geometries.

SOLEX has been equipped with a rotation system, thus the same monochromatic beam can be sent successively towards two different directions. The second output is equipped with a gas proportional counter; it has a front and a back Be window of which attenuation coefficients as well as the Ar+CH4 gas mixture were measured in order to estimate the gas detector efficiency. This detector is used as a reference to calibrate the efficiency of any energy-dispersive detectors. Several automated procedures running under a LabView® program allows energy-scans for different kind of measurements such as efficiency calibration.

Several other studies can be considered such as the detector response function taking advantage of the monochromatic character of the beam. This can be combined with a surface scan of the detector with the X-Y stages mounted on the output to test its homogeneity. Some other tests can include characterization of absorbing layers or escape effects.

Studies performed with different kinds of detectors will be presented. These include conventional commercial detectors (HPGe, Si(LI), SDD, CdTe) and detectors developed for specific applications such as DUVEX [2], Caliste and XRDPIX.


Preliminary studies on the X-ray emission from an innovative plasma-trap based on the Bernstein waves heating mechanism

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The radiation emission from ECRIS (Electron Cyclotron Resonance Ion Sources) is a well-known process. In particular, X-ray emission has been largely used as passive plasma diagnostics. However, the possibility of using ERCIS as a potentially high-brightness X-ray sources has been not deeply investigated. The X-ray emission intensity would grow dramatically with the plasma density, but electromagnetically-heated plasmas are intrinsically density limited because of the well-known cut-off effect; large plasma volumes (i.e. large device dimensions) would be needed in order to get intense X-ray beams. In the present work a pilot study about intense X-ray emission from a very compact plasma-trap (a cylindrical chamber of 24x14 cm dimensions) based on the Electron Bernstein Waves (EBWs) heating is presented and discussed. EBWs are plasma waves able to sustain extremely overdense and energetic plasmas. EBWs experiments have been recently performed in fusion reactor devices [1] but never in compact-size linear systems. Our prototype operates in a low power range (P\textsubscript{RF}<150 W) and it is characterized by a quasi-flat magnetic field profile; EBW are triggered by microwaves at 3.747 GHz and their generation takes place via inner-plasma electromagnetic-to-electrostatic waves conversion. This effect has been recently investigated and demonstrated by the LNS group [2,3] in the aforementioned compact trap. The activation of the EBW-heating regime was manifested by an intense X-ray emission mainly in the soft X-ray domain from 0.1 to 3 keV, but extending up to about 25-30 keV. The emission is highly time-stable. A threshold (in terms of applied RF power) was found out, above which the mode conversion took place and the plasma modified suddenly its shape (a high-brightness annulus became visible thus starting the X-ray emission). Experiments reveal that a “typhoon-shaped” plasma vortex develops, due to BWs propagation in the cylindrical symmetric magnetic field. A huge amplification of a factor $10^5$ in the X-ray emission rate was observed during the EBWs-heating mode with respect to the standard ECR-heating regime. Different gases (D, N\textsubscript{2}+O\textsubscript{2}, N\textsubscript{2}, Ar and He) were used to investigate the X-ray emission at different pressures (i.e. different plasma densities). Measurements were performed with a 80 mm\textsuperscript{2} SDD detector by extracting and collimating in air the X-rays emitted by the plasma vortex. In this way X-rays starting from an energy of 1-2 keV can be directly detected, even if with low efficiency. Simulations about the total plasma emission over the entire solid angle provide an intensity of about $10^{14}$-$10^{15}$ photons/sec in the 0.1-3 keV region. A pin-hole X-ray camera is currently under development for X-ray imaging and for characterizing the low energy component (below 1-2 keV) of the X-ray spectrum. Finally, a new high performing plasma-trap for BWs studies is under installation and will be commissioned in summer 2012 at the LNS. Larger X-ray intensities are expected to be produced.

The DEPFET detector-amplifier structure possesses several unique properties which make it very attractive as basic element in semiconductor sensors to be used in X-ray astronomy, X-ray spectroscopy, optical and X-ray imaging and in particle tracking.

In its basic form it is a field effect transistor located on a fully depleted silicon bulk. By suitable crystal doping an electron potential minimum is formed below the transistor channel, so that signal electrons generated anywhere in the fully depleted bulk are collected in a very small region below the transistor channel, thereby inducing mirror charges in the channel and thus increasing its conductivity. The device is simultaneously a detector and an amplifier with very low input capacitance and therefore low noise. In addition it is simultaneously a charge storing device so that the same signal charge can be read out repeatedly. A measurement precision of 0.25 elementary charges has been demonstrated experimentally. The DEPFET is a natural basic element of a pixel detector and therefore an excellent device for spectroscopic imaging. A variety of concepts have been invented in order to optimize it for specific applications.

The presentation will cover the basic functionality and properties of DEPFETs, demonstrate experimental achievements and present some advanced concepts and designs. These include DEPFETs with strongly nonlinear characteristics providing simultaneously single (low energy X-ray) photon sensitivity and high dynamic range as well as DEPFETs with gating capability.
SDD Detectors with Minimized Input Capacitance

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In recent years, SDD based detectors set the performance benchmark for silicon based spectroscopic X-ray detectors. By now, the trend towards larger sensitive detector areas and larger solid angle coverage generates the need for SDDs capable of processing the involved elevated photon intensities. Increased photon throughput requires an operation of the SDD devices at short shaping times while maintaining the superior spectral purity and energy resolution of the SDD. This means that the effective input capacitance of the SDD readout node has to be reduced to the lowest possible value, as it affects the way all kinds of noise impact the spectral resolution. Minimizing this capacitance allows for improving the energy resolution for given timing or, correspondingly, reducing the optimum shaping time drastically without compromising spectral performance.

The recent introduction of the Silicon Drift Detector Droplet (SD3), which, among other benefits, also had a modified readout node geometry with lower capacitance, already demonstrated impressively the performance scaling power of the input capacitance. Now, efforts made to further reduce the input capacitance lead to the introduction of a new generation of SDD devices, the so-called SDD\(^{\text{plus}}\) series. Advancements in technology permitted topological optimizations of the structure of readout anode and integrated JFET, which reduce the input capacitance by a factor of 2. The optimized FET of the SDD\(^{\text{plus}}\) structure can be integrated into all SDD geometries and sizes and applies to both standard circular and droplet configuration. The leap in performance is impressive: 122 eV FWHM at 5.9 keV for -20°C can be achieved for medium shaping times of 1 - 2 μs; the same device can cope with count rates up to 800 kcps with 127 eV FWHM at shaping times of 0.25 μs only. Structures of up to 30 mm\(^2\) sensitive area have been built and tested, larger size SDDs with SDD\(^{\text{plus}}\) FET are in preparation and await qualification. The principle will be illustrated; results from test and qualification measurements will be presented.

Reducing the input capacitance by scaling the size of the readout FET, however, can not arbitrarily continue. For structures below the SDD\(^{\text{plus}}\) FET size, technological and conceptual challenges generate the need for alternative concepts to decrease the input capacitance further. Here, the combined detector-amplifier structure DEPFET [1,2] (Depleted P-channel FET) is a promising candidate. DEPFET based readout nodes can easily be combined with an SDD like drift ring structure, combining the traditional advantages of SDDs, like scalability and optimized QE, with the properties of the DEPFET cell, e.g. charge storage capability and a readout capacitance lower than 20 fF. Recently, single cell SDD devices utilizing DEPFET based readout nodes have been designed to make the advantage of the reduced input capacitance become effective for high rate X-ray detection applications.

References
The Hard X-ray Micro-/Nano-Probe beamline P06 at PETRA

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The Hard X-ray Micro/Nano-Probe beamline P06 at PETRA III has become operational in 2012. Here, different techniques can be applied for 2D- and 3D-imaging, including X-ray fluorescence (XRF), X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD), small angle X-ray scattering (SAXS), and coherent X-ray diffraction imaging (CXDI) as well as ptychography. The photon energy can be selected and scanned in a wide range of 2.4 - 100 keV.

Two endstations exist: The Microprobe offers a focus of (sub)-micron size, while its large working distance optics allow to use special sample environments like cryochambers for biological specimens, diamond anvil cells or heaters. The Nanoprobe achieves sub-100nm focussing, achieving sub-10nm resolution using scanning coherent diffraction imaging techniques ("ptychography"). This contribution will introduce into the capabilities and current status of both endstations, exemplified by a few first results.
High Throughput Pulse Processing Electronics Using Model Based Signal Processing

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In many practical applications of X-Ray Spectrometry the rate at which data can be analysed is severely limited by the efficiency of the X-ray detectors. Detection efficiency, including throughput and resolution, degrades rapidly at medium to high radiation flux.

Traditional pulse shaping electronics use linear filters to produce trapezoidal pulses with variable rise and peaking times. However, the short shaping times required to operate at high count rate also attenuate the signal energy reducing signal to noise ratio and consequently the energy resolution. Furthermore, closely spaced pulses cannot be separated and pulse pile-up remains a problem. Recently there has been interest in implementing more complex signal processing methodologies to further extend the operational limits of radiation detection and measurement systems.

We present a novel approach to pulse processing electronics. Using Maximum Likelihood Estimation techniques, implemented in real-time, we demonstrate the ability to accurately recover information from pulse pile-up. To implement this pulse pile-up recovery technique, the detector data is digitised and modeled as the sum of an unknown number of events (n), each with random arrival time (t) and unknown energy (e). It is assumed the detector response function to a single event is known a priori. By solving, on-line and in real-time, for each of the unknown parameters n, t, and e, it is possible to accurately recover information from piled-up pulses.

The real-time pulse pile-up recovery algorithm enables high throughput, low dead-time pulse processing by recovering rather than discarding detector data corrupted by pulse pile-up. It has been implemented on a Spartan-6 FPGA and the performance evaluated with a range of radiation detectors. Key performance metrics include throughput greater than 1 million counts per second at less than 10% dead-time; and a pulse pair resolution of less than 60 nano seconds.
Analyzing Nanoscaled Materials with a Wavelength Dispersive Spectrometer

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Nanolayered structures as well as nanoparticle become more and more important in current industrial applications. The analysis of these materials is challenging due to low concentrations or mass depositions. The use of a wavelength dispersive spectrometer (WDS) enables the possibility of revealing information about the chemical speciation by means of the fine structure in X-ray emission spectra of the respective elements of interest. But these measurements, in general, involves extraordinary long measuring time.

The extension of the WDS to be presented, in particular the refocussing of soft X-ray radiation down to a 10 µm beam profile with single-bounce monocapillary, allows for the usage of the spectrometer without any entrance slit. This drastically increases the efficiency of the WDS so that not only the measuring time is decreased but also fluorescence radiation with low transition probabilities can be detected.

By means of two 10 nm thick titanium and nickel layers, the sensitivity of the improved WDS arrangement could be confirmed whereas a larger deposition of titanium dioxide nanoparticles could demonstrate the speciation capabilities.
Characterizing and modeling the diffraction properties of a new type of Highly Oriented Pyrolytic Graphite (HOPG) - X-ray optics for high energy resolution spectroscopy


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Highly Oriented Pyrolytic Graphite (HOPG) as a polycrystalline material offers high integral reflectivity [1]. This high reflectivity however is achieved at the expense of spectral resolution. Recent advancement in the annealing process allows for the production of Highly Annealed Pyrolytic Graphite (HAPG), a novel type of PG with very low mosaicity and improved intrinsic reflection properties [2]. Compared to HOPG, the resolving power E/ΔE of HAPG is improved. Resolving powers of 2000 in first order and 4000 in second order could be demonstrated. The mosaicity can be as low as 0.05°.

HAPG allows for the manufacturing of efficient X-ray optics of virtually arbitrary shape for the application in the energy range from approximately 3 keV up to 60 keV. Furthermore, applications of HAPG as polychromator have facilitated X-ray tube based X-ray absorption and X-ray emission experiments [3]. Compared to state of the art HOPG optics, high resolution HAPG optics make higher demands on their fabrication as well as on their characterization and simulation of their diffraction properties.

The contribution will present an overview of recent achievements in characterization methods, modeling, simulation, and manufacturing of HAPG optics. Experimental results of synchrotron based characterization experiments as well as those obtained with an X-ray tube are presented. The peculiarities and properties of HAPG's structure will be discussed.

Influence coefficient algorithms in X-ray fluorescence analysis of thick and intermediate-thickness samples

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X-ray fluorescence spectrometry (XRF) is a versatile tool in many analytical problems. Major, minor and trace elements can be qualitatively and quantitatively determined in various kinds of samples: metals, alloys, glasses, cements, minerals, rocks, ores, polymers, thin films etc. However, the quantitative analysis is rather complicated because the measured intensities depend not only on the analyte concentration but also on matrix elements, method of sample preparation, thickness of the analyzed sample and measurement conditions.

Numerous methods, both empirical and theoretical, have been proposed for quantitative XRF analysis. Due to the increasing power of computers during the past few years, the theoretical methods, both fundamental parameters and theoretical influence coefficients, became the most popular in routine XRF analysis. The serious advantage of fundamental parameter methods is their versatility: the analysis of bulk, thin samples and multilayers is possible. Unfortunately, the fundamental parameter methods are like “a black box”. Therefore, the influence coefficient algorithms are widely applied in routine analysis [1-3]. The matrix correction and calibration is clear and interpretation of data is very easy. The most popular influence coefficient algorithms will be reviewed and discussed. Although, these algorithms are widely applied for quantitative analysis of infinitely thick samples, the idea of influence coefficients can also be used in quantitative analysis of intermediate-thickness samples [4,5]. Both empirical and theoretical influence coefficient algorithms for simultaneous determination of thickness and composition of samples of less than ‘infinite thickness’ will be presented. The presentation will show that the complicated problem of matrix correction in XRF analysis of intermediate-thickness samples can be simply solved using the concept of influence coefficients.

Light matrix specimens emit X-ray fluorescence (XRF) spectra having a prominent spectral background. Particularly for element-rich specimens the knowledge of the background is critical and may cause significant errors at the extraction of net peak areas for the XRF quantification. Usually, mathematical or empirical backgrounds are taken into consideration. Based mainly on the modeling of the X-ray scattering a physical background has been recently demonstrated in our lab as being accurate enough [1] to be exploited for gaining more accurate analytical information on XRF figures of merit as a method or on the specimen.

One very attractive application of the physical modeling of the XRF spectral background is the possibility to predict limits of detection for particular conditions such as excitation, specimen matrix or geometry. Once the model established, the consideration of the effect of the X-ray polycapillary optics, i.e. of the transmission, in the case of µ-XRF is also feasible. The effect of the use of well defined filters in the excitation channel can be predicted, too. The exercise of prediction of detection limits is possible only by having also a model for the calculation of the X-ray fluorescence line intensities, so that signal-to-background ratios and signal-to-noise ratios, respectively, can be predicted. The good agreement of predicted and experimental limits of detection will be highlighted on representative examples.

Another interesting implementation of the scattering model for practical analytical purposes is the exploitation of the dependence of the X-ray scattering on the average atomic number of the specimen. For defined excitation and geometrical conditions the ratio of the two components of scattering, i.e. inelastic and elastic (or Compton and Rayleigh) ones, can be synthesized for various mean Z in form of a calibration curve. The sensitive dependence on the mean Z in the low-Z range makes the approach attractive to derive concentration of heavy elements in known light matrices, in differentiating “similar” light matrices or calculating element concentrations “by difference” for light elements which are “invisible” for XRF.

Other unwanted effects which might occur in the XRF spectra such as refraction peaks can be better identified by applying the physical model above. Also the lack of special reference materials can be suppressed by using the predictions above in combination with results obtained by electron probe microanalysis [2].

Quantification of ED-XRF datasets through iterative Monte Carlo simulations: new developments

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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 modelled 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 new software package XMI-MSIM, based on the Monte-Carlo code by Vincze et al[1], 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[2] 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 multithreading and multiprocessing has led to a significant increase in computational efficiency and allows for the deployment on supercomputers, which is recommended when operating in brute-force mode.

Optionally, the code can be called as a plugin from PyMca[3], 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 ANSI-C and Fortran 2003, and makes extensive use of several open source packages such as the GNU Scientific Library, libxml2, HDF5, OpenMPI and GTK. XMI-MSIM is available from www.github.com/tschoonj/xmimsim and is distributed under the GNU General Public License (GPL).

Quantification of SXRF microscopy imaging of intermediate thickness plant specimens

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The SXRF microscopy enables the mapping of element distribution on cellular level in the μm or sub-μm scale. The quantification of step-by-step scanning of the sample on the basis of the measured full spectrum in each pixel is very important if the data are to be properly interpreted in different plant physiology studies.

The samples of different plant organs were prepared by cryo-fixation and cut by cryo-microtome to 20 μm. Afterwards the cuttings were freeze-dried under controlled conditions in order to minimize the shrinkage of the samples. The experiments were performed at the TwinMic beamline of synchrotron Elletra (Trieste, Italy) and ID21 beamline at the ESRF (Grenoble, France). For the excitation the monochromatic beams of 2.2 keV and 3.55 keV respectively, with the spatial resolution in a micrometer range were used. The X-ray fluorescence spectra in each measured pixel (usually 100x100 pixels scanned) were measured by the SD detectors (up to 8 detectors at Twin-Mic and one at ID21 beamline) and stored in the H5 file.

The quantification of scanned elemental distribution maps started with deconvolution of X-ray spectra using PyMCA software [1] and elemental intensities with uncertainties were obtained in the matrix form (*.CSV file) with data for each measured pixel in a single row. These data included also the intensity measured at each pixel by the CCD camera and/or photodiode positioned behind the sample in the direction of the beam, which in principle offered the information about the sample thickness and absorption of the primary beam in this particular pixel.

The quantification procedure applied was the extension of the quantification used in the conventional XRF analysis and was based on FP and the Emission-Transmission method in order to be able to assess the absorption in the so called “dark matrix” of the sample, and make in this way the quantification fully quantitative. The FPs used were taken from the recent database of Elam et al. [2] and the system of equations for measured elements was based on the relationship firstly developed by Sherman et al [3].

The calibration of the XRF system was performed by a set of thin, few 10 μg.cm⁻² thick standard samples from Micromatter and the respective geometry and/or instrumental constant was obtained [4]. On the other hand the same constant was also obtained from measured incident photon beam by the CCD camera and/or photodiode and considering the solid angles extended from the sample to the detectors. Using FPs the respective elemental sensitivities were then calculated. The uncertainties introduced by FPs and calibration procedure were partially compensated if experimental sensitivities were used in further quantification.

The quantification using the measured elemental intensities was performed in an iterative way by considering the absorption of the primary beam in the sample, which yielded in each pixel the experimental value of $\mu_S \cdot \rho_d$. The iteration included beside elemental concentrations of measured elements and the area weight also the absorption in the iteratively varied “dark matrix”, which was proportional in composition to the one obtained from conventional analysis of the same bulk sample. The iteration procedure ended, when the calculated product of area weight with absorption in analyzed elements and resulting “dark matrix” did coincide with the experimental value.

For the validation of the applied procedure a specially prepared standard sample in TFM was used and also the comparison with the results of analysis of the same sample by micro-PIXE technique.

Advanced Scattering X-ray Correction for Oils in XRF

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X-ray fluorescence spectrometry is commonly known as a suitable analytical technique for inorganic element analysis in oils due to its precision and easy applicability. However, in several kinds of base oils analytical errors occur particularly in biofuel, waste oil and lubricating oil. This is caused by the fact that fluorescent X-ray intensities are affected differently depending on the oxygen content and the CH ratio in the base oil. In addition, similar problems are often observed when commercially available oil standards with high contents of mixed stabilizers are used because the matrix of base oil changes thereby as well.

In order to avoid the base oil problem, methods exist to correct for the CH ratio differences by utilizing scattered X-rays or correct for the influence of the oxygen by using Compton scattered X-ray intensities. However, to our knowledge no reports exist about a method that corrects for the influence of both the CH ratio and the oxygen content. We have developed a new method to correct for both influence factors by utilizing the scattered X-ray intensity of the continuum and the absorption effect by inorganic elements.

The scattered X-ray intensity of the continuum depends strongly on the energy of those X-rays. We found that the influences of both, the CH ratio and the oxygen content, can be corrected by selecting an appropriate energy of scattered X-rays of the continuum. With respect to the influence of inorganic elements we found that this was particularly high in case of high sulfur oils and lubricating oils where the content of inorganic elements is high. The correction is achieved in this case by accounting for the resulting inter-element effects by obtaining the pertinent alphas by a fundamental parameter method in addition to scattering X-ray intensity correction. The newly developed correction method requires no special standard samples.

We will discuss the theoretical background of the new correction method and show its validity for various oil samples such as bio-diesel, bio-ethanol by using a wavelength dispersive X-ray fluorescence (WDX) spectrometer.
Monte Carlo techniques are powerful tools to simulate the interaction of electromagnetic radiation with matter. One of the most widespread simulation program packages is Geant4. But it is not evident which accuracy can be obtained by a simulation. The accuracy of electromagnetic processes within Geant4 has already been investigated by several authors, but mainly in comparison to other simulation codes, usually based on the same cross sections. For a really quantitative validation, a direct comparison to absolute experimental data has to be accomplished, requiring a known incident photon flux and a calibrated detection system in a well-defined geometry.

In this work, results of experiments using monochromatized synchrotron radiation in the X-ray regime are quantitatively compared to the results of simulations using Geant4. For the quantitative measurements a cadmium telluride detector was used, that had been fully characterized and calibrated in the laboratory of the Physikalisch-Technische Bundesanstalt (PTB) at the electron storage ring BESSY II. The detector was deployed to study angle and polarization dependence in the X-ray regime using different scattering foils. For the simulations the detector was modeled with high accuracy, and both the results of experiments and of the simulations were normalized to the same number of incident photons.

For most set-ups good agreement of experimental and simulation results was observed, and it was found that Compton and Rayleigh scattering are described well by Geant4 as well as the photoeffect, including fluorescence. However, for some orientations a dominant Rayleigh-scattered contribution was observed only for the simulations, indicating the need to reassess the Geant4 differential cross sections for polarized Rayleigh scattering. For small scattering angles, prominent deviations were observed, which were caused by diffraction in the experiments.
Qualification of quantitative grazing incidence X-ray fluorescence for the analysis of nano-particular surface contamination


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The major challenge for the analysis of ambient aerosols is the characterization of the chemical properties of the particles in dependence of their physical dimensions, especially in the nanometer regime. This issue may be approached by reference-free quantitative grazing incidence X-ray fluorescence (GIXRF) analysis for size-selected particles deposited on a flat surface. When changing the incident angle the periodicity of the X-ray standing wave field (XSW) can be varied and information can be obtained on the elemental composition of nano-scaled sample systems [1] and the size of deposited mono-disperse particles [2].

Reference-free quantification is enabled by the use of calibrated instrumentation [3]. In addition, for GIXRF measurements, a reliable calculation of the XSWs properties is necessary. For multi-layered sample systems it has recently been shown that GIXRF yields quantitative results very much comparable to those of conventional XRF [4]. If, on the other hand, the samples are not layer-like, as is the case for structured surfaces or deposited particles, the interaction between the sample and the XSW can become more complex and additional parameters may have to be taken into account for the quantification.

To identify and to quantify individual effects of the interaction between particle-like surface contaminations and the XSW, different artificial surface structures were manufactured by means of electron beam lithography and investigated with GIXRF in the PTB laboratory at the electron storage ring BESSY II.

The artificial structures are designed to address different crucial parameters of the sample-XSW-interaction, such as particle areal density or particle height and mass. Results obtained from those structures are presented and compared to measurements at nanoparticles deposited directly from aerosol phase.

Simulations and backward calculation strategies for angle-resolved measurements of graded CIGSe thin films

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Materials with chalcopyrite structure, like Cu(In,Ga)Se₂ (commonly referred to as CIGSe), are promising for thin-film solar cell absorber layers. The distinguished property of this semiconductor is the dependency of the band gap on the ratio of gallium to the sum of gallium and indium. A gallium concentration gradient perpendicular to the surface gives way to improved charge collection and, therefore energy conversion efficiency.

For non-destructive investigations of such element gradients, angle-resolved XRF measurements arise as a method of choice. Hereby the information depth can be altered by a variation of the incident or detection angle, where more shallow angles lead to a higher contribution from upper layers to the fluorescence spectrum. Streeck et al. showed [1] the principal suitability of the method by comparing measurements using a synchrotron source and grazing incidence (GIXRF) geometry to fundamental parameter based forward calculations.

Those forward calculations are further investigated by including polychromatic excitation and the contribution of secondary effects. The final aim is to find a reliable backwards calculation strategy to determine the concentration gradient of a specimen from angle-resolved measurements at different excitation conditions and geometries. We present our approach for developing such a scheme and discuss the problem of unambiguity. The simulations are compared to reference-free measurements at the four-crystal monochromator (FCM) beamline in the laboratory of the Physikalisch-Technische Bundesanstalt (PTB) at BESSY II.

Quantification of X-ray fluorescence confocal imaging

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A novel quantitative reconstruction model for synchrotron based confocal micro X-Ray fluorescence data has been developed. The theoretical model uses generalized Fundamental Parameter (FPM) approach in an iterative procedure to calculate 2D concentration distribution of the detected elements in biological samples. The FPM based model considers the matrix effect for determination of concentrations in the analyzed sample volume. The algebraic reconstruction procedures of 2D quantitative µXRF analysis always suffer from the numerical difficulty in the solution of huge number of non-linear equations describing the absorption and excitation processes in the sample. In order to neglect this serious calculation problem a new type of FPM algorithm software was developed in MATLAB environment for 2D confocal imaging using monoenergetic synchrotron radiation for sample excitation.

X-ray fluorescence (XRF) microtomography and confocal imaging based on synchrotron radiation were used for the determination of 2D/3D distributions of composition elements in small sized biological samples (1-2 mm) at HASYLAB beamline L. The energy of the incident beam was set between 17 keV and 22 keV providing optimal condition for excitation of the investigated elements from Mn to Mo. In order to focus the primary X-ray beam polycapillary optics was applied providing lateral resolution of 10-20 µm for the measured elemental maps in biological samples. For validation of the numerical procedure confocal micro-XRF analyses were performed on NIST 612 and 1577 standard reference materials and real biological samples (cucumber roots and hypocotyls).

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Precise XRF Quantification by Means of Multiple Scattering Calculations plus Instrumental Background Correction

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In quantitative XRF analysis the Fundamental Parameters (FP) method uses the theoretical calculation of the intensity to avoid or reduce the need of certified standards materials (CRM). Since the object of the quantification is the determination of the specimen composition and not the calculation of the intensity, it becomes necessary to perform the iterative computation of the concentrations from the theoretical intensities. Obviously, the correctness of the obtained composition depends on the goodness of the FP model. The FP method described in literature computes deterministically the intensity in terms of the following pure photoelectric interactions: first-order (sometimes called primary), second-order (also known as secondary or enhancement), and third-order (or tertiary). It is apparent that the different orders of Rayleigh and Compton scattering and the combinations of scattering with photoelectric collisions are missing, leading to systematic errors in the calculated compositions.

In this article we use the code MULTISCAT® based on Multiple Scattering X-Ray Fluorescence (MSXRF), a very precise deterministic model that integrates multiple-order collision contributions involving the photoelectric effect (followed by atomic relaxation) and Rayleigh and Compton scattering. MSXRF is based on the analytical solution of the Boltzmann transport equation comprising all first and second-order collisions and some selected third-order ones, polychromatic excitation, polarization effects, Compton profile broadening, Lorentzian broadening of the characteristic lines, and coupled electron-photon corrections. Such a detailed description gives a very accurate picture of the XRF intensity emitted by an isolated specimen that needs to be complemented with the external determination of the instrumental background coming from the spectrometer or from the specimen-spectrometer interaction. In this article it is presented a strategy to determine the instrumental background both from physical and mathematical points of view.

It is introduced a simple test method to evaluate the accuracy of the complete model using a given set of CRM’s. The test makes it possible: (a) to understand when the instrumental background has been correctly estimated, and (b) to detect eventual anomalies in the measurement or in the registered standard compositions. The result of the test shows that the background correction is essential for a proper determination of low-concentrations.

1 MULTISCAT AB, Örsundsbro, Sweden
Selective membranes in X-Ray Analysis: A preconcentration step or a sensor?

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ABSTRACT

Analysis of environmental interesting elements in liquid samples at low concentrations is an important analytical task and various instrumental methods of analysis are devoted to this aim. X-Ray Fluorescence is an interesting approach but it suffers from two significant disadvantages: the limits of detection that usually needed (low ppb levels - or even lower) cannot be achieved, and speciation determinations are not possible. In order to overcome these disadvantages we developed various complexing membranes that can be used for selective analysis of important pollutants (including mercury [1], chromium [2], perchlorate [3] and bromate [4]). The possibility of detection limits lower than 1 ppb has been proved as well as speciation discrimination.

Although, at the first step, the method was applied in TXRF analysis (direct membrane preparation on quartz reflectors surface), last year the technique has been extended for mercury analysis with classical Energy Dispersive XRF with promising results. In this case the selective membrane was developed on the surface of a Prolene® (or Mylar®) thin film and the irradiation was performed in a commercial X-Ray Spectrometer.

Various experimental parameters are studied, including ionic charge (cation-anion), membrane composition (matrix, plasticizer, complexing agent), equilibration time, sample volume, pH, interferences, seawater analysis, linearity range, minimum detection limit etc. Future possibilities are also discussed.

References


Quality improvements of EDXRF instruments with close-coupled geometries by means of Monte Carlo simulations

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The repeatability, reproducibility and accuracy of XRF systems with closely coupled geometries can be influenced by several coexisting factors. For instance, it is known that the qualitative and quantitative characteristics of the excitation spectrum of an X-ray tube will not remain constant with time. Evaporation of W from the filament to the anode and/or to the beryllium window may heavily modify the primary tube spectrum in an unpredictable way. W deposition will eventually result into a top anode layer with a twofold effect: The addition of a heavy atomic number element will reduce the kinetic energy of electrons impinging on the actual anode material and will introduce W, M and L lines into the emitted spectrum. This effect will become more pronounced at lower excitation voltages. Furthermore, instabilities in the position of the anode focus have to be seriously considered. Also, when the size of the electron focus becomes a significant fraction of the anode to sample distance shadow effects can alter the intensity distribution on the irradiated sample’s surface depending on the shape and positioning of the collimating system. With a constant detector viewing area this may result to detected intensity deviations of a few percent. In addition, temperature and pressure changes play a significant role and have to be appropriately accounted and corrected for. Last but not least sample related parameters such as sample positioning and sample flatness can affect not only the observed fluorescence intensities but also the position of scattered peaks. The influence of such effects can be extensively studied by means of Ray–Tracing, Monte Carlo simulations. The use of Monte Carlo simulations allows us to isolate and quantify the contribution of each and every one of the aforementioned parameters separately, identify potential risks and set realistic design specifications that improve enormously the stability and analytical performance of XRF instruments.
ED-XRF analysis of SnPb solder alloys

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ED-XRF is a very suitable and well-proven method for the analysis of solder alloys. On the one hand Pb is restricted for numerous applications but on the other hand for so called “high-reliability” applications in the military, healthcare and aerospace industries a minimum of 3 wt-% Pb is required to avoid “whisker” formation. Whiskers are needle like Sn single crystals which can lead to short circuits and therefore to failures of electronic components.

The homogeneity of SnPb alloys is inherently determined by their metallurgy and influenced by manufacturing processes and aging effects [1]. Therefore, the availability and usage of homogenous reference materials is limited. The fundamental parameter based ED-XRF method of the WinFTM software [2] was applied without using calibration standards. Additionally a relative homogenous SnPb3 material was obtained with the help of a new manufacturing process, which is also suitable for micro XRF analysis and the production of reference materials.

For “high reliability” applications SEM-EDX is also a widespread method for determining the Pb concentration in Sn coatings and solder alloys. The suitability of the electron excitation technique (SEM-EDX) for characterisation of SnPb composition of solder alloys is investigated and compared to the standard less ED-XRF method for coating thicknesses and concentrations.

On the quantification of amoxicilline and clavulanic acid in binary commercial antibiotic solid drug by PIXE

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Amoxicilline is a β-lactamine anti bacterial molecule used as active ingredient in a large variety of antibiotic drugs. The potassium calvulanate is generally added as inhibitor of the β-lactames enzymes which can hydrolyze the β-lactame nucleus which is the active part of the amoxicilline.

The quantification, with high precision, of active ingredients in a commercial drug is one of the major steps followed in the quality control procedure. Active ingredients in drugs are generally analyzed by using classical analytical techniques based on the analysis under liquid form. Effort has been made during the last decay to develop and validate new analytical methods, like Raman or NIR spectroscopy and solide state NMR, that allow the quantification of active ingredients directly on the drug under its original solid form (80% of commercial drugs in the market).

We demonstrated in previous papers that if the chemical structure of the active ingredient contains at least one specific heteroatom (S, Cl, Br, F, K, Pt..), the quantification of the active ingredient, in solid drugs, is possible via the quantification of the heteroatom of interest, by using appropriate elemental IBA technique like PIXE and or PIGE.

In this paper, we discuss the analytical validation procedure of the PIXE technique for a rapid and accurate simultaneous determination of amoxicilline (via S) and potassium calvulanate (via K) in six commercial binary antibiotic drugs with different dosages and origins.

The degradation under beam irradiation as well as the distribution of the two active ingredients in the drug formulation are highlighted and discussed. Furthermore, quantification procedure (absolute versus relative quantification) and the role of the water content in the coated or decoated analyzed drugs is discussed in term of the development of a specific sample preparation procedure that can permit the quantification of ammoxicilline and potassium calvulanate simultaneously, in solid commercial antibiotic drugs, with high accuracy and high precision (~5%) for few minutes acquisition time by using 3 MeV proton beam.
Total reflection X-ray fluorescence spectrometry in the environmental field: A review of some recent investigations and applications

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The use of TXRF in the field of chemical analysis has been reduced in the last years mostly due to the increasing use of ICP-MS instrumentation. Although ICP-MS present sufficient sensitivity and multielement capability for the determination of elements at trace and ultratrace levels, the complexity of some environmental matrices significantly hamper the analysis. An additional shortcoming is that several mL of liquid solution are needed to perform analyses and thus, the application to mass-limited samples is restricted. For this reason, in some applications, above all concerning to the analysis of mass-limited samples and suspensions, TXRF is still unique [1]. Besides, taking into account the micro-analytical capability of TXRF spectrometry, its combination with miniaturized preconcentration procedures in which only few µL of liquid or µg of solid containing the target elements are available for the subsequent analysis, is also possible [2].

In the present contribution, the feasibility of several analytical approaches combined with TXRF for trace and speciation analysis of different type of samples in the environmental field is presented. These analytical strategies included the direct analysis of the samples by depositing some µL of sample on a reflective carrier and also the development of fast and simple chemical strategies to decrease matrix effects and improve the limits of detection for metal determination, such as liquid phase microextraction procedures (LPME) or the use of carbon nanotubes as solid sorbents. These analytical methodologies have been applied in combination with different configurations of TXRF spectrometers (Mo/W X-ray tubes), including laboratory instrumentation (X-ray tubes up to 3kW) and benchtop equipments (50W power), to achieve reliable analytical results for environmental analysis at many different scales.

Our results give insight into the possibilities and drawbacks of TXRF analysis and to a certain extent the potential applications in the environmental field. It is expected that future improvements in instrumentation and sample preparation procedures could increase, even more, the analytical sensitivity and thus, TXRF spectrometry could offer new possibilities in these fields in the upcoming years.

Elemental composition of PM$_{2.5}$ in Cairo city centre, Egypt

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Aerosol particles are one of the criteria pollutants in the legislation of many countries due to their influence on human health and environmental degradation. Information about the elemental composition of the aerosol particles aids in source apportionment and determination of possible negative effects of the particulate air pollution. In this study aerosol particles smaller than 2.5 µm in aerodynamic diameter (PM$_{2.5}$) have been collected for 24 hours once a week at roof level at the National Research Centre (NRC) in the central part of Cairo, Egypt. Collection took place between September 2010 and May 2011 using a cyclonic sampler. The site is representative for an urban residential area in the centre of this megacity. An Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometer with a secondary target of Mo was used for the elemental determination and the obtained concentrations were evaluated by the QXAS/AXIL software package [1]. Quality control was done using the standard reference material SRM2783 from National Institute of Science and Technology (NIST), USA. Concentrations of 16 elements were determined in the collected aerosol samples, although not above detection limits in all samples. As expected the concentrations of many of the elements are high compared to other urban environments. The concentration of Pb was 88 ± 102 ng/m$^3$, well below the Egyptian legal limit of 500 ng/m$^3$. The concentration has decreased from above 3 µg/m$^3$ in 1997, since Pb was banned in the fuel in 1997 and a Pb smelter was moved from the central part of Cairo in 2002 [2]. From the analysis of the elemental concentrations we are able to determine seasonal variations, possible sources and estimate some effects on human health.


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Air Filter Analysis Using Direct Excitation EDXRF with Si(Li) Detection – Methodology & Performance

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The United States Environmental Protection Agency’s (U.S. EPA) commitment to improving air quality across the U.S. as well as the European Community’s Directive 2008/50/EC has created a renewed and increasing demand for the monitoring of specific elements on air filters collected in residential, industrial and recreational areas. X-ray fluorescence is the preferred method to analyze samples related to air monitoring due to the non-destructive nature of the technique and the superior sensitivity achievable.

Over the years, Energy-Dispersive X-Ray Fluorescence (EDXRF) spectrometry in particular has proven to be the analytical technique of choice for the analysis of air filters. A low power X-ray tube (usually 50 Watt) in a direct-excitation geometry, combined with a lithium drifted silicon (Si(Li)) solid state detector allows for cost-efficient, non-destructive analysis without sample preparation. Thanks to the high stopping power of the Si(Li) detector, detection levels down to a few ng/cm² and less are not limited to light elements only but can also be obtained for heavier elements such as As, Cd, Hg and Pb.

This work focuses on the methodology to calibrate the instrument using commercial single and dual element thin film vacuum deposited standards from Micromatter, Inc. in addition to blank films. Verification of the calibrations is accomplished by analyzing a National Institute of Standards and Technology (NIST) thin film standard (SRM 2783). The results are compared to those specified in the U.S. EPA Compendium Method IO-3.3. For a majority of the elements listed, the MDLs achievable are as good as or better than those reported by the U.S. EPA in Compendium Method IO-3.3.
Identification of trace elements in ambient aerosols helps source apportionment, especially with a high time and size resolution. Emission sources, such as traffic and shipping are highly variable in time, and different sources emit aerosols in different size ranges. Traffic e.g. emits particles between 10 and 2.5 µm via resuspension of dust, but also between 2.5 and 1.0 µm via brake wear. A two-hour time resolution of coarse mode iron may indicate the resuspension of road dust, while antimony is associated with brake wear.

Synchrotron Radiation induced X-Ray Fluorescence Spectrometry (SR-XRF) is able to quantify ambient elemental concentrations with a detection limit for single element masses on the order of a few pg. During the last couple of years, the possibilities of these spectrometry measurements at different Synchrotron facilities have been shown [1, 2]. Such measurements are a big step forward in trace elemental identification compared to more conventional 24-h filter sampling methods.

Here we present 2-h resolved trace elemental measurements in three size ranges as part of the CalNex-LA field campaign. The measurements were performed with a 3-stage Rotating Drum Impactor at a roof-top urban site in Pasadena, CA, USA. Subsequent SR-XRF analysis reveals trace elemental concentrations from sodium to lead. Source apportionment by Positive Matrix Factorization is applied to the time series of the trace elemental concentrations and their relative contributions in the aerosol ranges 10-2.5 µm, 2.5-1.0 µm and 1.0-0.1 µm. Emission sources that are identified at the urban site are, among others, mineral dust from resuspension by traffic, shipping and secondary sulphate aerosol.

Elemental Characterization of Airborne Particulate Matter Sampled in Kenitra City (Morocco) using Total-Reflection X-Ray Fluorescence

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A major component in air urban pollution is particulate matter (PM), which can be coarse or fine. Coarse particulates can be regarded as those with a diameter greater than 2.5 μm, and fine particles less than 2.5 μm. Coarse particles usually contain materials from the earth’s crust and dust from vehicles and industrial plants; while fine particles contain the secondary formed aerosols, combustion particles and re-condensed organic and metallic vapors. Air pollution is an increasing threat to human health and the environment, affecting the quality of life of millions of persons around the globe [1, 2].

In Morocco, the study of air pollution attracts more and more interest and attention during the last years, either by the government or researchers. As a consequence, many studies on air quality have been developed and implemented in several Moroccan cities [3-5]. In this context, the present study aims to evaluate the air quality and to quantify emission sources in Kenitra City located about 50 km from Rabat (the kingdom of Morocco) in the border of Atlantic Ocean. So, this study consists in estimating contents of heavy metals and particulate matter (fine and coarse), in the atmospheric aerosols, collected using Gent and Dichotomous samplers. The analysis of collected samples was carried out using Total-Reflection X-Ray Fluorescence (TXRF).

The obtained results show that contents of airborne particulate matter in Kenitra City exceed those recommended by World Health Organization (WHO) and European Union (EU) [6, 7]. The identification of emission sources using Model Receptor, more particularly Positive Matrix Factorization (PMF), reveals the predominance of traffic, soil dusts and resuspension of deposited particles as emission sources.

X-RAY FLUORESCENCE DETERMINATION OF MANGANESE VALENCE STATE IN NODULES

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Nodules contain manganese mainly in form of Mn$^{4+}$ and sometimes in Mn$^{3+}$ and Mn$^{2+}$. Manganese valence state is usually determined in mineral objects by wet chemistry and potenciometric techniques, but those techniques are laborious. X-ray spectra can be used for simultaneous determination of the concentration and speciation of elements [1]. Dependence of the ratio of XRF line intensities of K-series on manganese valence state was reported in the paper [2]. Preference was given to ratio of FeK$\beta_5$ and FeK$\beta_{1,3}$ line intensities as the analytical parameter for XRF determination of iron valence state [3].

This study was performed to estimate the accuracy of manganese valence state determination in standard reference materials (SRM) of nodules and manganese ore. The measurements have been implemented by a conventional XRF spectrometer, S4 Pioneer. Dependence of ratio $R^c = \frac{C(MnO_2)}{C(MnO^{10\%})}$ on the ratio of MnK$\beta_5$ and MnK$\beta_{1,3}$ line intensities ($R^I$) in the second orders of reflection is approximated by the linear regression equation, that includes term of $C_{Fe,O^{10\%}}$ because of spectral overlapping of FeK$\alpha_{1,2}$ and MnK$\beta_{1,3}$ lines:

$$R^c = a_0 + a_1 \cdot R^I + a_2 \cdot C_{Fe,O^{10\%}}$$

Relative standard deviation (RSD) of equation (1) was 7%. In the case of excluding of $a_2 \cdot C_{Fe,O^{10\%}}$ term RSD was 30%. The RSD of MnO$_2$ content was 1.8 % for the range of MnO$_2$ content 24 - 41 %. SRM of nodules and ore were used as calibration samples for estimation of Mn$^{4+}$ content in SRM of nodules (GMK-1, GMK-2) and cobalt-manganese crusts (KMK-1, KMK-2). The estimation of valence state proved that manganese occurs mainly in high valence state Mn$^{4+}$. In Baikal lake nodules in which total iron content is about of 40–50% and total manganese content is about of 1-2%, XRF determination of manganese valence state is complicated because of spectral overlapping.

The XRF method is fairly fast and low costly for sample preparation and can be used for manganese valence state determination in nodules.

Scanning SRXRF analysis in the investigation of the proglacial lake bottom sediments of the Baikalsky Ridge for reconstruction of glacier fluctuation for the last 160 years

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In the present study authors show the reconstruction of glacier fluctuation of Chersky Mountain of the Baikalsky Ridge about 18 km western of the northern basin of Lake Baikal (Russia). It has been made on the basis of study of the element composition of drill samples of bottom sediments which have been taken from proglacial Lake Gitara.

X-ray fluorescent technique with synchrotron radiation (SRXRF) was used by means of total scanning of unreformed wet drill sample. The goal of this investigatio is the reconstruction of the response of the Baikal region glaciers (glacier of Chersky Mountain, as example) to the climate changes during last 160 years on the basis of the detailed study of the element composition of drill samples of bottom sediments from proglacial lake Gitara. The records of this period comprise important climatic reconstructions.

As for the data on the changes of element composition of drill samples from proglacial lake, the following main groups of elements, which describe the changes on the territory under study during last 160 years, could be mentioned: the 1st group (Ca, Ti, V, Fe, Mn, Cu и Sr), which reflects intensity of chemical rock and soil decay of lake Gitara drainage basin; the 2nd group (K, Br и U) connected with the organic autochthonous component of the lake; the 3rd group (Y, Th, Ga, Rb, Zr, Nb и Rb/Sr ratio), marking physical decay processes, and surge of glacier, in particular. Glacier fluctuation has been defined by the level of delivery of “terrigenous” group of elements into proglacial lake by melt waters. We consider five episodes (~1880, 1905, 1918, 1950 and from 1968 to the present day), when glacier underwent big advances during last 160 years.
X-ray microspectroscopic investigation of the uptake of Cs(I), Ni(II), Nd(III) and U(VI) by argillaceous rocks of the Boda Siltstone Formation, Hungary

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Argillaceous rocks are being considered in many radioactive waste management programmes as suitable host rock formations for the deep geological disposal of radioactive waste. Clay minerals such as illite, smectite, illite/smectite mixed layers and kaolinite are important components in such rock types and can often make up 50 wt.% or more of the total mass. One of the most important characteristics of many clay minerals is their generally strong radionuclide retention properties.

Transport in natural barriers depends strongly on retardation like chemical sorption or other physical processes. Consequently, an understanding of sorption processes, and of the physico-chemical parameters, which influences them, is becoming increasingly important. The present study focuses on the interaction of escaped radionuclides with the host-rock surrounding the planned high-level radioactive waste (HLW) repository in Hungary (Boda Siltstone Formation – BSF).

The aim of our study is to investigate the uptake mechanisms of key radionuclides representing transuranium elements, fission and corrosion products on clay and other minerals of the host rock, as well as to identify the mineral phases responsible for the uptake on the microscale. For this reason, combined synchrotron-radiation micro-XRF mapping, micro-XRD and micro-EXAFS measurements were performed on thin sections subjected to sorption experiments using 5–20 µm spatial resolution at the ANKA FLUO beamline (Karlsruhe, Germany) and the HASYLAB Beamline L (Hamburg, Germany). Cs(I), Ni(II), Nd(III) and U(VI) were selected as inactive or natural analogues for the key radionuclides.

The rocks investigated were prepared from geochemically characterized cores from drillings in BSF. Thin sections were prepared on 350-µm thick high-purity silicon wafers. The average thicknesses of the sections are 30-60 µm. Samples were subjected to 72-hour sorption experiments with one ion of interest added, using a 0.1 M NaCl solution as background electrolyte to block cation exchange processes.

The micro-XRF elemental maps indicate a correlation of Cs, Ni and Nd with Fe- and K-rich regions suggesting that these elements are predominantly taken up by these phases. Micro-XRD identified the Fe- and K-rich regions as illite and iron oxides, respectively. For U, secondary mineralisation around carbonate filled veins and vugs was also observed. X-ray absorption spectroscopy demonstrated that under the experimental conditions employed inner-sphere complexation of Ni(II) to clay minerals prevail, indicating that illite and iron oxides are an effective sink for Ni(II) in BSF.
Evaluation of metal distribution in a *Solanum lycopersicum* plant located in a coastal environment using \( \mu \)-ED-XRF imaging

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Metal homeostasis is an emerging topic in the analysis of metals in plants. The location of different metals in specific parts of the plant can give information about the mobilization and transport of metals. Moreover, this information can also be used to improve the nutritional value of crops, prevent the cultivation in soils with high content of toxic elements, implement phytoremediation processes, etc., which are important issues to consider for human health. The interest of metal distribution in plants has gradually increased since it was established that hyperaccumulation in edible plants could be dangerous for human health. Tomato plants, one of the most consumed vegetables worldwide, are inside this group. Nowadays, the distribution and speciation of metals in tomato plants is not completely understood. The principal way of metal uptake in plants could be from air depositions and transport through the roots. After absorption, metals can migrate and be distributed throughout the plant.

A crop field located in a coastal town (Barrika, Basque Country, North of Spain) and influenced by marine aerosol was selected as sampling area. Different tomato plants (*Solanum lycopersicum*) were collected in this orchard and thin-sections of their roots, stems, leaves and fruits were prepared. For the fruit, superficial analyses were also performed on previously dried fragments. Pellets of around 3 mm of diameter were considered for the \( \mu \)-XRF analysis of soils. \( \mu \)-X-ray fluorescence analyses were performed using an ArtTax \( \mu \)-XRF portable spectrometer. Spectra were acquired at voltage/current of 50keV/700 \( \mu \)A for 800 seconds using a collimator of 650 \( \mu \)m. To determine elements with \( Z<20 \) (Ca), helium purging in the excitation and detection paths was used. The average mapped area for each part of the plant ranges from 8 to 1.5 mm\(^2\). The common metals present in each section of the plants were S, Cl, Br, K, Ca, Ti, Mn, Fe, Zn, Cu, Sr and Sn. Elements such as Cl and Br related with marine aerosol particulate matter show clear coincident distributions (accumulation in the leaves main nerve, accumulation in the cortex of stems, etc.). Metals such as Cu, Zn and Sn show a uniform distribution in each part of the plant. On the contrary, Zn is not present in the vascular cylinder of the stem, as Cl, K, Zn, Br, Cu and Mn are. Moreover, Ca, Sr and Fe show a coincident distribution in the stem, localized in the most external part of the cortex and in the vascular cylinder.
Antimony (Sb) is a non-essential element and toxic to most living organisms; however, its toxic effect depends on oxidation states. Sb is released anthropogenically mainly to the terrestrial environment; thus it is crucial to investigate the fate of Sb in the soil system [1]. Moreover, humic substances are the most chemically active compounds with high cation and anion exchange capacities, and are long lasting, key components of soil. It is anticipated that a significant proportion of Sb is retained in soil organic layer; therefore, the oxidation state of Sb is controlled by the soil humic acid (HA) to some extent which influences Sb solubility and ecotoxicity. The coordination chemistry of Sb to soil HA has both theoretical and practical interests. For example, it may explain existence of reduced Sb form in oxic conditions, and Sb immobilization in soil organic layer; furthermore, this research may be essential to Sb detoxification procedure.

The extraction efficiencies of Sb compounds from environmental and biological matrixes are insignificant, and also stability of Sb compounds is low during the overall analytical process including sampling, extraction and determination. Therefore, determining Sb species in aqueous media is not straightforward. X-Ray Absorption Fine Structure (XAFS) spectroscopy is a powerful technique that could identify metal speciation and chemical coordination in various medium including solid, and is well suited for use directly with bulk materials.

In the present study, HA-Sb (III) composite was obtained based on HA extracted from soil. The native soil, soil-derived HA and HA-Sb composite were studied by Nuclear Magnetic Resonance (NMR) and XAFS spectroscopy. The Sb (III) binding to soil derived HA mainly contributed to its open chains through carboxyl and hydroxyl moieties as revealed by the $^1\text{H}$ and $^{13}\text{C}$ NMR spectroscopy. In addition, it was estimated that the cyclic structure of the HA nucleus remained unchanged during Sb (III) association. Based on the absorption edge energy and coordination numbers, Sb oxidation state in a native soil was interpreted as pentavalent, meanwhile the HA-Sb composite contained both Sb (III) and Sb (V). Tri- and pentavalent oxidation states of Sb are distinguished by the Sb K-edge energy differences of 4 eV [2] and O-coordination numbers, which were around three and six, respectively. The absorption edge energy of the HA-Sb composite was intermediate compared to those for tri- and pentavalent oxides taken as reference. For the soil samples, the first Sb shell yielded 6 oxygen atoms at a radial distance of 1.96 Å and around 4 oxygen atoms were calculated for the HA-Sb at 1.99 Å (Table 1), again indicating that the composite contains a mixture of Sb (III) and Sb (V), which means the initially taken Sb (III) partly converted to its higher oxidation state. It is concluded that HA catalyzes Sb (III) oxidation to Sb (V) but the process was slow.

Table 1. Structural parameter for the soil sample and HA-Sb composite

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_0$ (eV)</th>
<th>CN$^a$</th>
<th>R(Å)$^b$</th>
<th>$\sigma^2$Å$^2$</th>
<th>R-factor$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native soil</td>
<td>30497</td>
<td>6.0±1.5</td>
<td>1.96±0.03</td>
<td>0.001±0.004</td>
<td>0.02</td>
</tr>
<tr>
<td>HA-Sb composite</td>
<td>30493</td>
<td>4.2±0.4</td>
<td>1.99±0.01</td>
<td>0.002±0.001</td>
<td>0.008</td>
</tr>
</tbody>
</table>

$^a$Coordination number; $^b$Inter-atomic distance; $^c$Debye-Waller factor; $^d$Scattering amplitude.

Carbon nanotubes as solid sorbents in X-ray fluorescence analysis of trace elements

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Carbon nanotubes (CNTs) are recently used as an excellent material for preconcentration, separation and speciation of metal ions. CNTs are ideal as solid-phase extraction adsorbents because of their large specific sorbing surface area and the hexagonal arrays of carbon atoms, which are profitable for strong interaction with organic compounds and metal ions.

The application of CNTs as solid sorbents in X-ray fluorescence analysis (XRF) compared to other analytical spectroscopy techniques offers important advantages. The analytes do not have to be eluted from CNTs for XRF analysis and samples can be stored and analyzed many times. Moreover, since samples are prepared as thin layers errors resulting from matrix effects can be neglected.

A wavelength-dispersive as well as energy-dispersive X-ray spectrometry were used for the measurements of Cr, Mn, Fe, Co, Ni, Cu, Zn and Pb adsorbed onto multiwalled carbon nanotubes (MWCNTs). After the adsorption process the aqueous samples are filtered and loaded MWCNTs are collected onto a cellulose filter for XRF analysis. The preconcentration was carried out using raw and oxidized MWCNTs with and without APDC as chelating agent. The proposed procedure allows obtaining detection limits in range of 0.5-2 ng mL⁻¹. The method was applied successfully to determine Cr, Mn, Fe, Co, Ni, Cu, Zn and Pb in water samples. The proposed sample preparation is easy and non time-consuming. The the risk of contamination and loss of analytes are reduced to a minimum. The proposed combination of the solid phase extraction using CNTs and XRF spectrometry was proved to be an alternative to other techniques commonly used in the analysis of liquid samples.
Challenges and Status in the Development of ICT-Based Learning and Training Modules on Nuclear Instrumentation and Spectrometry

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Nuclear-related techniques are proven technologies which have been applied in the environmental, medical, agricultural, mining, petro-chemical, educational, and other sectors of national economies. These technologies can be utilized effectively and on a sustainable basis, through the careful and systematic employment of ICT-based modules for human resource development. This paper therefore discusses challenges and current status in the development of ICT-based materials for learning, teaching and training in Nuclear Instrumentation and Spectrometry (NIS). It draws extensively on experiences at the Instrumentation Unit of the IAEA Seibersdorf Laboratories, in Austria, and the School of Nuclear and Allied Sciences (SNAS) in Ghana.

The significant challenges posed in the development of the ICT-based modules in NIS are: the wide spectrum of technical background of intended users, different authoring tools employed, synergy between subject and software specialists, modes and formats of presentation, and copyright issues of available input resource materials. Furthermore, the requirement of integrating text, scientific equations, chemical formulae, graphics, curves, logic diagrams, and animations perfectly in one document still presents a daunting task to developers of ICT-based modules.

About fifteen ICT-based modules in NIS have been developed by the Instrumentation Unit of the IAEA through contractual service agreements with selected technical consultants. The different approaches in the development of these modules, and efforts at harmonization of these modules have also been discussed. The topics covered by the modules include radiation detectors, power supplies, analog electronics, digital electronics, maintenance of liquid scintillation counters and TLD readers, alpha-, gamma-, and X-ray spectrometry, ion beam analysis and applications, and quality management procedures and practices in EDXRF spectrometry [1]. Also discussed are the strategies for integrating some of these modules into the teaching of selected courses in the Applied Nuclear Physics program at SNAS, development of new, customized ICT-based modules in NIS, as well as possibilities for their utilization in an e-learning platform, such as CLP4NET being set-up at SNAS for the AFRA member states of the IAEA.

Appropriate combination of pedagogy and ICT technology will therefore go a long way in consolidating capacity building [2] in the thematic areas of Nuclear Instrumentation and Spectrometry.


Intensity Ratios of Pb L\(\beta_1/L\alpha_{1+2}\) XRF Spectra as a Fundamental Parameter

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In X-ray fluorescence (XRF) analysis technique, As K\(\alpha\) spectrum overlaps with Pb L\(\alpha_{1+2}\) spectra when arsenic and lead both exist in specimens. We have to separate the overlapped spectra to know correct As K\(\alpha\) and Pb L\(\alpha_{1+2}\) spectral intensities to achieve an accurate quantitative analysis. The intensity ratio of Pb L\(\beta_1/L\alpha_{1+2}\) is an important fundamental parameter to separate the overlapped spectra appropriately. However L lines in XRF spectra are easily affected by factors such as a self-absorption effect, Coster-Kronig transitions, or measurement conditions\(^{[1]}\). The intensity ratio of Pb L\(\beta_1/L\alpha_{1+2}\) is not a constant value. The intensity distribution of incident X-rays is one of the most important parameters for explaining such changes in the L lines. We measured the Pb L XRF spectra of Pb metal and Pb compounds under various measurement conditions, and we discuss the fluctuations in the ratios of not only L\(\beta_1/L\alpha_{1+2}\) but also Pb L\(\eta/L\ell\), since L\(\beta_1/L\alpha_{1+2}\) and Pb L\(\eta/L\ell\) constitute same multiplet arising from the electric dipole transitions which is related to the probability of hole creation in the inner L\(_2\) and L\(_3\) shells, using the scattered X-ray spectra of an acrylic plate that are considered to be the incident X-ray spectra\(^{[2]}\).

We conclude that the scattered X-ray spectra of the acrylic plate facilitated the understanding of the changes in L spectral lines without measuring the direct incident X-ray spectra.

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[Fig. 1] Pb L XRF spectra of Pb metal with the change of X-ray tube voltage. Intensity normalized to Pb L\(\ell\) peak top. L\(\eta\) lines are magnified 50 times and indicated by dotted lines.

[Fig. 2] XRF spectra of an acrylic plate with different filters at 50kV X-ray tube voltage: (a) without filter, (b) Al filter, (c) Ti filter, (d) Cu filter, (e) Zr filter.


Examination of forensic traces by the use of X-ray spectrometry

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X-ray spectrometry, either alone or in conjunction with scanning electron microscopy, have been often applied in criminalistic examination of different kind of traces as it provides information about chemical composition and is helpful in identification of the examined materials. It can help to establish if the suspected person was involved in a crime. Great expectations are currently linked to the µ–XRF technique as it does not involve complicated sample preparation prior to the examinations and it enables one to examine evidential traces directly on the substrate on which they occur.

Physicochemical investigation of traces, i.e. microchips of paint coat, single fibers, glass fragments, oil stains, metal attrition, soil and building materials as well as inks (in documents) are especially difficult as such samples are very small (thin) and, in addition, they are not usually possible to be entirely separated from the substrate. What seems to be preferably used as an analytical tool in such cases, is application of microtechniques that are nondestructive for the examined samples and may be used in situ.

Application of X-ray spectrometry enables one to determine the elemental composition of the trace and in comparative analysis makes it possible to show similarity or dissimilarity of samples in a clear and relatively easy way [1,2]. The method is an ideal tool for identification of gun shot residue – an important evidence in shooting cases [3,4]. The application of X-ray analysis in the examination of selected traces for forensic purposes will be presented in detailed.

In recent years, scientists are racing to harness billion-dollar synchrotron facilities to generate and use ever-smaller hard X-ray microbeams and nanobeams (5 to 100 keV). Synchrotron radiation X-ray fluorescence analysis is for many samples the most sensitive nondestructive way to measure composition distributions, and X-ray fluorescence and X-ray absorption spectroscopies provide details about oxidation state, local coordination, and bond distances. Furthermore, the relatively weak interaction of X-rays with matter provides the opportunity to characterize samples nondestructively in the presence of air, water, or other environments with little or no sample preparation in life science.

Over the past three decades, specialized sources and instrumentation have evolved to meet the scientific challenges of X-ray micro/nanobeam experiments. For example, X-ray source brilliance, the merit for X-ray micro/nanobeams, continues to improve exponentially with a doubling time of 10 months. Similarly, achievable spot size is also improving by a factor of 2 every 22 months. Indeed, it is now practical to make sensitive, quantitative measurements on volumes $10^3$ to $10^5$ times smaller than possible just a decade ago; fluorescence measurements on volume elements approaching $10^{-6}$ µm$^3$ are now possible. In addition to the ongoing revolution in source brilliance and focusing optics, specialized monochromators have been designed to maintain focal spot position during energy scans and to switch easily between monochromatic and broad-bandpass modes. As the sample is moved under the beam, absorption processes are observed by various specialized X-ray detectors.

Driven by the characterization opportunities afforded by micro–x-ray fluorescence spectroscopy (µXRF) and micro–x-ray absorption near-edge spectroscopy (µXANES), these methods have evolved into sophisticated tools for mapping elemental distributions and chemistry to understand how cells segregate heavy metals under normal and toxic conditions. Spatial resolution of 30 nm is now available, which opens important opportunities for understanding how trace elements are distributed in healthy and diseased cells. The companion tool, µXANES, represents a quantitative technique for spatial mapping of the oxidation states of elements. This capability reveals chemical variations needed to understand how biological and chemical processes proceed at the microstructural or intracellular level. For example, several scientists are using µXRF and µXANES to locate and explore the role of transition metals in neurodegenerative disorders such as Alzheimer’s and Parkinson’s diseases.

In this lecture talk the recent development of the synchrotron radiation micro/nanobeam XRF and XANES techniques will be briefly reviewed. Then some typical applications in life science will be shown, and a few examples of applications in China will be also introduced.
SR µ-XRF Imaging of Human Osteoporotic Bone


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Osteoporosis (OP) is characterized by a low bone mass and a micro architectural deterioration of bone tissue leading to increased bone fragility and fracture incidence. The general prevalence of OP raises in women rises from 5% at age of 50 years to 50% at age of 85 years. Many risk factors have been found which are associated with osteoporotic fracture, including hormonal factors, low intake of calcium and vitamin D and a history of fracture. Little is known about where Pb and other trace elements, e.g. zinc (Zn) and strontium (Sr), are incorporated within the bone tissue. Previous studies on the local distribution of Pb in bone only differentiate between cortical und trabecular bone tissues [1]. Finding new ways of treating osteoporosis and reducing the negative impacts (e.g. vertebral and non-vertebral fractures) of this disease is one of the urgent topics in medicine. Strontium ranelate (SrR) has been approved for the treatment of postmenopausal osteoporosis a couple of years ago. This agent is described to have both anabolic and antiresorptive effects in bone, but the exact mechanism of its action is not yet fully understood. Strontium (Sr) is incorporated in bone during the mineralization process. A set of five human femoral necks from patients suffered osteoporotic femoral neck fractures and five age-matched non-fractured controls (taken from a previous study [2]) have been analyzed. Additionally four femoral head samples were measured, obtained from patients undergoing a hip replacement surgery at the Trauma Centre Meidling (Hospital of the AUVA, Vienna, Austria) after suffering osteoporotic femoral neck fractures. Furthermore we had the opportunity to analyze two human bone biopsies (iliac crest, femoral neck) from patients receiving SrR therapy. The undecalcified samples were examined by quantitative Backscattered Electron Imaging (qBEI) using a pixel resolution of 1µm. Grey-level images were generated to differentiate between bone packets and osteons of different mineral content separated by cement lines. Areas of interest were analyzed with Synchrotron Radiation induced confocal micro x-ray fluorescence analysis (SR µ-XRF) to determine the distribution of Ca, Sr, Zn and Pb in subchondral and cortical bone. Measurements were performed at the FLUO beamline at ANKA using a beam size of 17x12µm and a depth resolution of 19µm at Au-Lα, with primary excitation energy of 16.7keV. We could show that confocal micro SR µ-XRF is well-suited to determine the trace element distribution in the different histological structures of subcondral and cortical bone. Pb and Sr were found to correlate positively with the Ca content among the bone packets, while Zn did not show any correlation. Furthermore an accumulation of Pb and Zn was found specifically in the cement lines (borders between bone packets), as identified in the XRF-maps by overlaying them with the corresponding qBEI. No significant differences in the elemental distributions between fractured and controls could be observed. The samples from the SrR treated patients showed high Sr accumulation in bone packets build during the therapy, which is in very good agreement with the findings of our recent study [3] analyzing samples of an experimental osteoporosis treatment model in rats [4].

K shell x-ray fluorescence of Pb in bone: Problems encountered and some solutions

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The first \textit{in vivo} bone Pb measurements were conducted 40 years ago, using \(\gamma\)-rays from \(^{57}\)Co to excite the Pb K x-rays. The now more widely used technique that relies on the 88 keV \(\gamma\)-rays from \(^{109}\)Cd for excitation has been in operation for nearly 30 years. Many thousands of people have had their bone Pb measured successfully and the technique has proved robust in the field. However, not every measurement goes as smoothly as the large majority of typical studies.

What happens when there is unexpected evidence of Pb contamination in flooring? What about lead shot still in the leg years after the argument ended? We routinely measure left tibia and right calcaneus: what about the one legged subject? What is the origin of Hg x-rays appearing prominently in what we thought was a bone Pb spectrum? How does one recognise cross talk between two systems and ensure that data quality is nevertheless maintained?

This talk is predicated on the dictum of learning from one’s mistakes. So it will explore a set of examples in which there has been a particular challenge presented to making a bone Pb measurement or in interpreting the resulting spectrum.
Energy-dispersive X-ray fluorescent analysis in human prostate gland studies

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Analytical studies of chemical elements in normal and neoplastic prostate tissue were done in the second half of 1970s in the Medical Radiological Research Center of Russian Academy of Medical Sciences (MRRC RAMS) using instrumental nuclear methods. Nondestructive methods of analysis avoid the possibility of changing the content of chemical elements in studied samples, which allows, for the first time, to obtain reliable results. In particular, we showed that the average content of Zn in prostate cancer (PCa) tissues is 7 times lower than in healthy or hyperplastic (BPH) prostate tissue [1]. Moreover, Zn concentration of prostatic fluid for PCa is 13-17 times lower, on the average, than that for normal, chronic prostatitis, or BPH [2]. Obtained results formed basis for a new method for differential diagnosis of BPH and PCa. Our method allows accurate measurement of zinc content in the material of transrectal needle biopsy of prostate or in expressed prostatic fluid samples obtained by digital rectal massage. For the first time, it is proposed to use radionuclide-induced energy-dispersive X-ray fluorescence (EDXRF) to determine zinc content in needle-biopsy cores. This method has been successfully used in clinical trials of MRRC RAMS, and they were patented in Russia [3,4]. All data on the new method of diagnosing prostate cancer were classified by the Ministry of Health of the USSR, and publications were made possible only in the 90's, after the radical political changes in the country. Publications in international scientific journals [1,2] and presentations at international medical conferences [5,6] have stimulated the interest in new approaches for early diagnosis of prostate cancer based on the phenomenon of sharp reduction in the ability of prostate to accumulate Zn in its malignant transformation. Currently, work in this direction is carried out in several research centers and hospitals in Israel, the United States, and other countries [7-10]. To a large extent, the resumption of the search for new methods for early diagnosis of prostate cancer was due to gained experience in a critical assessment of the capacity of the PSA serum test [11].

Our presentation will include new data on the possibilities of using radionuclide-induced EDXRF for differential diagnosis of BPH and PCa.

Development of a $^{170}$Tm source for mercury monitoring studies in humans using XRF

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Mercury is a non-essential element and its toxicity means that its concentration is not only of concern to the human body but also for many living beings. Studies on health effects of exposure to mercury suggest the need for developing a system for biological monitoring that can measure Hg body stores in vivo. K shell XRF is the preferred technique for monitoring studies of mercury and its success clearly lies in using the most suitable excitation source. $^{170}$Tm is promising because it emits 84.25 keV gamma-rays; this energy is suitable, because it is close to and greater than the mercury K shell binding energy of 83.1 keV. $^{170}$Tm can be made efficiently by the $^{169}$Tm(n,γ)$^{170}$Tm reaction. However pure Tm foil was found to contain significant quantities of tantalum (Ta), due to its typical manufacturing procedure and the Ta introduced an important radioisotopic impurity. Hence a compound of thulium; Tm$_2$O$_3$ was considered for developing $^{170}$Tm radioisotope. As the compound was a powder, a special method was used to develop a radioisotope out of it. A sample XRF spectrum was generated using the radiation source thus developed.

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Nanomaterials and in particular nanoparticles have opened attractive broad application opportunities in biomedicine [1,2] but their expanding use has raised the growing concern about the health hazards related to their possible toxic effects. For instance magnetic NPs such as ferrites (Fe$_3$O$_4$) and cobalt ferrites (CoFe$_2$O$_4$), are used in biomedicine as drug delivery carriers, hyperthermia treatments in cancer therapy and magnetic resonance imaging (MRI) contrast enhancement [3, 4]. The lacking information about the NPs impact on environment and on human health, as well as data on risk assessment, requires development of a reliable methodology for control and prediction. Among the promising detection methods synchrotron radiation X-ray Fluorescence (SRXRF) has already demonstrated its potential in bio-medical research for exploring e.g. neurodegenerative disorders [5, 6]. The application of SRXRF with soft X-rays [7] has also provided access to light elements, which are major constituents of the living matter. In this work we report a SRXRF investigation of the distribution and chemistry of Fe$_3$O$_4$ and CoFe$_2$O$_4$ NPs in balb/3T3 mouse fibroblast cells exposed to NPs concentrations ranging between 40 and 1000 µM for 24h [8]. The SRXRF maps and micro-spot spectra indicate that, for concentrations below 500 µM, Co and Fe are localized in cytosol, indicating that the NPs are localized in the perinuclear region. On the other hand, at higher concentrations, the Fe and Co are present also in the nuclear region of the cell, with sensible accumulation of Co. A co-localization of P, Ca and Fe at high concentration has also been observed indicating intracellular sequestration mechanisms as a response or in an attempt to reduce the nanoparticles toxic effects.

Role of Ca, Fe, Cu and Zn in breast cancer: Study by X-Ray Fluorescence techniques and Immunohistochemical analysis.

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In recent years, several studies have shown that concentrations of trace elements (TE) are altered in neoplastic breast tissues [1-6]. However, the microenvironment and metabolic changes caused by tumors are complex and still not completely understood [7]. These changes may be due to biochemical changes in the tumor and the presence of some important growth and metastasis factors such as vascular endothelial growth factor (VEGF) that stimulates the formation of new blood vessels within the tumor [8], as well as matrix metalloproteinases (MMPs) that degrade extracellular matrix and basement membrane [9]. Under this aspect, the combination of different techniques to investigate the role of TE in promoting and/or maintenance of tumor is interesting once the combination of information obtained by X-Ray Fluorescence (XRF) techniques with the immunohistochemical expression of some proteins may allow a better metabolic understanding of TE in breast cancer [10].

In this work the role of trace elements Ca, Fe, Cu and Zn in neoplastic breast tissues was investigated by XRF techniques and immunohistochemical analysis. By using Energy Dispersive X-Ray Fluorescence, we determined trace elements concentrations in 106 samples of normal and breast cancer tissues. Cut-off values for each TE were determined through Receiver Operating Characteristic (ROC) analysis from the TE distributions. These values were used to set the positive or negative expression of elements in normal and neoplastic tissues. These expressions were correlated with the spatial distributions of TE (evaluated by micro-XRF) and with immunohistochemical expression of MMPs and VEGF. The results reveal that trace elements Fe, Cu and VEGF expression are correlated, indicating that higher levels of these elements can be associated with angiogenic process in breast cancer. Also, correlations between Ca, Zn and MMPs and TIMPs expression have been observed, possibly due those metals are present in these proteins.

Energy dispersive X-ray fluorescence analysis of the “Gates of paradise” in the baptistery of Florence

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The east door of the Baptistry of Florence, dubbed by Michelangelo the “Gates of Paradise”, was done by Lorenzo Ghiberti between 1426 to 1452. It is composed of 10 panels made on gilt bronze. The gilding was produced with an amalgam of gold. The panel “Abraham” was systematically analyzed by using Energy Dispersive X-Ray Fluorescence (EDXRF) analysis. Two portable EDXRF equipments were transferred to the “Opificio delle Pietre Dure” where the panels of the Door were under restoration. The panel Abraham (Figure) was analyzed in many areas, both to analyze again the bronze composition, and to analyze the gilding composition and thickness. This last parameter was determined using the Cu(Kα/Kβ) and AuLα/CuKα)-ratios, which both depend on the gold-thickness. The aim of the analysis was to re-analyze the bronze composition and to analyze the gilding composition and thickness. Following bronze composition was measured: Cu: 92.4% ; Sn: 1.8% ; Pb: 0.7% ; Zn: 3.8% ; Sb: 0.9% ; As: 0.2% ; Ag: 0.2%. The gilding is probably on almost pure gold, with a mean thickness of about 4.0 ± 0.5 µm.
Energy dispersive X-ray fluorescence analysis of pre-Columbian copper from the north of Peru

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The earliest useful metal objects in any region are nearly always of copper. From 6000 to 4000 BC was the period when copper came into common use everywhere, and particularly in the Mediterranean basin, from where the word copper comes (from the Latin cuprum, deriving from the island Cyprus). Sometimes copper was employed in the form of native copper, characterized by high purity, more often it is crude copper produced by smelting. Frequently the crude copper in use in early period contained sufficient arsenic to harden the metal. In fact 0.65% arsenic in copper is sufficient to give to Cu resistance to deformation; when arsenic is < 2% the alloy is called arsenical copper. The presence of arsenic was at first, with high probability, the accidental result of smelting certain copper ores.

Concerning metal and alloys produced in the pre-Hispanic period of the north of Peru, copper is present in various forms in all type of alloys: copper and arsenical copper, gold, gilded copper, copper-gold tumbaga, silver, silvered copper, copper-silver tumbaga, where tumbaga is a poor gold (or silver) alloy with copper as main component, enriched at the surface by depletion gilding, i.e. by removing copper from the surface.

Portable energy-dispersive X-ray fluorescence equipments were employed in the various campaigns of measurements, carried out in Peru from 2007 to 2011. They are mainly characterized by a small-size X-ray tube (at the beginning a tube with Ag-anode was employed, working at 30 kV and 100 μA maximum voltage and current, finally a tube was employed with W-anode working at 40 kV and 200 μA) and a Si-detector (first a Si-PIN detector with about 300 μm thickness, 7 mm² area and an energy resolution of about 180 eV at 5.9 keV, then a Si-drift detector with about 500 μm thickness, 25 mm² area and an energy resolution of about 125 eV at 5.9 keV.

Following may be concluded concerning the copper and copper-alloys in the pre-Hispanic north of Peru from about 1000 BC to 1375 AD:

- The Chavín (1000-200 BC), possibly employed almost pure copper with small quantities (<1%) of Zn, Fe and Pb;
- The Vicús and Frías (200 BC – 300 AD), seem to have employed arsenical copper. However, in this case, only one significant object could be analyzed;
- The Moche (400 BC – 700 AD), from the tomb “Señor de Sipán” employed almost pure copper, with only traces of Fe and Ni. In this case, many objects basically on copper could be analyzed;
- The Moche from the site Museum “Huaca Rajada” employed almost pure copper, but also, in two cases, arsenical copper;
- The Sicán (700 – 1375 AD) systematically employed copper containing arsenic and iron.
- The Chimú (900 – 1470 AD), employed almost pure copper and, in two cases, arsenical copper;
XRF Analysis of nine Renaissance Nuremberg Trombones

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Nuremberg was from the beginning of the 16th century till the end of the 18th century the centre of brass wind instrument making *par excellence*. The high-quality standards achieved by the Nuremberg renaissance brass wind instruments makers are testified by a group of ten preserved trombones made between 1551 and 1598. One of the issues on this group of instruments is related to the material they were made of. Scholarly references stay brief on historical brass alloys as they apply to these pre-1600 brass wind instruments; consequently many questions arise as to the material one should use in making reproductions of such instruments. X-ray fluorescence (XRF) analysis has proven to be a useful method for the determination of the chemical composition of a brass alloy and has been used by several scholars for this purpose.

This poster presents the results of a systematic X-ray fluorescence analysis of a group of nine of the earliest surviving Nuremberg trombones. The measurements had been carried out by a handheld XRF Spectrometer [1] which is equipped with a special museums adapter to guarantee a secure and repeatable setup. With the included software it was possible to quantify these measurements and therefore classify the different pieces of the samples.

With the help of these measurements a characteristic alloy has been identified which differs considerably from the material used in modern reproductions of Renaissance instruments. Additionally it was possible to identify the replaced pieces in the samples.

Characterization of Au-Thong glass beads using XRS

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It was proved that non-destructive and non-sampling methods were used to analyze the composition of the archaeological objects. Differences of archaeological objects found in Thailand such as glasses, pottery and metal wares. They are highly heterogeneous. Due to the complex nature of materials and objects, extremely sensitive, spatially resolved, multi-elemental and versatile analytical instruments are needed. In this work, the composition of the ancient glass bead samples excavated from Au-Thong archaeological site in central area of Thailand was analyzed by using Particle induced X-ray emission spectroscopy (PIXE) and scanning electron microscope coupled with energy dispersive X-ray fluorescence spectroscopy (SEM-EDS). The composition analysis showed that the glass matrices were found mostly to be an alkali-lime silicate glass and agreed with ones which found at various archaeological sites. Transition metals such as copper and iron were mainly presence as the colorants. Some were ancient-like glass beads because their compositions were significantly different. Furthermore, this type of glass demonstrated the long distance or exchange connections. Finally, PIXE and SEM-EDS have been used to be the efficient techniques to analyze the archaeological objects, especially the glassy materials, to understand their characteristics and how they were produced in ancient times.

KEYWORDS: AU-THONG GLASS BEAD, PIXE, SEM-EDS
Research on applications of XRF spectrometry in non-invasive investigations of cultural heritage

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The characterization of cultural heritage materials is essential for the comprehension of their degradation mechanisms. X-Ray Fluorescence spectrometry (XRF) allows a rapid and simple determination of the elemental composition of a material. As a non destructive tool, it has been extensively used for analysis in art and archeology since the early 1970. Whereas it is commonly used for qualitative analysis, recent efforts have been made to develop quantitative analysis even with portable systems. The use of differential X-Ray attenuation can allow to model the various layers: indeed the absorption of x-rays through different layers will result in modification of intensity ratio between the different characteristic lines.

In this paper we present results obtained using XRF spectrometry in the analysis of metal liturgical objects, textiles religious icons on wood and writing inks.

The analyses have been made with the help of a portable X-ray fluorescence spectrometer Innov X Alpha Series. Source excitement: X-ray tube, the anode Ag W, 10-40 kV, 10-50 µA, up to 5 filters. Detector: Si PIN diode, <230 eV FWHM at 5.95 keV Mn K-alpha line and FTIR spectrometer Vertex 70 Bruker, 30 – 25 000 cm\textsuperscript{-1}.

<table>
<thead>
<tr>
<th>Element</th>
<th>%</th>
<th>+/-</th>
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</thead>
<tbody>
<tr>
<td>Cu</td>
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<td>0.09</td>
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<tr>
<td>Au</td>
<td>0.96</td>
<td>0.09</td>
</tr>
<tr>
<td>Ag</td>
<td>98.15</td>
<td>0.74</td>
</tr>
</tbody>
</table>
Non-destructive pXRF analysis of rock art paint

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South Africa has a very rich heritage of rock art paintings. These rock art paintings are found in caves or on rock faces, with visibility varying from very bright to barely visible. Some of the rock art paintings are rather contemporary but some are thought to be as old as 3000 years. Research is carried out for preservation purposes and to determine the type of materials they used for the rock art paintings.

The non-destructive measurements technique pXRF together with Fundamental Parameter analysis were used to analyse the elemental composition of a rock art fragment. The fragment was found on the shelter floor of a cave near Mount Ayliff in the Eastern Cape after natural exfoliation of the rock. The elemental analysis of such sample is not trivial due to the non-homogeneous nature of the material. Eight paint and two rock surface samples were analysed and the results are discussed.
Comparative study of cinnabar from historic Spanish deposits (SEM/EDX). The collection of the Geomining Museum (IGME)

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(3) Cultural Heritage Institute of Spain, c/ Pintor El Greco, 4, 28040 Madrid, Spain.

The study presented here is part of a cross-disciplinary project currently being pursued by at the Complutense University in conjunction with the Geomining Museum of Geology and Mining Institute of Spain (IGME) and the Cultural Heritage Institute of Spain (IPCE) -all members of the Campus of International Excellence at Moncloa-. The aim of the proposed research project is to establish a design for a data base of Spanish pigments of natural origin in the historic deposits represented in the Geomining Museum. This includes a complete characterization of each mineral species: preliminary morphological study (LM, SEM) and microanalysis (SEM/EDX); individualized characterization (TEM/SAED) and nanostructural characterization (HRTEM). The work for this ambitious project falls into various stages, but the ultimate object is to furnish the scientific and professional communities with a reliable source of information for consultation, expansion and verification of experimental data derived from studies of pigments on real works.

The findings reported here are from morphological analysis and microanalytical characterization of cinnabar, a mineral found widely in Spain and much used throughout Europe as a pigment for artworks since Roman times. The samples come from seven different deposits, among them the important mines of Almadén (Ciudad Real). The samples were examined without prior inclusion in resin in order to observe the morphological characteristics of the fractures in detail (crystal aggregation, porosity, density, etc.). The capture of images is a fundamental part of the study; a photographic data base has been built up, making it possible to conduct an exhaustive examination of each sample, from general areas to a large number of individual details. At the same time, microanalytical examination was carried out, with analysis of previously-demarcated areas (1000 magnifications), yielding data on areas of around 1500 μm²; these spectra were accompanied by semi-quantitative evaluations in all cases. This system made it possible to determine what associated minerals are present and their quantity and distribution in the sample. That information is supplemented by point-to-point microanalysis of individual particles. The results highlight the particular features of each mineral, and that information -supplemented by subsequent studies as noted above- can be used to establish a reference pattern for each mineral for use in the study of artists’ pigments.

[1] This work has been carried out with funding from the Ministry of Science and Innovation (Secretaria de Estado de Investigación), National Plan for Scientific Research and Technological Development Projects (R&D) (Ref.: HAR2010-19814).
EDXRF techniques for the safeguard of the Riace Bronzes

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The Riace bronzes are among the highest examples of the art of Greek culture in Italy. They were found in the sea of Riace in Italy in 1972 and the archaeologists believe that they can be dated to the fifth century BC.

Many measurements have been done after their discovery in the Ionian Sea in order to plan a conservation project after the long stay into the sea: more than 2000 years.

The present research performed by an EDXRF equipment showed significant presence of sulphur (mass concentrations up to 12.5\%) and chlorine (mass concentrations up to 15.7\%) on the surface of the two bronzes, in different amounts for the statue A versus B.

The high presence of these two elements has allowed to understand the composition and the formation of patinas and some mechanisms of corrosion of the surfaces.

The ultimate goal of the measurements was to identify the most suitable environmental conditions for the conservation of the bronzes in the renewed museum of Reggio Calabria where they will be exposed after restoration.
DEMOnSTRATION AND COMPARISION OF VARIOUS ANALYTICAL TECHNIQUES SUITABLE FOR THE IDENTIFICATION OF PLASTICS IN CONSERVATION WORK

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Huge development and production of plastic materials in the last century resulted in increasing number of such kind of objects in the museums collections. Conservation of plastic artifacts has been a relatively new field of interest since 1990. Ageing and environmental conditions of storage of plastics influencing to the quality of archived artifacts. The conservators task is to prevent degradation of objects and maintain them in good condition. Deterioration processes are different and specific and related with plastics type and status of the storage. Information about the chemical composition of plastic artifacts is thus necessarily and improve conservation work. The validation of the simple nondestructive identification model for unknown plastics by Energy Dispersive X-ray fluorescence spectrometry with monochromatic excitation based on incoherent/coherent scattering excitation index (1) was performed. In this way, the comparision with Fourier Transform Infrared spectroscopy and solid state Nuclear Magnetic Resonance were investigated for possible characterization of the plastic materials used in artifacts from museum collections. Sampling, sample preparation and analysis were key issues which were critically evaluated for the purpose of identification of plastic material in the conservation work. A set of plastic artifacts, such as souvenirs, household wares, toys, etc. were characterized in this way according to their chemical composition.

Analysis of ancient Egypt funerary servants using XRF and multivariate statistical

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The scientific examination of archaeological objects, belonging to museum collections, has gained increasing interest in the last years. It can supply important information that makes possible to identify past technologies, migration of peoples, possible trade routes, and also to date an artifact, identifying modern forgeries. However, the fact that every artifact is an unique piece emphasizes the necessity of working with non-destructive techniques. In this work, EDXRF technique was used to analyze 124 funerary figurines belonging to the Egyptian Collection of the National Museum (Rio de Janeiro/Brazil). These figurines are known as shabtis, shawabtis or ushabtis and represented servants of the deceased or personal substitutes for its master, performing agricultural labor in order to pay tribute to the gods. The National Museum houses probably the oldest Egyptian collection in the Americas. Most pieces of this collection were acquired in 1826, when the Italian trader Nicolau Fiengo brought from Marseille (France) to Rio de Janeiro various antiquities excavated by Giovanni Battista Belzoni in the necropolis of Thebes, at Karnak Temple. The artifacts were bought by the Brazilian Emperor Dom Pedro I and donated to the Royal Museum (established in 1818). Nowadays, the collection comprises 700 objects like human and animal mummies, coffins, funerary masks and stelae, statues, canopic vases, necklaces, etc.

The analyses were carried out with an EDXRF portable system developed in the Nuclear Instrumentation Laboratory, consisting of an X-ray tube Oxford TF3005 with W anode, operating at 25 kV and 100 µA, and a Si-PIN XR-100CR detector from Amptek. In each sample were obtained several spectra, with an acquisition time of 300 s and a beam collimation of 2 mm. The spectra were analyzed using the software QXAS-AXIL from IAEA. The results revealed the elemental composition of the Egyptian faience (blue or green) used in most of the figurines and the pigments used in a decorated one. An additional analysis employing multivariate statistics (PCA and HCA) was performed to identify groups of samples that presented similar behaviors or different characteristics, in order to provide a more accurate classification of these artifacts.

Figure 1. Shabti during the analysis.
The preservation of cultural heritage has acquired increasing interest in the last decades and many scientific techniques have been employed to analyze paintings, manuscripts, ceramics, glasses, statues, coins and metal artifacts in order to solve problems related to restoration, conservation, dating and attribution of artworks. In this work, XRF was used to analyze altars, sculptures and paintings in the Saint Anthony Convent (Rio de Janeiro, Brazil). The cornerstone of this convent was launched in 1608, by the Franciscan friars, and the construction of the church was finished in 1620. The Saint Anthony sculpture in the main altar is one of the few remaining pieces from the XVII century in Rio de Janeiro. The splendid Baroque carvings of the chapel, covered with integral gilding, in the national Portuguese style, dates from 1716 to 1719.

The analyses were carried out with an EDXRF portable system developed in the Nuclear Instrumentation Laboratory, consisting of an X-ray tube Oxford TF3005 with W anode, operating at 25 kV and 100 µA, and a Si-PIN XR-100CR detector from Amptek. In each sample were obtained several spectra, with an acquisition time of 300 s and a beam collimation of 1.5 and 2 mm. The analysis of the golden carvings of the altars, in the main chapel, revealed the original gold covering (hidden by commercial paint) and also the original layer of red color, at the ground, obtained by the use of vermilion. The analysis of 15 sculptures - dating from XVII and XVIII centuries - revealed the original pigments, the elemental composition of the clay and materials employed in recent restorations. The analysis of 14 wood panels (XVIII century), at the vault and side walls of the chapel – representing nine episodes of the saint's life - revealed original pigments and retouchings regions.

Figure 1. Saint Anthony sculpture during the analysis.
Two panels by Pedro Villegas Marmolejo (16th century) 
analysed by portable XRF

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(2) Centro nacional de Aceleradores (University of Seville), Avda. Thomas A. Edison 7, 41092 Sevilla, Spain

Pedro Villegas Marmolejo was a Spanish painter, born in Seville in the first half of the 16th century and known as one of the intellectuals of that time. His style was considered academic and shows influences of contemporary Roman and Flemish art. Between 1560 and 1580 he became one of the leading artists in Seville and his workshop carried out also orders for the New World [1, 2]. Two of his interesting panels are conserved in the Fine Arts Museum of Seville, representing St. Thomas of Aquileia with St. Catherine of Siena and the Holy family with St. John the Baptist. Both panels belong to the same art piece, which is not conserved in its integrity.

The relation between both panels was of interest, not only from the art historical point of view, but also considering painting materials applied. For this purpose, both panels were studied with a non-destructive X-Ray Fluorescence system, which is a very helpful technique in the first material characterization of artworks [3]. The portable equipment used has an X-ray tube of 30 kV with anode of W and one SDD detector with energy resolution of 140 eV. It was applied directly in situ in the exposition room for the analysis of support and pigments.

Both panels present very similar colour palette, characteristic for that time [4]: lead white (identified by Pb peaks), yellow and red ochres (Fe), vermilion (Hg), a copper based green pigment (Cu), azurite (Cu) and smalt (Co, Ni, As), umber (Mn, Fe) and probably red and black organic pigments, which are not possible to identify by XRF due to low Z numbers of their characteristic elements. In very low quantity also a lead-tin yellow can be observed. Golden elements were confirmed to be carried out by real gold leafs (Au) applied on a layer of red bol (Fe). Small retouches were detected on the bases of Ba, Ti and Zn peaks, revealing the use of modern titanium and zinc whites. The similarity of the results confirms, also from the analytical point of view, that both panels belong to the same artwork. The results form part of a bigger database on Spanish 15th and 16th century painting, which is being prepared in collaboration between the Museum and the Centro nacional de aceleradores.

Application of X-Ray Imaging to study soil blocks: a case study from Crustumerium (Italy)

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In this paper, we show the application of the X-Ray Imaging technique (XRI), Radiography and Computed Tomography (CT), associated to X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD) to study soil blocks. The soil blocks analyzed come from Crustumerium, a Latin settlement founded in the IXth century B.C. on the edge of Sabine territory, 9 miles north of Rome.

We present several examples to show how all these techniques can give complementary information on the artifacts within the soil blocks allowing us to provide a complete documentation, to characterize their composition and to determine their state of decay. Furthermore, the collected data can support the work of archaeologist and can help to choose the best procedures for restoration.
Spectroscopic studies of Greco-Roman coins

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The metallurgical features of several coins representative of a 1st century AC Greco Roman copper coin collection, found in the course of archaeological excavations at the site of Lithochori-Kavala, Greece, were investigated non destructively by laboratory X-ray (XRD), synchrotron diffraction (SR-XRD) and SEM-EDX. The aim of this work was first to obtain, through microstructural analysis, off the surface information of the metallic phases present in the samples, second to collect high resolution data, using point sampling, of the structure and compositions of the corrosion products and third to identify uncommon additions / growths, observed on the surface of the bronze coins that may have been deposited during burial [1-3]. Analysis of the diffraction patterns suggests that the main phases are Cu-alloys namely CuSn / CuZn with compositions greater than 75% (wt). Additional high amounts, of cuprite 12 % (wt) and of nantokite 6% (wt) indicate a significant degree of corrosion of the coins. Secondary - traceable phases of pyromorphite, chalcopyrite, and Fe-oxides suggest extensive environmental interaction with either phosphorous enriched or anaerobic and humus reach soil [6]. Elemental SEM-EDX analysis of the surface revealed that the chemical composition of the alloy varies from 68 to 75 % (wt) of Cu, and 16 % to 29 % (wt) Sn, while the Zn amount remains almost constant around 2% (wt). The corresponding tin/zinc content in the Cu-alloy for each coin has been estimated from the refined lattice parameters [7-9] and it is in fair agreement with the value determined by SEM-EDX. This is due to the limited information depth of only about 20µm and the method emphasises the signal from the patina covering the coins, so that, in some patterns, the Cu peaks are either vanish or severely reduced. Therefore the phase analysis based only on a diffraction pattern taken from a surface may sometimes lead to incorrect conclusions concerning the phase composition of the sample. This deficiency can be remedied by the neutron scattering methods, which are sensitive to the bulk material.

References
Medieval glasses were analyzed by particle induced x-ray spectroscopy (PIXE) using in-air proton milli-beam and x-ray fluorescence spectroscopy (XRF) using a mobile spectrometer developed for in-situ analysis of objects of cultural heritage.

The glass fragments were found in the area of the medieval county town Ete located in Sárköz, Hungary. Ete was inhabited since the 9th century AD and it became a market town in the 15-16th century. During the Turkish invasion in the beginning the 17th century Ete was destroyed and it was not rebuilt since then. The first excavations in the area were in 1933, 1935 and were continued throughout 1996-2009 by Zs. Miklós and M. Vizi [1].

The aim of the study was to map the characteristic groups in the collection of glass fragments and to provide information in addition to the stylistic properties for the further investigation of the medieval glassworks in Hungary.

The matrix elements in the glass fragments were measured by in-air PIXE. The samples were mounted on an X-Y-Z positioning stage, the AMPTEK SDD x-ray detector was applied at 45° backward angle with respect to the proton beam. The x-ray absorbers and the detector to sample distance could also be varied. The minor and trace elements of lower and medium atomic number were also detected by PIXE, while those of higher atomic number were measured by XRF.

The CaO/K₂O ratio in the samples indicates that the glasses are wood-ash type with varying Ca content. In some samples higher Mn and Cu concentrations were measured, these elements may have been applied as glass colorants.


Acknowledgements

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Comparative Study of Pigments on Post Byzantine Icons in Krusedol Monastery

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In this work we presented results of nondestructive investigations of icons which are selected as representative ones regarding different periods of their origin. Krusedol Monastery is founded in 1509 and it is one of the most important sacral buildings in Serbia with very turbulent history and is undergone several interventions including rebuilding the exterior and decorating the interior of the temple. As a consequence of this, iconostasis is consisted from icons from several periods starting from XVI century and followed by extensison of dimensions in the middle and late XVII century. The oldest XVI century icons were attributed to masters from Walachia region. Most important complex restoration of the interior was performed in mid XVIII century during the Baroque period. The painting of these icons have been attributed to Jov Vasilijević, a Ukrainian painter. The old church mobiliar was replaced with new pieces, which added Baroque features to the monastery church, in accordance with the then prevailing style in European art. The latest added icons in the socle are attributed to the Zemun painter Konstantin Lekic in 1829.

The aim of this investigation was to supplement the present knowledge about the Krusedol icons and on the basis of their characteristics to establish differences between the technology of creating icons of the post Byzantine period (XVI and XVII century) and that of the Baroque era (XVIII century), which is the period of great changes in Serbian sacral art. Nondestructive EDXRF techniques with mobile equipment is used along with two imaging techniques (IR reflectography and UV fluorescence photography). In total 10 icons are analyzed and for more then 200 points spectra was collected. Results of the investigation gave us useful information about pigments used including some so far unknown facts as a very early usage of smalt (glass paste with cobalt) in icons from the beginning of XVI century. Pigment identified on icons revealed the major differences in painting techniques through art history and this work can be considered as a foundation for future investigation of the icons in Serbian sacral temples whether they will be performed for conservation or characterization purposes.
Micro analytical study of the fresco “The Good and the Bad Judge” in the medieval village of Monsaraz (Southern Portugal)

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The so-called fresco “The Good and Bad Judge” at the medieval village of Monsaraz is unique in Portugal and still raises questions in terms of Art History and History in general. Discovered on the walls of the ancient City Hall in 1958, it has been studied since 1960 by several researchers. To the present no consensus was attained concerning the date (the range goes from the first half of the 14th century to late 15th century) and because of the lack of historical documentation there has been speculation about the real meaning and, lately, about the chronology of the two painted scenes. The technical and material characterization (pigments, binders and mortars) have been initiated in 1996 in order to clarify some of these questions[1,2]. The present work was undertaken to complete the previous data through the analysis of twenty eight micro-fragments by Scanning Electron Microscopy (SEM) equipped with an EDS detector, optical microscopy in visible and ultraviolet light, µ-Raman spectroscopy and Fourier transform infrared spectroscopy (FT-IR).

Preliminary results show that the mortars of both scenes seem to be similar and are made of aerial lime with siliceous aggregates of different granulometry. A thin layer of pure lime was applied in the carnations. The pigments identified in both scenes were cinnabar (HgS), red and yellow ochre (Fe₂O₃ and FeOOH as chromophores), carbon black (C) and a green copper pigment (probably malachite). The pigments were used pure and mixed to obtain different shades. An interesting feature is the use of red ochre over the most expensive pigment cinnabar in the shadows of Christ mantle. The identification of animal glue in some samples and the extensive areas of chromatic losses seem to indicate that a mixed technique (fresco and secco) was used by the painter.


Acknowledgments

The authors wish to acknowledge the Fundação para a Ciência e Tecnologia for financial support (Post-doc grant SFRH/BPD/63552/2009) through program QREN-POPH-typology 4.1., co-participated by the SocialEuropean Fund (FSE) and MCTES National Fund. The authors would like also to acknowledge the City Hall of Reguengos de Monsaraz, Direcção Regional de Cultura do Alentejo and Dr. Herminia V. Vilar and Dr. Maria Teresa Amado.
Semi-quantitative analysis of the formation of a calcium oxalate protective layer for monumental limestone using combined µXRF/µXRPD


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The aim of this study was to investigate the effects of the application of ammonium oxalate (AmOx) as to form a protective layer of calcium oxalate (CaOx) on the surface of cretaceous limestone samples. Solutions of different concentrations were employed, as well as various treatment times and application methods (poultice, immersion and brushing). In order to determine the thickness of the resulting CaOx layers, line scan measurements over cross-sections of treated samples have been performed using combined micro X-ray fluorescence and micro X-ray powder diffraction (µXRF/µXRPD) at the DIFFABS beamline, SOLEIL synchrotron, France. Signals were recorded in reflection geometry using a collimated X-ray beam of 12.5 x 7.5 µm² (H x V) in size.

The diffraction measurements allowed for the identification of calcium oxalate monohydrate (CaC₂O₄·H₂O, whewellite) and calcium oxalate dihydrate (CaC₂O₄·2H₂O, weddellite) as the two oxalate phases formed. The misalignment of the sample outer surface relative to the direction of the beam, caused a notable shift in the reflections of the crystalline phases. This misalignment, however, was taken into account during the analysis. Weddellite was found only close to the treated surface (max. depth: 21 ± 6 µm), while whewellite was found over a larger depth in the sample (< 200 µm). The maximum depth at which CaOx formation took place was shown to be dependent on both the treatment time and the AmOx concentration used. Using a procedure for semi-quantitative XRPD analysis it was possible to determine both the thickness of the layer, as well as the relative amount of CaOx formed under different treatment conditions. The obtained results showed that brushing treatment could be considered as an effective and economically more feasible alternative to poultice treatment for the creation of a protective CaOx layer on less porous large surfaces [1].

Comparative study of two laboratory setups for micro X-ray powder diffraction

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This study reports on the use of a laboratory setup for micro X-ray powder diffraction (µXRPD) comprising a microfocus Mo anode X-ray tube equipped with a doublefocussing polycapillary lens as beam forming optic, a zirconium foil (50 µm) as β-filter and a Smart1000 CCD detector (Bruker) for capturing two-dimensional diffraction patterns. Different beam size and divergence of the X-ray beam can be obtained by changing the distance between the polycapillary lens and the anode. In this way, the spatial and angular resolution of the laboratory setup can be altered (respectively between 200 – 420 µm and between 0.3 – 0.75° or 5.4 – 14.0 mrad) at the cost of longer measurement time (from ~10 to 100% relative intensity).

The laboratory setup was used for the analysis of different pigments in a fifteenth or sixteenth century illuminated manuscript showing its capability for the identification of different phases in a complex sample. The obtained results were similar to previous synchrotron measurements [1], however a much longer measurement time was required. A comparison is made with a commercially available microfocus Mo anode X-ray tube equipped with Möntel optics (IµS, Incoatec). This source offers a small spot size (~110 µm) with 5 mrad divergence resulting in a slightly higher angular resolution for the diffraction signals. The higher flux of the IµS makes it possible to perform scanning µXRPD imaging experiments in a laboratory environment.

"Portuguese-Flemish Painting" is a common expression used in the history of Portuguese art of the first third of the sixteenth century and in its most basic meaning designates the work of Flemish masters who settled in Portugal during the reign of King Manuel (1495-1521) contributing decisively to the process of renewal of Portuguese painting at the time [1]. Frei Carlos, one of the most important “Portuguese-Flemish Painters”, working in the region of Évora (active between 1517 and 1539-40), left a large number of works mainly that come from the Espinheiro’s Convent where he made the Profession of Faith (in 1517). The painting known as “Ecce Homo”, acquired in 2006 by The National Museum of Ancient Art (MNAA) in Lisbon, is considered the ex-libris of Espinheiro’s painting workshop, and probably the master piece of Frei Carlos.

The material characterization of the “Ecce Homo” was first performed by non-destructive X-ray fluorescence spectrometry. The microsampling was supported by physical imaging techniques namely macrophotography, visible light photography, raking light photography, UV-vis fluorescence photography, Infrared reflectography and X-ray radiography [2]. Microfragments were collected and mounted in epoxy resins in order to expose the paint layers for further analysis by optical microscopy and scanning electron microscopy coupled with energy dispersive x-ray spectrometry. FTIR spectra were obtained giving further information about binders and pigments applied in the technical execution of the painting. The investigation enable the study of the pigments, paint layers and colour effects with the aim of understanding the painter’s technique and the influence of the Flemish schools.

The micro analytical research allowed the identification of the main artist palette: lead white, ochre, vermilion, azurite, lead tin yellow and green earths. Gold was also found on the splendor of Christ. The preparatory layers are composed mainly by calcium sulfates (gypsum and anhydrite) which is associated to the southern European technique.


Acknowledgments
The authors wish to acknowledge the Fundação para a Ciência e Tecnologia for financial support (PhD grant SFRH / BD / 66068 / 2009) through program QREN-POPH-typology 4.1., co-participated by the Social European Fund (FSE) and MCTES National Fund.
SR-µXRF in the analysis of iron gall ink parchments

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Many of the documents and artworks significant to Western Civilization have been written or drawn using iron gall inks on either parchment or paper. These acidic inks continued to be used until the late nineteenth century to create public and private documents which are now in varying states of degradation around the world. The Royal Commission of Assent signed by Queen Victoria enacting the Australian Constitution was written using iron gall ink on parchment.

To determine how best to conserve these important documents and artworks it is essential to understand the iron gall ink composition and mechanisms of degradation of the inks on parchment supports.

Experiments are proceeding at the Australian Synchrotron on the X-ray fluorescence microprobe (XFM) beamline to enable us to understand aspects of the iron gall ink/parchment system using using µ-XRF to study the spatial migration of potentially harmful elements of the ink within the ink line and into the surrounding parchment. Sample cross-section and top surface elemental mapping using a nanoprobe with Vortex detector is being used to detect elements in the ink of most interest in potentially causing metal catalysed oxidation and catalysed hydrolysis of the collagen; Fe, Cu, Zn and S. Experimental configurations and preliminary results are discussed.

SR-µXRF top surface elemental maps (line of ink on the right), 1 µm step, 2 µm spot size
Raising the temper - µ-spot analysis of temper inclusions in experimental ceramics

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Provenancing of ancient ceramics is a highly important scientific tool for archaeological studies. In general, ceramics are not made from the original clay, as it can be found in deposits. To produce the needed physical properties in the finished product, the clay has to be either tempered by adding sands or biological materials or levigated, to remove the coarse fraction. Thus, the chemical composition of the finished ceramic differs from the composition of the original clay bed. To overcome this obfuscation, any information that can be gained about the temper used is useful. In a small series, several pieces of ceramic were produced from known clay and tempers and the resulting ceramics analysed by INAA. As many attempts to physically separate the temper from the clay matrix have failed, µ-spot analysis of temper inclusions were performed at the µ-PIXE (Particle induced X-Ray Emission) facility in Rossendorf and by LA-ICPMS (Laser ablation Inductively coupled plasma mass spectroscopy) in Aberystwyth. It could be shown that from a small number of measurements, a general impression of the temper used could be gained, showing if the temper consists mainly of quartz, feldspars or other main components. With this information, dilution calculations can be greatly facilitated, and a close resemblance of the chemical composition of the clay matrix can be calculated.
Hand-held XRF analysis of a 16th century Mexican feather headdress

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Handheld XRF analysers are of extreme value for the study of art works in museum environments. The capability of inspecting objects in a non-destructive manner facilitates the study of artefacts that cannot be moved either due to their high fragility, large size and/or weight. In addition, for extremely valuable archaeological or historical objects invasive sampling techniques are usually not recommended or at least very restricted.

An in-situ XRF analysis of an object presenting most of the above restrictions was recently conducted at the Vienna Museum of Ethnology (MVK), an affiliated institution of the Kunsthistorisches Museum (KHM) in Vienna. The object is a 16th century feather headdress from Mexico, requiring different conservation measures. To conduct the work the feather headdress was placed lying flat on a supporting transparent plate to be studied and to avoid damages.

The in-situ XRF analysis was part of a research project carried out by professionals from Mexico and Austria who also applied other non-destructive methods such as x-ray radiography. The present contribution focuses only on the results obtained from the in-situ XRF examination. The measurements were aimed at: a) revealing the presence of inorganic toxic elements that could be associated to the use of pesticides in the past, b) identifying pigments on the structural elements of the object and c) distinguishing the authentic gold and the gilded brass elements, which were added in the 19th century.

Despite the diversity of analytical questions posed, the use of the handheld XRF analyzer offered rich qualitative and even quantitative information: The use of certain types of inorganic pesticides and pigments was suggested and the composition of the authentic gold decoration elements was confirmed. An analytical methodology was proposed to determine the thickness of the gold layers of the gilding as well as the composition of the brass alloys.

The results of this study demonstrate the capabilities of handheld XRF analysers, when used following a well-designed analytical strategy. Fast screening results can be produced on the spot to answer different questions arising from the in-situ investigation, whereas a more detailed interpretation of the measurements carried out can be performed “off-line” to enhance significantly the quality of the analysis.
In 1975 two Old-Slavonic liturgical manuscripts in Glagolitic script (Euchologium and Missale Sinaiticum) from the 11th century were found in a so far unknown room of the St. Catherine's Monastery on Mount Sinai [1]. Their investigation and edition lead to further questions also concerning used writing materials in comparable manuscripts from that period. The current research project (FWF-P23133 „The Enigma of the Sinaitic Glagolitic Tradition“) aims not only to the edition of hitherto inedited manuscripts of the Glagolitic finds but also to the comparative analysis of several manuscripts in Glagolitic script from the 10th-11th/12th centuries. In order to classify analogous objects from various collections [2], used materials were identified to find hints on differing recipes for inks and parchment-manufacturing as well as to evaluate storage-conditions influencing the stability of the objects. As the mentioned manuscripts are very sensitive due to their age as well as due to the fact that they were in intense use, it was highly aimed that collecting data of used writing inks and parchments must involve non-destructive techniques. This means that methods with the ability to measure in-situ are needed. XRF covers the demands mentioned and can be applied under specific conditions also as air-path systems. A handheld XRF-device of Spectro Analytical Instruments, type xSORT, designed in the first place for commercial application, was used for non-destructive in-situ analysis, as it offers several advantages: its lightweight and the fast measuring procedure as well as the detection of light elements with Z even below 20, such as Mg, Al, Si and P.

The poster presents preliminary results of the measurements done within the current project including also the evaluation of the qualitative results from different XRF devices used in former and current projects in order to achieve further adaption of the hand-held instrument for the analysis of objects of art and archaeology.

[2] Tyrolean State Museum Ferdinandeum (Austria), Biblioteca Comunale di Trento (Italy), Austrian National Library, Graz University Library (Austria), Library of the Rila Monastery (Bulgaria) as well as St. St. Cyril and Methodius National Library (Bulgaria)
Quantification of in-situ scanning Micro-XRF analyses of Late Bronze period gilded figurines.

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Scanning micro-XRF analyses have been applied in-situ at the Damascus archaeological museum for the characterization of three unique gilded bronze figurines. The figurines belong to the late bronze age (1400-1300 B.C.) and were discovered at the Ugarite site. The one figurine presents poor preservation state whereas the other two have been recently conserved (2007) and protected with wax coating. The in-situ campaign was conducted within the FP6 project PROMET (Protection of Metals) that evaluated the applicability of mobile LIBS (Laser Induced Break down Spectroscopy) and Micro-XRF techniques in diagnostic analyses of museum metal collections [1].

The present work focuses on combined and complementary analytical methodologies developed to provide non-destructive characterization of the gilded layer thickness and its elemental composition including the bronze metal. The micro-XRF spectrometer used is a customized version of an Artax spectrometer (Bruker-AXS) providing a typical spatial resolution of 80 microns at CuKα. The scanning measuring option of the spectrometer was utilized to provide average compositional results for the gilding layer on a few mm² area, improving the reliability of the micro-spot analyses and identifying local compositional variations and contamination problems. The Ag-K/Ag-L intensity ratio served to estimate the gold leaf’s thickness, whereas the results obtained using unfiltered versus hard filtering excitation conditions are compared. For the bronze metal, the main problem encountered towards a reliable compositional analysis was related to the presence on a surface patina or corrosion products. The Sn-K/Sn-L ratio was explored to provide analytical criteria of universal nature (independent of the spectrometer type/experimental condition) to assess the suitability of the spot analysis measurements for quantification. The method proposed was validated by measuring with different XRF spectrometers/excitation conditions nine (9) standard bronzes of varying Sn concentration. As a result, the composition of the bronze figurines was determined with certain level of uncertainty. The results obtained are compared and discussed with respect to available bibliography data.

Insight into gilding and silvering techniques applied to parchment by Optical imaging, EDXRF and SEM-EDS

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At the beginning of the 16th century, King D. Manuel I of Portugal promoted a large restructuration of the historical written memory of the realm, by copying old juridical documents from the 12th century onwards into renewed codices. The Manuelin foral charters, as they became known, are part of this inestimable heritage from the Portuguese Renaissance art. All these texts on parchment are supplemented by the addition of decoration, the most important ones having a full page illuminated frontispiece (Typology I), a large number being ornamented with a precious initial and marginalia (Typology II) and some comprising only a painted initial (Typology III) [1].

As part of a larger research project on foral charters, the present work aims at studying these illuminated manuscripts, decorated in the strictest sense with gold and silver, in order to broaden our understanding of the gilding and silvering techniques applied to parchment between 1501 and 1525, in Portugal.

Six Manuelin foral charters, well representative of the existing typologies, were selected to provide the characterization of the parchment and metallic coatings used, and seek to elucidate the layered structure involved in each metallic coating according to the iconographic aspects and aesthetical effects to be achieved. A thorough examination of the manuscripts was performed in the National Archives, at naked eye, by means of stereoscopic microscopy (60-120x), equipped with normal and raking light and a digital camera, and also by digital microscopy (Dino-Lite) equipped with visible and ultraviolet radiation for high magnification images (220x). Non-destructive analysis was carried out in situ by Energy Dispersive X-ray Fluorescence (EDXRF) with portable equipment, for elemental composition. Complementary analysis was performed on a very limited number of micro-samples by Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS) in order to assess: 1) the vestigial materials remaining from the parchment making; 2) the inert surface finishing to obtain a more opaque and whiter support; 3) the quality of the parchment/gilding and parchment/silvering interface; 4) the metal alloys used (semi-quantitative evaluation).

By crosschecking the dataset, it was possible to determine which of the two sides of the parchment – hair side or flesh side – was illuminated, the way gilding and silvering were implemented – with or without preparatory layers, with metal leaf or metal in powder form –, the gold and silver grades thus considered appropriate according to the heraldic and ornamental needs, and how the surface of the motives was perfected.


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Relativistic K shell fluorescence yields of hollow atoms with $50 \leq Z \leq 92$

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The fluorescence yield of an atomic shell is defined as the probability that a vacancy in that shell is filled through a radiative transition. The experimental and non-relativistic or semi-empirical data on the K X-ray fluorescence yields of many elements with a single vacancy in the K shell are available in literature. However, though relativistic calculations on the fluorescence yields of doubly ionized K shell of some elements with $Z \leq 54$ were reported [1, 2], to the best of our knowledge, no experimental data on such hollow atoms are available. In this work, using fully relativistic wavefunctions with the inclusion of Breit interaction, self energy and vacuum polarization [3] the radiative transition probabilities for the significantly contributing decay channels of empty K shell have been computed for some selected ions in the range $50 \leq Z \leq 92$. The radiationless decay rates have been evaluated using available relativistic radial matrix elements [4]. The K Auger hypersatellite rates have been calculated only for KK-LL transitions. The obtained transition probabilities are then used to calculate the K shell fluorescence yields.

References:
An Attempt of Exploiting the Compton-to-Rayleigh Intensity Ratio for Improved Analysis with µ-XRF at a SEM

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The µ-XRF as an attachment at a SEM/EDS offers the possibility to improve the analytical capabilities of a conventional SEM/EDS system – especially due to the much lower limits of detections [1]. An XRF spectrum consists of the fluorescence lines and a scattering spectrum of the incident excitation spectrum on the specimen to be analysed. The fluorescence lines are usually evaluated for the determination of the elemental concentration of the specimen. In addition, information about the material can be found from the Rayleigh (or elastic) and Compton (or inelastic), scattered fraction in the detected µ-XRF spectrum [2].

The Compton-to-Rayleigh intensity ratio is dependent on the average atomic number Z of the material [3]. Thus, it can be possible to distinguish between materials with close Z, particularly in the case of light matrices. Furthermore, elements which cannot be detected by their fluorescence lines with XRF can be identified and even quantified from the shift of the average Z relative to the average Z assumed. With this motivation, in the present study, the dependence of the Compton-to-Rayleigh intensity ratio on the average Z has been experimentally determined in the Z range between 5 and 24. The Compton and Rayleigh lines considered have been Rh Kα lines. With the resulting calibration curve (Compton-to-Rayleigh intensity ratio vs. average Z) the XRF quantification of specimens with a high proportion of "invisible" elements can be improved. This will be demonstrated for several examples. Validation of selected results with electron probe microanalysis (EPMA) at the SEM will be also given.

An own developed software package for the analytical computation of the Compton and Rayleigh scattering intensities has also been employed for checking and completing, respectively, the experimentally determined Compton-to-Rayleigh intensity ratios.

The *xraylib* library for X-ray–matter interactions:

recent developments

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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 not only present the features of the original *xraylib* package, but also introduce some recent additions [2], such as partial photoelectric effect cross sections, cascade effect corrected X-ray fluorescence production cross sections, atomic level widths, Compton broadening profiles 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 and .NET, and have created versions compatible with all major operating systems.

The *xraylib* package is available from [http://www.github.com/tschoonj/xraylib](http://www.github.com/tschoonj/xraylib) and is distributed under a BSD license.

\[2\] T. Schoonjans *et al.* Spectrochimica Acta B, 66(11-12), 2011, 776-784
Polynomial approximation to universal M-shell ionisation cross-sections

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The calculation of ionisation cross-sections in efficient ways for inclusion in simulation programs to determine the X-ray yields are still extremely useful, in spite of the significant computer power available nowadays. Particle Induced X-ray Emission studies have been mostly done using K- and L-shell X-ray emission. However, the new microcalorimeter detection systems available will make M- and higher shell X-ray emission data increasingly important. Quantification and simulation of X-ray yields require one to be able to compute the ionisation cross-sections, which can be carried out using the ECPSSR theory [1]. Nevertheless, this is not an efficient process and, therefore, in previous work, K- and L-shells universal ionisation cross-sections curves were found as well as polynomial approximations to the universal curves [2].

In this work, polynomial approximations to the M-shell universal ionisation cross-sections are presented and calculated ionisation and X-ray production cross-sections based on the polynomial approximations are compared with results from literature. These polynomial approximations were included in the X-ray yields simulation program DT2simul, based on LibCPIXE [3], and the results obtained are compared with experimental data for several elements and compound samples.

New measurement of L XRF fluorescence cross-section and relative intensities for Ag, Au, Pb and Bi elements

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We have measured $\sigma_\alpha$, $\sigma_\beta$, $\sigma_\ell$, $\sigma_\eta$, fluorescence cross sections for Ag, Au, Pb, Bi using Cd$^{109}$ and Am$^{241}$ sources. Thin samples have been prepared by evaporation with thickness less than 1000 A° to reduce the self-absorption effect. The experimental data will be compared with the theoretical predictions existing in the literature [1] and using the atomic parameters. Relative intensities are also determined for L X-rays of the studied elements [1], [2].

Kβ₅, Kβ₂, KMMRAE and Sawada lines of some medium Z elements

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The energy and relative intensity of the diagram lines Kβ₅, Kβ₂, the low energy Kβ x-ray satellites KMMRAE of Ge, As, Se, Br, Sr, Zr and Mo, and that of Sawada lines for the first five of these elements are determined (relative intensity for the first time except in the case of Mo) using a wave length dispersive spectrometer with LiF 420 (2d= 1.8 Å) as the analyzing crystal and Scintillation detector (NaI) as the detector of X-rays.

The measured energy shifts and relative intensities of these lines with respect to the Kβ diagram line are compared with different theoretical estimates and previous experimental values for the cases available. The KMM RAE edge energies are calculated using the corresponding semi-empirical auger electron energies of F.P. Larkins[1] and the energy shifts are estimated from these values. Comparing these theoretical energy shifts with the energy shifts of experimental edge energies of the KMM RAE peaks, they are interpreted as KM₁M₁ - ¹S₀, KM₁M₂ - ¹P₁, KM₂M₂ - ³P₁, KM₂M₃ - ¹S₀, KM₁M₃ - ³P₁, KM₃M₃ - ³P₂. The energy shifts of Sawada line Kβ₅[2] of Ge, As, Se, Br and Sr, measured for the first time for these five elements, agree well with the theoretical values computed using L and M edge energy values from the compilations of Storm & Israel [3].The theoretical values of Kβ₂relative intensity of Storm & Israel [3] are lower than the experimental values. But in the case of Kβ₅relative intensity, theoretical estimates based on formalisms of both Storm & Israel [3] and Scofield [4] are higher than the experimental values. The present experimental integrated KMM RAE X-ray relative intensity values are higher than the theoretical values computed based on Scofield’s RHF theory.

In the Z range of the present study, the energy shift of all these lines, except KMMRAE increases linearly with atomic number Z. While the relative intensities of the diagram lines Kβ₅, Kβ₂ increase quadratically with Z, those of the satellites KMMRAE and Sawada lines decrease exponentially with Z.

[1] F.P.Larkins, Atomic Data and Nuclear Data Tables 20, 1977, 311
K-shell X-ray Production cross section for S, Fe and Cu

By 4.2 MeV Alpha Particles

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K-shell X-ray production cross-sections for S, Fe and Cu by 4.2 MeV alpha particle have been measured using Si(Li) windowless X-ray detector with a resolution of 146 eV at 5.9 keV. The efficiency of the X-ray detector was determined using standard radioactive sources. The experimental results are compared to the prediction of the ECPSSR theory and the K–shell empirical database of Paul[1]. Measured and calculated X-ray production agreed well within reasonable limit of experimental errors.

FPM model for portable X-ray fluorescence spectrometer

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The ultimate goal of this work is to develop a new portable X-ray fluorescence spectrometer for quantitative determination of elements in solid waste samples. The radiation source of the spectrometer is a low powered AMPTEK Mini-X Ag tube and a silicon drift detector (Canberra X-PIPS) is applied. A new algorithm and computer code have been developed to perform quantitative analysis using Fundamental Parameter Method approach.

The FPM system of equations describes exactly the mathematical relationship between the concentration of sample elements and their characteristic intensities. This system consists of non-linear integral equations; therefore the mathematical solution is obtained only by numerical iteration algorithm. New software was constructed in MATLAB environment for calculation the concentration values of the sample based on the FPM model that considers the enhancement effect as well.

Due to the polychromatic excitation mode the model calculates the characteristic intensities of the sample elements for every individual energy channel of the primary X-ray beam instead of using theoretical or fitted function describing the primary X-ray tube spectra [1]. The white spectrum of the X-ray tube was measured under vacuum condition using an evacuated tube closed by polymer windows on both sides.

In order to verify the FPM model-calculation standard reference material of alloy samples were measured. The results of the analysis had a good agreement with certified concentrations in range of 0.001-100 w%. According to these numerical results the new FPM method is successfully applicable for quick and non-destructive quantitative analysis of metal waste materials in 4-5 orders of magnitude of concentration range without using standard samples.

The current version of the FPM software is able to calculate the concentration of elements in range of Z=20-58. Future plans are to improve the algorithm and computer code for error estimation, calculation of elementary composition in undetectable dark matrix and to complete the calculation procedure for L-lines.

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An internally consistent self-calibration approach to fundamental parameter x-ray fluorescence analyses

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The inconsistencies and unreliability of the basic atomic parameters \cite{1,2}, as well as the inaccuracies of the precise description of the equipment parameters, make for a daunting task in applying the fundamental parameter (FP) approach to x-ray analysis.

With a quality assurance capable signal processor \cite{3,4}, we have overcome the limitations of the signal processing approaches clearly described by Dr. P Statham \cite{5}, and the detection arm can be properly handled, even at very high input rates. The other arm of the XRF equipment is the excitation arm that provides the x-rays striking the sample. It is crucial to accurately know the x-ray spectrum at the sample position. This demands the precise knowledge of the x-ray tube function, the absorbers and the geometry. Usually the x-ray tube function along with the effect of the filters and geometry is not well known and is difficult to determine experimentally.

We have developed a user friendly approach, where an inverse FP method is used to determine the synthetic tube function at the sample position, from a multi-element standard spectrum. This method will accommodate the inconsistencies and inaccuracies of the basic physics parameters to first order. However, the inaccuracies in the atomic parameters and system description will not be sufficiently compensated with layered targets, and will give limitations in the layer accuracy.

The experiences and observations will be presented.

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Characterization of a PIN diode detector and Quality assurance capable Digital signal processor system for FP analytical work

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It is difficult to assess the reliability of the basic physics parameters, on which the fundamental parameter methods analytical techniques are based [1]. Some of the measurements report striking observations, like strong deviation from Feynman’s Golden rule [2], or strong chemical effects for which an explanation is yet to be given [3]. Beyond that the detector performance and detector models have large variations [4,5]. Therefore it is important to have as much detailed information about the detection system and equipment parameters as possible.

We have characterized a Si PIN diode x-ray detector response function. It is customary to characterize the detector response function and parameterize it in terms of the hypermet function and exponential tailings [6], or the double exponential plateaus derived from the electron energy loss processes [5]. Characterization of the absolute counting capability and the rejection ratio are also required but this has never been presented. We have characterized the Si PIN diode detector with a digital signal processor, which has the unique capability to create several spectra, retaining all events, and sort them into different spectra. This allows a determination of the energy dependent electronic efficiency curve as well.


The research has been supported by the Marie Curie International Reintegration Grant within the 7th European Community Framework Programme.
ABSTRACT

The Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife, Nigeria, has recently acquired a NEC 1.7 MV Pelletron tandem accelerator for Ion Beam experiments. This paper presents an overview of the accelerator and its capabilities. A full description of the end-station designed and built at iThemba Labs, South Africa, is also presented. A number of preliminary PIXE and RBS experiments have been carried out using this facility and the results are also presented. This paper further discusses the other diverse areas of application of the accelerator, including solid minerals/geological and biomedical samples analysis; agriculture, materials science and, environmental pollution studies.

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Dual energy alpha beam RBS and PIXE measurements for in-depth elemental profile characterization of Cu(In,Ga)Se₂ thin film solar cells


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There is a growing interest to use Cu(In,Ga)Se₂ (CIGSe) thin films as absorber cells in photovoltaic applications due to their high performance versus low cost feature. The preparation results in an in-depth gradient of In and Ga concentrations. With this the band gap and free carrier density are modified influencing critically the optoelectronic properties of the solar cell. The non-destructive characterization of such a thin film stack is a rather challenging task requiring the application of a technique with depth resolved capabilities in the nm scale and probing depth up to few micrometers. Reference-free grazing incidence X-Ray Fluorescence analysis at two exciting energies has been demonstrated as a very promising new technique to resolve the In/Ga concentration gradient in the CIGSe thin films [1, 2].

The present work explores the potential of Rutherford Backscattering Spectrometry (RBS) and Particle Induced X-ray Emission (PIXE) using helium ions at two different energies to provide in-depth elemental profile characterization of Cu(In,Ga)Se₂ thin film solar cells. The measurements were performed at the IAEA PIXE/RBS scattering chamber of the 6.0 MV accelerator at Ruđer Bošković Institute, Zagreb, Croatia. About twenty (20) thin films were prepared onto 500 nm Mo back contact and 2 nm glass substrate including either complete solar cells or single/double absorber cell combinations (prepared by Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany [3]).

The experimental methodology included alpha beam RBS measurements at two energies, 10.8 and 3.0 MeV respectively and PIXE at 3.0 MeV. The high energy alpha beam was carefully selected to separate In from other elements, maintaining the Rutherford character of interaction. The synergistic application of RBS/PIXE techniques resulted in complementary information: The high Energy RBS revealed the detailed in-depth profile of In and the total thickness of the absorber cell, whereas in the case of a complete solar cell the thickness of the ZnO window layer was also estimated. Low Energy PIXE analysis provided total average elemental concentrations to be used as initial parameters for simulating the RBS spectra. Finally, the previous results were properly fused to simulate using SIMNRA code the low energy RBS elemental profiles and to estimate elemental gradients. Interesting features were revealed such as diffusion of In into the ZnO window layer in the case of a complete solar cell and the diffusion of Se into the Mo back contact, which forms an intermediate MoSe₂ layer. The analytical possibilities of dual energy combined RBS/PIXE measurements and the uncertainties induced in the quantification methodology are discussed and assessed.

We present the analytical features and performance of a proton-induced XRF experimental set-up designed and installed at the 5.5MV Tandem accelerator laboratory of the Institute of Nuclear Physics, N.C.S.R. “Demokritos”, Athens. The set-up includes a two-level UHV chamber that hosts in the lower level up to six primary targets in a rotatable holder; the irradiation of pure element materials used as primary targets with few-MeV high current (~uA) proton beams, produces intense quasimonochromatic X-ray sources of selectable energy. In the upper level, a six-position rotatable sample holder hosts the samples considered for X-ray Fluorescence Analysis. The PIXE induced X-ray beam is guided to the sample position after proper collimation, whereas various filters can also be inserted along the beam’s path to eliminate the backscattered protons or/and to absorb selectively components of the X-ray beam. The apparatus incorporates an ultrathin window (AP1.7) Si(Li) spectrometer (FWHM 136 eV at 5.89 keV) coupled with low-noise electronics capable of efficiently detecting photons down to C-Kα. Exemplary soft X-ray spectroscopy studies [1, 2] and results of selective XRF analysis of geological samples will be presented, whereas the pros and cons of the method are discussed.


PS1-39
SAXS INVESTIGATION OF THE SURFACE STRUCTURAL INHOMOGENEITIES AND FRACTAL PROPERTIES OF MnO₂ SEMICONDUCTOR THIN FILMS

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The theory of scattering by a porous solid was developed by Wong [1], and the theory main formula is as follows:

\[ I(q) \sim \text{constant} \times q^{-D} \]  

(1)

Here D is the surface fractal dimension that shows fractal behavior.

The relationship shows the fractal behaviour. Indeed, on the graph, the coefficient of the curved part slope, which can be closely approximated by line \( \alpha \), is:

\[ \alpha = -\frac{\text{d} \log I(q)}{\text{d} \log q} = 2.87 \]  

(2)

Comparison result (2) with the formula (1) gives (for \( \alpha = D \)) the value of D=2.87.

Obtained D value coincides with the previously [1] found value of surface fractal dimensionality in a sintered niobium powder pellet (Nb) with high accuracy, \( D_{(Nb)} = 2.81 \).

So far, the authors are at a loss and cannot say whether it is a mere coincidence or the result of some specific generation features of the capacitor MDS structure. But it as was noted earlier, in case of sintered niobium the scattering is stipulated by the sample surface.

Micro X-ray beam produced with a single glass capillary 
and a metal small ball for XRF analysis

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XRF analysis has the advantage of nondestructive analysis, however, SEM-EDS gives
elemental maps with a spatial resolution of a few micrometers. Thus, it is important to
improve the micro-XRF instrument to have better spatial resolution. A single glass capillary is
the effective x-ray optics for micro-XRF in the laboratory [1]. Actually, a beam diameter of
10 micrometers is available with commercial instruments such as x-ray analytical microscope
[1]. In our research group, a combination of a single glass capillary and a metal small ball has
been studied for improving a spatial resolution in a micro XRF analysis [2].

In this presentation, another approach is discussed. We used a micro-focused x-ray tube (x-
ray emission size: 50 x 50 micrometers, Mo anode, 50 kV, 0.5 mA) and a single glass straight
capillary with a metal small ball (400 micrometer). A center part of x-rays emitted from the x-
ray tube was stopped by the metal ball, while the outer part of x-rays were totally reflected on
the inner wall of the single capillary. A focused x-ray beam was observed at a distance of
5–15 mm from the output of the glass capillary. In our analysis, the length of the glass
capillary could be reduced, leading to a long working distance (~50 mm). This long working
distance will be a practically useful advantage of this x-ray optic. The detailed results will be
shown on the poster.

polycapillary x-ray optics combined with glass conical pinhole for micro x-ray fluorescence spectrometry", X-
Confocal Micro-XRF Spectrometer for Light Element Analysis

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Micro X-ray Fluorescence (Micro-XRF) analysis is a well established tool to determine the spatial distribution of major, minor and trace elements in a sample. It is widely used to investigate samples from different fields (biology, geology, life science, etc.). Most available micro-XRF spectrometers operate in air which does not allow the analysis of low-Z elements. In order to extend the analytical range down to light elements, a special micro-XRF spectrometer has been installed at the Atominstitut of the TU Wien [1].

Recently the spectrometer has been extended to confocal micro-XRF geometry by installing a second polycapillary X-ray optics (XOS) in front of the energy dispersive detector. Alignment of both optics is now fully automated using two xyz-stacks of attocube ANPx/z101 piezo positioners. This allows the alignment process to be done under vacuum condition, like the measurements. In this work the modifications of the spectrometer, characterization of the modified spectrometer and test measurements are presented.

The energy dependent size of the effective measurement volume (resolution) ranges from about 35x35x35 µm³ for ZrKα to about 85x85x85 µm³ for AlKα. The lower limits of detection are in the range of ppm. 3D scanning capabilities are demonstrated using a special test structure (microscopic Cu cross on an X-ray screen). As an example depth profiling of historic paint layers has been performed to show the spectrometers capabilities. Several test samples were measured.

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Quantitative analysis of low concentration elements in a human biological substratum by TXRF.

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The results of the research work on element structure of biological substratum (BS) of human organism, brought by using TXRF spectrometer "XFS" [1] are considered. The samples of hair and urine had been selected from males and females at the age of 18-22 and 40-55. The results of investigation were processed statistically and were structured on human ages, sex, field of work, and areas of living. It is established, that microelement structure of hair is the indicator of ecological conditions and features of a functional state of the human. Last years in Russia sharp deterioration of a condition of the public health, connected in many respects with influence of factors of ecological character is marked [2]. The increase of concentration of toxic bio-elements (BE) of the technogenic nature (for example Pb, Hg and Cd) and the naturally caused deficiency of essential elements (for example Fe, Cr, Zn, Se, I, etc.) was created with prospects for long-term deterioration of health of the population.

At the first stage of researches values of concentration of trace elements in BS, collected from men and women with the account of age gradation were examined. Their fluctuations have been compared to the data of the literature which are not ranged according to sex and age [2]. The attention has been drawn to the fact, that in the received results of the research the sparseness of concentrations of the trace elements is less expressed, results were more "compact". This is probably connected with the fact that the researched material has been grouped on homogeneous attribute. It has been received from individuals, basically, the same social layer (students, office workers), living in the nearby areas of city which are not distinguished on intensity of technogenic pollution. The surveyed used approximately the same food assortment distinguished by a similar set of micronutrients. In this connection BS of the same ten students – first-year students constantly living in the same area of city, in the middle of a semester and during the first examination period have been surveyed. It is found, that girls to the greater degree, than young men, had under stress the level of the listed essential elements in urine reduced, and in hair remained former. Judging by the dynamics of parameters concentration of lead did not undergo any appreciable changes, while all students’ nutrition was identical. Appreciable differences in the quantitative respect between a range of concentrations of chemical elements for men and women are not revealed. It is established, however, that such trace elements as Se, Rb and Cu participating in young women reproduction biology, were in bigger concentration, than at more senior generation. At the same time men of mature age had higher parameters of a range of fluctuations of Fe concentration, that is probably connected with the fact, that the level of hemoglobin containing the most part of Fe, is at men’s organism higher, than at women’s. At the third stage of work it has been decided to estimate a level of concentration of some elements which are included in molecules of some enzymes, on a background of stressful reactions of any aetiology. Changes in concentrations of Fe, Se, Cu, Zn, metals which are part of ceruloplasmin (copper), glutationperoxidas (selenium), alkaline phosphas (zinc), i.e. enzymes of antioxidant system – the main protection of an organism from distress and intoxication have been analysed. Parameters of lead – the main polluter of the environment, taking place with above mentioned bio-elements in antagonistic relations in aspect of their biological effects are also investigated.

The evaluation of the earth worm (*eisenia fetida*) for the removal of uranium, lantanum and cerium from a contaminated substrate and the effect on biological parameters

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The use of the earth worm (*Eisenia fetida*) for the removal of uranium, lantanum and cerium from a contaminated sediment was evaluated. An experimental random design was carried out during 18 days with ten treatments with 15 replicates (one control with bovine manure with five worms per replicate, one control without worms, four experimental treatments with mixtures of manure (BM) and sediment (UCS) in proportions of 12.5%, 25%, 37.5% and 50% of UCS with five worms per replicate and four experimental treatments with the same proportions of BM and UCS without worms).

The elements were determined in the substrates of the treatments and in the worm tissue as function of time using the TXRF technique. The parameters mortality, number of cocoons and biomass were also determined. The measurements of the element concentrations were performed using a PICOFOX spectrometer after the wet digestion of the samples. For the quantification were selected the L lines of La, Ce and U, excited with a Mo anode during a live counting time of 100 s. The element Selenium was selected as internal standard.

The monitoring and statistical comparison of the concentrations of La, Ce and U in the substrates of the treatments and the worm tissue demonstrated that under the conditions of the experiment the elements were not removed. No significant differences \((p<0.05)\) were observed in the biomass production. There were found significant differences regarding the number of cocoons for the treatment with 12.5% respect the other treatments. It was observed a higher production of cocoons. The mortality was absent in all treatments with worms. The individuals survive at U concentration of 170 mg/Kg, and La and Ce of 900 mg/Kg.
Reduction of Ar Kα peak in TXRF measurement by flowing nitrogen gas

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We improved the sensitivity of total reflection X-ray fluorescence (TXRF) spectrometer, which Kunimura et al. developed [1], by reducing noise from the TXRF spectrometer [2]. However, it is still difficult to detect trace elements of which characteristic X-rays have energies near those of Ar Kα line (2.96 keV) with the TXRF spectrometer. This is because TXRF measurement is generally performed in air and the TXRF spectrometer will detect the 0.9 vol.% of argon gas contained in air. Holtkamp et al. [3] reported that they succeeded in decreasing Ar Kα line by placing the TXRF spectrometer (S2 PICOFOX, Bruker) in a gas-tight box and flowing nitrogen (N₂) gas into the box. It will take more than half an hour to complete the replacement of air in the gas-tight box with N₂ gas. In the present study, we placed polyethylene tubing at the gap between the X-ray detector and the sample stage of the TXRF spectrometer, and then flowed N₂ gas through the polyethylene tubing in order to sweep the air. In this case, TXRF measurements can be carried out without waiting for the replacement of air with N₂ gas. When 1 μL of solution containing 10 ppm of Cd was measured with the TXRF spectrometer, clear peak of Cd Lα line was obtained by flowing 800 ml min⁻¹ of N₂ gas as shown in figure 1. The signal-to-background ratio of Cd Lα line was improved from 1.7 to 3.4 and the lower limit of detection of cadmium was improved to 1.7 ng.


![Figure 1. EDX spectra of 1 μL of a solution containing 10 ppm of Cd before (filled dot) and after (open dot) flowing N₂ gas.](image-url)
Simulated comparison of grazing incidence and grazing emission geometry for angle resolved X-ray fluorescence analysis with a X-ray tube

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A flexible multi-purpose experimental chamber for X-ray fluorescence (XRF) analysis with a special focus on grazing incidence (GIXRF) and grazing emission (GEXRF) geometry is built up at the Berlin Laboratory for innovative X-ray Technologies (BLiX) at the Technical University Berlin in cooperation with the research group X-ray and IR Spectrometry at the Physikalisch Technische Bundesanstalt (PTB). The aim is a versatile set-up for angle resolved XRF measurements which provides access to different information depths. Under grazing incidence or grazing emission conditions the information depth is tunable with the variation of the incident angle of the exciting radiation or the angle of detection of the fluorescence photons.

For highest flexibility the experimental chamber is designed for being connected with a synchrotron beamline and also for being operated with a laser-plasma-source in the laboratory. As a supplementary source a X-ray tube is integrated into the chamber.

For this purpose we like to present a simulated comparison of grazing incidence and grazing emission geometry for angle resolved X-ray fluorescence analysis with a laboratory X-ray tube set-up. The decisive quantities here are angular resolution, penetration depth, solid angle of detection and fluorescence photon yield. Pure geometrical considerations as well as fundamental parameter-based calculations are done. The intention is to determine the best possible compromise between the given quantities. Also the use of capillary optics for micro-analysis is taken into account. Further the strengths and fields of application for different geometries will be demonstrated for GIXRF and GEXRF. The calculations are carried out for several thin film multilayer systems like solar cells containing photovoltaic absorber layers which consist of Cu(In,Ga)Se\(_2\) or nano- and microcrystalline silicon.

With these simulations the optimal experimental geometry has been figured out.
A new multi-purpose XRF experimental chamber for UHV conditions has been built up at the Berlin Laboratory for innovative X-ray Technologies (BLiX) in the frame of the photovoltaic competence centre Berlin (pvcomB) excellence initiative at the Technical University Berlin (TUB). The chamber is developed by the Physikalisch-Technische Bundesanstalt (PTB) and adapted to our needs. It will offer various possibilities for measurement geometries, both for excitation and detection. The following measuring methods are planned with this chamber:

- conventional 45°/45° XRF
- grazing incidence X-ray fluorescence (GIXRF)
- grazing emission X-ray fluorescence (GEXRF).

Inside the chamber an UHV qualified seven axis goniometer is positioned, for most flexible sample positioning and geometry variations. Two axes are used for monitoring diodes. Possible excitation sources include laser plasma X-ray sources, various laboratory X-ray tubes as well as synchrotron radiation at an electron storage ring. Therefore, the vacuum chamber is mounted on a base designed as a four axis goniometer. For laboratory sources the use of different X-ray optics, like polycapillaries or multilayer mirrors to focus the X-ray radiation onto the sample is also accounted for. Detection of the fluorescence radiation is realized with a peltier cooled silicon drift detector (SDD) which can be mounted to the chamber in various positions. For the soft X-ray range below 1 keV, a compact reflection grating spectrometer can be attached. The sample can be changed quickly and without venting or polluting the chamber by a load lock. An overview of the chamber design and its various modes of operation will be given.
Reconstruction of the structure of La/B₄C and LaN/B₄C multilayer mirrors using X-ray Standing Waves

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Application of La/B₄C multilayer optics for λ = 6.7 nm, as can for instance be used at near normal incidence in a next generation photolithography equipment requires substantial improvement of both the reflectance and the bandwidth. La/B₄C multilayers suffer from layer intermixing, diffusion and significant structural imperfections. In recent research we have shown that the formation of La-nitride by N-ion treatment of the La layers helps to reduce the compound formation, thus leading to an increase the multilayer mirror reflectivity. Here we present positive and negative influences of the N-ion treatment on the multilayer structure.

Using the Grazing Incidence X-ray Standing Waves technique for model waveguide structures, it was observed that, depending on the thickness of the La layer, the La density in a B₄C/La/B₄C stack is found to be reduced significantly with respect to the literature value for bulk La. This can be explained by LaB₆ interlayer formation. The density of LaN in B₄C/LaN/B₄C stack was found to be similar to the bulk LaN value.

To analyze the multilayer structure we combined the Grazing Incidence X-ray Reflectivity (GIXRR) technique with the analysis of the X-rays fluorescence from the La atoms excited with the X-ray Standing Wave (XSW) at the first order Bragg reflection. The analysis confirmed that nitridation of La significantly improves localization of the La atoms inside the multilayer period which significantly increases the optical contrast of the multilayer mirror. Analysis of the off-specular X-ray reflection however shows that depending on the nitridation process, interface roughness can be increased in LaN/B₄C multilayers.

In this paper we will present details of the multilayer structural analysis and discuss the influence of interface intermixture and roughness on multilayer reflectivity.
Investigation of microelementoses of rat's organism by
using TXRF

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Main goal of this article was a polymicroelementoses in rat’s hair modeling. A Polymicroelementoses (sharp growth of chemical elements concentration) in hair may be an early marker of chronic radiation sickness [1]. For this dynamic of concentration of chemical elements which is systematically irradiated by x-rays at special created camera. Obtained chemical composition dynamics data has been compared with bio chemical indexes of bloods and ovaries of animals. Investigation of rat’s hair investigation provides on TXRF spectrometer «XFS» [2]. Typical TXRF spectrum of rat’s hair is shown at figure. It is established that with increase in time of radioactive defeat concentration of elements which participate in exchange processes in an organism sharply grow. The more received dose is more than concentration of chemical elements. The conclusion says that changing of any chemical elements concentration in hair of rats signal about development of symptoms of chronic radiation sickness. And TXRF technique is a very useful technique for resolution of medical screening in areas of radiation damage like Ukraine Chernobyl and Japan Fukushima.

Authors are grateful to professor Kozhin for useful discussions

![Typical TXRF spectrum of rat's hair](image)

**Figure.** The typical TXRF spectrum of rat’s hair.

Investigation of the improvement of angle-resolved XRF-measurements by including L-lines for graded CIGSe thin films

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Thin film solar cells based on Cu(In_{1-X}Ga_X)Se_2 (CIGSe) absorber layers with 0 ≤ X ≤ 1 are multi-layered systems with a variable band gap. The ratio of the matrix elements In to Ga determines the band gap within the absorber layer and can be varied through its thickness of about 2 µm. This gradient in the elemental composition of CIGSe thin films influences the respective photovoltaic properties, i.e. it can modify the solar cell efficiency.

To determine these gradients, angle-resolved X-ray fluorescence (XRF) measurements can be performed, for example in grazing incidence (GIXRF) geometry [1]. Angle-resolved XRF uses the effect that information originating from different layer depths can be kind of partially discriminated when varying the incident angle of the exciting radiation. Because of the low thickness of the investigated CIGSe layers, incident angles in the range of 0° up to 5° are chosen.

In the experimental set-up, employed having an energy dispersive SDD detector the X-ray beam penetrates the sample at shallow incident angles and the generated characteristic radiation is detected at a steep angle of 90°. The beam source provides monochromatic synchrotron radiation of up to 12 keV. In the detected fluorescence spectra the L-lines of Cu, Ga and Se are in the energy range of up to 1.5 keV, the L-lines of In have energies from 3.2 keV up to 4 keV, and the K-lines of Cu and Ga are in the range of 8 keV up to 10.3 keV. This means, that both sets of fluorescence lines have considerably different information depths. Because of their larger photon energy, the excited K-lines can provide information from deeper regions than the L-lines.

The previous analysis [1] only includes the Cu and Ga K-lines and the In L-lines. We calculated fluorescence line intensities (of Cu, Ga and Se) as a function of the incident angle in order to investigate, which kind of additional and complementary information the L-lines can provide. The incident angle and the line energy determine the information depth and the count rate of the detected fluorescence photons. Our goal is to optimize the measurement strategy for the incident angles and the measurement time. Simulations were performed on the basis of known experimental and fundamental parameters for differently graded CIGSe systems.

Complementary Characterization of Buried Nanolayers by Quantitative X-ray Fluorescence Spectrometry under Conventional and Grazing Incidence Conditions

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The determination of the thickness and elemental composition is an important part of the characterization of nanolayered structures. For buried nanolayers, X-ray fluorescence spectrometry is a qualified method for the thickness determination whereas conventional electron emission based methods may reach their limits due to rather restricted information depths.

The aim of the presented investigation was the comparison of reference-free X-ray fluorescence spectrometry under conventional and grazing incidence conditions offering complementary information with respect to quantification reliability, elemental sensitivity, and layer sequences. For this purpose, buried boron_carbon layers with nominal thicknesses of 1, 3, and 5 nm have been studied using monochromatized undulator radiation in the laboratory of the Physikalisch-Technische Bundesanstalt (PTB) at the synchrotron radiation facility BESSY II. The results for the two beam geometries are compared and show particulate good agreements, thus encouraging the complementary use of both methodologies.

Evaluation of the applicability of total reflection X-ray spectrometer S2 PICOFOX to analysis of rocks

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Total reflection X-ray fluorescence (TXRF) analysis is a versatile tool to determine the trace element contents in various materials. However, its application to the analysis of powdered geological samples is reported relatively rarely [1, 2].

The aim of this work is to evaluate the applicability of benchtop total reflection X-ray spectrometer S2 PICOFOX to the analysis of suspensions of the powdered geological samples. The instrument is equipped with a Mo target microfocus tube, operated at 50 kV/750 µA, a multilayer monochromator and 30 mm² XFlash® silicon drift detector.

Theoretical and experimental investigations the intensity of scattered primary radiation and fluorescence versus the chemical composition and the surface density of the sample were carried out using acrylic and quartz glass sample carriers [3]. As the sample carrier the quartz sample carriers were chosen.

All studies were performed using Certified Reference Materials (CRMs) of different composition rocks. The optimum conditions for the sample preparation and measurements were chosen. 50 mg of each rock sample powder was suspended in 2.5 ml of a 1% aqueous solution of Triton X-100. 10 µl of the suspension was transferred onto the quartz glass carrier and dried on a heating plate. The measurement time was 1000 s per sample.

The TXRF results showed good agreement with the reference values. The estimated relative deviation (ΔC/C) was less 0.1 for Cr, Y, Ce, Pb, and 0.2-0.3 for K, Ti, Mn, Fe, Ni, Zn, Ga, Rb, Sr, Ba, La, Nd, Th, U.

For the chosen measuring conditions the estimated detection limits of TXRF were in the range from 1 to 16 ppm. The experiment was designed according to the one-factor dispersion analysis scheme for the estimation of errors in preparing samples.

Application of a low power TXRF spectrometer for aerosol analysis

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The construction of a compact TXRF spectrometer, which is not bound to the stationary use in a laboratory, opens the door to a multitude of new applications. Thus a compact spectrometer, operating with a 50 W low power x-ray tube with Mo anode, a Mo/Si multilayer monochromator unit and a Peltier cooled silicon drift detector (SDD) with 80 mm² active area, which therefore does not require liquid nitrogen for cooling, has been constructed by the Atominstitut x-ray laboratory.

The applicability of this new low power TXRF spectrometer for quantitative analysis of indoor aerosols has been tested. By using a Dekati impactor, that discriminates particles with cut-off diameters of 10 µm, 2.5 µm and 1 µm, the deposits of aerosols had a larger area than seen by the detector. The samples were directly collected on siliconized quartz reflectors and form two concentric rings with individual sample spots. Quantitative analysis required estimation of geometry factors by using a modified nanoliter application unit of the x-ray laboratory in order to reach defined points on the surface of quartz reflectors with satisfactory accuracy. Thus the point patterns of the aerosol samples could be reproduced and simulated by pipetting of standard solutions with known concentrations and a droplet volume of 500 nl for each point, which created a good basis for quantification. The measurements of the aerosol samples carried out with the commercially available spectrometer Atomika 8030C led to comparable results. Detection limits of less than 10 pg/m³ could be achieved for most of the elements determined.
Modelling shallow dopant distributions as layered samples for grazing incidence x-ray fluorescence analysis

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The characterization of shallow dopant distributions in semiconductors has historically been a challenge for microelectronics technology. Advances in the fabrication have been connected to shallower and shallower distributions and increasing dopant concentrations.

Grazing Incidence X-Ray Fluorescence Analysis has been used in the past for the evaluation of dilute near surface dopant profiles. The physical models used for the simulation of the fluorescence intensities and the quantification of the dose have not considered the modification of the x-ray optical constants of the substrate material due to the dopant. Technological interest in the analysis of higher dopant concentration drove us to study the theoretical limits of applicability of the original approach and quantify the differences with an approach where the dopant profile is translated into a stack of layers with different dopant concentrations and hence different optical constants.

Simulations have been performed following the two different paradigms. Secondary Ion Mass Spectrometry depth profiles of arsenic in silicon for samples produced by low energy ion implantation or plasma ion immersion implantation have been used as input for the definition of the sample model. Results will be compared and discussed.
First set of imaging diagnostics for the LMJ


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The Laser Mégajoule (LMJ) facility, now under construction at CEA/CESTA, will be with the National Ignition Facility (NIF) one of the world’s largest laser driven fusion facilities in operation in the 2010’s. We present here the design of the first set of diagnostics to be implemented on LMJ. This set includes three imaging diagnostics with high spatial, temporal and spectral resolution. They will give basic measurements, during all the life of the facility, such as position, structure and balance of beams, but they will also be used to diagnose implosions in indirect drive. Thus, the design requires a vulnerability approach, because components will operate in a harsh environment induced by fluxes of neutrons, gamma rays, debris and shrapnel. Grazing incidence X-ray microscopes as far as possible from the target are a good way to mitigate this environment.

All microscopes include toroidal mirrors and reflect x-rays up to 10 keV using W/SiC non-periodic multilayer coatings (Super mirrors). Metrology on X-ray tubes and at synchrotron radiation facility BESSY II and SOLEIL is presented.
X-ray elemental imaging by using two dimensional X-ray detector

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Development of an X-ray focusing device enables elemental imaging by scanning micro X-ray beam. However, this scanning type XRF imaging method needs a long acquisition time. Therefore, the projection type XRF imaging has been required. Sakurai and Eba developed a projection type XRF imaging technique at SR facility [1]. In our research group, a new wavelength-dispersive XRF imaging spectrometer equipped with a two-dimensional X-ray detector and a dispersive crystal was developed in the laboratory [2].

We used an X-ray tube (Mo anode, 40 kV, 40 mA), straight-type poly-capillary optics, metal foil and the X-ray CCD camera with a Gd$_2$O$_2$S:Tb scintillator. A straight-type poly-capillary, which was placed between the sample and the CCD camera, was used as collimator of X-ray fluorescence. The metal foil placed between the straight-type poly-capillary optics and the CCD camera was used as X-ray filter. We obtained several images by replacing the filter for 3 mm plates of Zn, Cu and Ni. When Ni foil was applied, the XRF image of the plate of Zn disappeared. When Co foil was used, the XRF images of the Zn-Cu plates disappeared. The detailed results will be shown on the poster as well as the results obtained by WD-XRF imaging spectrometer.

References

Laboratory-based recording of holographic fine structure in x-ray absorption anisotropy using polycapillary optics

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X-ray absorption anisotropy (XAA) results from interference of the direct incident wave on a crystal with the waves scattered inside the sample. Two dimensional maps of XAA can be interpreted in terms of x-ray holograms and can be used for 3D imaging of local atomic structure with element sensitivity [1].

Due to weak fine structure in XAA (approx. 0.1% of the total signal) intense synchrotron sources are usually used in such experiments. Only few laboratory based attempts were reported [2].

In this work it was demonstrated that XAA patterns can be efficiently recorded using a tabletop system based on polycapillary optics and a HOPG monochromator (Figure 1a). For Mo Kα radiation, the implementation of polycapillary optics resulted in a two order of magnitude gain in the radiant intensity (photons/s/solid angle) as compared to a system without optics. Element sensitivity was demonstrated by acquisition of distinct XAA signals for Ga and As atoms in a GaAs(111) wafer by using x-ray fluorescence as a secondary signal. Presented results indicate the possibility of performing laboratory-based XAA experiments for heavily doped single crystals or thin films.

Holographic reconstruction of XAA patterns was performed by means of a numerical procedure (Figure 2b, c). Even thought the XAA data had a high quality, due to imperfect existing reconstruction algorithms proper real-space images could be obtained only for particular bond lengths as in Figures 2b, c. Work on improvement of holographic data processing is in progress.

**Figure 1.** Stereographic projection of x-ray absorption anisotropy pattern obtained for Ga Kα fluorescence in a GaAs sample. Holographic reconstruction of the local structure around Ga atoms at distances of 2.25 Å (a) and 4 Å (b). A green circle marks the positions of the nearest As atom. Red circles mark the positions of nearest Ga atoms.

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Prospects of x-ray absorption anisotropy analysis with the wavelet transform

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The interference of waves scattered inside the sample with the incident plane wave gives rise to x-ray absorption anisotropy (XAA). When recorded with broad-band polychromatic x-rays XAA angular maps can be interpreted as quasi-real space projections of atomic planes and directions [1]. Recently, it has been shown that the acquisition of white beam XAA maps by means of fluorescence radiation is experimentally feasible [2]. Thus, current research is strongly focused on data analysis i.e. structure determination around absorbing atoms with atomic resolution.

In this work we present the prospects of analysing XAA maps with the continuous spherical wavelet transform which was first presented in [3]. The results are based on simulated XAA patterns which take in to account the parameters and experimental conditions corresponding to modern operational x-ray wigglers. The skewed nature of a typical white beam synchrotron spectrum is taken in to account for. Exact analytical formulas for the resolution of reconstructed atomic sites in both the radial and angular directions are presented. Possible applications of the method are explored by studying the GaN crystal (Figure 1). It was shown that the wavelet filter can be effectively used to obtain projections of the local atomic structure around Ga atoms which in turn allows one to obtain e.g. polarity information. The possibilities of studying the location of magnetic ions in the GaN matrix are presented.

![Figure 1. (a) XAA simulated for the GaN wurzite crystal, (b) the wavelet transform of XAA corresponding to the real-space image of the local structure around absorbing Ga atoms.](image)

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Interferometer for Fourier Transform Spectral Imager in Soft X-ray Region

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The development of Fourier Transform (FT) spectral techniques in the soft X-ray (FTXR, 100eV to 500eV spectral region) has been advocated in the past as a possible route to constructing a bench-top size spectral imager with high spatial and spectral resolution. The crux of the imager is the soft X-ray interferometer. The auxiliary subsystems include a miniature soft X-ray source, focusing optics and a CCD-based detection system. When tuned over a sufficiently large range of path delays, the interferometer modulates a spectrum of a wide-band X-ray source centered at the core wavelength of interest. The spectrum illuminates a target, the reflected signal is imaged onto a CCD, and the data acquired for different frames is converted to spectra in software by using FT methods similar to those used in IR spectrometry, producing spectral images per each pixel. The use of short wavelengths results in dramatic increase in resolution over that for IR. With the predicted <0.1eV spectral and <100 nm spatial resolution, the imager would be able to map core-level shift spectra of light elements such as Carbon to determine chemical compound fingerprint and image intracellular structures. Efficient use of beam energy enables a bench-top instrument, unlike for grating monochromator based techniques.

We have initiated development of FTXR spectral imager based on a Mach-Zehnder type interferometer. The enabling technology for the interferometer is beam splitting mirrors. Not available commercially, attempts by other researchers using parallel slits based beam splitters met with a very limited success. In contrast, our efforts using thin membranes perforated with a large number of small (μm-scale size) holes produced beam splitters with very low surface roughness and high planarity at sub-nm level. Low micro-roughness and high planarity are needed to obtain high wave coherency for the split-off beams and image forming; we reported on progress in beam splitter preparation using state-of-art micro-fabrication techniques at a previous conference.[1] The mirrors are incorporate into the interferometer. Here, we report on design, modeling of performance and assembly of the interferometer, and the results of beam-line experiments at ALS, LBL, to acquire fringes in 40eV-90eV X-ray region. The interferometer was assembled using all vacuum-compatible parts with the four reflecting mirrors resting on a movable flexure stage. Piezo-actuation was used to control stage displacement and mirror alignment. The acquired data exhibited intensity oscillations compatible with interfering beams.

References

Due to diffraction, the resolution of conventional optical microscopes is limited to about 200 nm. Electron microscopes on the other hand, with sub-Angstrom resolution, lack a good penetration depth and thus are mainly restricted to the investigation of surfaces. X-ray microscopes are a complementary tool for scientists enabling sub 50 nm resolution and thereby opening new fields of research.

One of the main requirements of x-ray microscopes is a highly brilliant light source and up until now synchrotrons are by far the best sources available. To improve the availability of x-ray microscopes for a broad community there is the need to further develop table top devices with comparative brightness, which is determined by the photon flux and the source size.

The concept and characterization of a laboratory zone plate based full field x-ray transmission microscope in the so called “water window” is presented. The Lyα emission at 2.478 nm of a liquid nitrogen jet laser plasma source operated with a high repetition thin disk laser system is used as light source ensuring a high natural contrast between carbon and oxygen.

Characterization measurements were performed by using a 10000 lines/mm transmission grating spectrograph for determining the source efficiency. The source size was measured by directly imaging the 2.478 nm x-ray emitting part of the plasma with the multilayer condenser mirror on a CCD camera. High quality pictures of test samples as well as biological specimen with a sub 40 nm resolution were taken. Additionally the feasibility of image enhancement methods for reduced exposure times has been explored.
A new digital radiography system for canvas paintings: a case study from Racconigi Castle

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Within the neu_ART project (“neutron and X-ray tomography and imaging for cultural heritage”), funded by Regione Piemonte (Italy), a team of specialists in different scientific fields coming from University of Torino, Istituto Nazionale di Fisica Nucleare (INFN) and Centro Conservazione e Restauro “La Venaria Reale” is developing a new digital X-ray system expressly designed for painted canvas and panels up to 3 m × 4 m. This system is based on the usage of both linear and time delay integration (TDI) digital X-ray detectors, which allow high spatial resolution and high dynamic range. Moreover, differently from traditional X-rays and computed radiography (CR) plates based systems, scanning time is extremely fast and images are shown in real time.

This system has been widely tested on several XVII, XVIII and XIX century canvas property of the Racconigi Castle and now exposed at Venaria Reale Castle: more than 20 paintings have been analyzed with this new digital radiography apparatus to optimize the acquiring and source parameters. The concrete possibility of testing the apparatus on real cases gave the chance to start the evaluation of its limits and potentialities, thanks to the constant dialogue between the scientists and the professionals involved in the activities of conservation and restoration of these works of art.

Results have been also compared with other imaging techniques based on IR reflectography.
Minimum detection time in XRF images

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A new parameter associated with the acquisition time of a 2D XRF image, which we called the minimum detection time per pixel (MDTP), is presented in this work. XRF images of different biological samples were acquired by a low-cost scanning EDXRF device developed by the author [1,2]. The MDTP depends on the distribution of the elemental concentration, pixel size, the matrix of the sample and the scanning device. Although the XRF scanning can be carried out in a multi elemental mode, the MDTP establish criteria to determine the time of acquisition of an image corresponding to a certain element.

The MDTP results achieved for our device EDXRF on different elements and various types of heterogeneous samples are shown. Values ranging from fractions of miliseconds to several seconds were obtained. For a defined geometry and matrix, a correlation between the MDTP and the concentration of a given element in a X,Y point (pixel) of the sample can be established, as well as a correlation between the intensity of each pixel and the concentration at that point.


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In vivo XRF image in human nail

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The human nail may contain other chemical elements, different from those of its matrix, whose presence and level of concentration could provide interesting and dynamic information in respect of any contamination or disease through the chemical elements accumulated in it during its continuo growth process. In vivo knowledge of the distribution of elements along the nail is very important, since we could point to some kind of health problem, which occurred within the last three or four months time it takes to grow a fingernail from root to end.

This paper presents a new in vivo XRF method in human nails with a quick scan. For this we used a scanning device EDXRF 2D which is particularly adapted for application to human nails elements such as S, Ti, Fe, Cu, Zn and Pb were found in different nails. XRF is possible to achieve two-dimensional images of complete nails as well as partial images along the growth direction of the nail. Exposure times ranging from 5 to 15 s; showing XRF imaging results of the various elements detected in various human nails dead and alive. Prior to in vivo applications the dose absorbed in the tissue by calculations analytically and Monte Carlo simulation [1] was carried out, these results were consistent and are at a tolerable dose level, which makes it possible to use this technique to applications in vivo.


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X-ray μCT study of the Proceratophrys bigibbosa group


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In this paper, we report the preliminary results for comparative morphological characterization of the Proceratophrys bigibbosa species from Brazil using the X-ray computed microtomography (μCT) through SkyScan 1174 system [1]. In south Brazil there are three species in this group: P. avelinoi, P. brauni and P. bigibbosa. The main difference between these three is the body size: it varies from the smaller P. avelinoi to the larger P. bigibbosa, and P. brauni with an intermediate body size [2]. Since the external appearance of these of the group members is very similar, and the body size is not a strict criterion, it is interesting to discover a specific morphological categorization. In this work we tried to use cranium proportions for this aim.

Eighty museum samples were scanned by SkyScan 1174. The reconstructed 3D images were used to visualize and measure the cranium proportions. The main result is that it is already possible to detect differences in the skulls through a qualitative analysis of visual images of the three species. From a frontal view, there are differences in the projection of the tubercles above the ocular cavity between P. brauni and P. bigibbosa, more developed in P. brauni. From a dorsal view, it is possible to see that the surface of the frontoparietals, including their ridges side in P. avelinoi, is much smoother than that of the other two species, and in P. bigibbosa there is a greater projection of the ridge of the frontoparietal, reaching squamosal. It is important to note that our μCT based osteological analysis have been done without destroying the samples.

Application of a portable EDXRF Spectrometer for In-Situ measurement of pollutants in overbank sediments of Mati River (Northern Albania)

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The recent interest in assessment of environmental pollution has created a growing need for in-situ analysis of a variety of pollutants in samples of different kind. Field portable EDXRF instruments offer great possibilities in this kind of activities.

The measuring head of the portable EDXRF spectrometer assembled at our laboratory includes a Peltier-cooled Si-PIN X-ray detector (XR-100CR, AMPTEK INC., USA) and a Cd-109 disc source (740 MBq) mounted in an orthogonal geometry. The spectrum acquisition system consists of the power supply and amplifier (PX2CR), Pocket MCA 8000A and laptop. The spectrometer allows the multielement analysis of soil and sediment samples with acceptable analytical parameters. The calculated detection limits vary from about 2500 ppm for K to about 25 ppm for Cu and up to about 5 ppm for the elements from Rb to Zr. The precision for major elements is generally better than 5%, while for most of the minor and trace analyzed elements its values are within 10%. Generally a good agreement is observed between the measured and recommended concentrations of standard reference materials (SRM).

Overbank sediments of the Mati River are contaminated due to former Cu mining and metallurgical activities in the drainage basin. The concentrations of four major and twelve trace elements are determined by in situ measurements of the different cross sections of overbank sediments. The results show that the main pollutants are Cu, Zn, Fe, As and Se which as confirmed by Factor Analysis are related with two main sources: discharges from copper metallurgy and copper tailings from ore processing plant. In the same time the results permitted not only the evaluation of the contamination but also the possibility to give an indication of the contamination history of the studied sediments.
Fluorochemical Concentration and Distribution Analysis

Using Portable XRF Instrument in Carpet Industry

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The carpet industry applies fluorochemical solutions on carpet fibers during its manufacturing process as a soil resist and stain blocker. To be effective as a soil resist and stain blocker, fluorochemical solutions have to be carefully applied with proper penetration depth and chemical concentration. Fluorochemical solutions from various manufacturers have different chemical formulae, but the same essential element fluorine. Manufacturers use a certified chemical burn test to assure the proper amount of fluorochemicals has been applied on the carpet fibers. This test is performed off-line on randomly selected carpet samples, and it can take several hours at best, even when performed on-site.

This research introduces the use of a portable XRF instrument as a non-destructive tool to rapidly determine fluorochemical concentration on carpet fibers. Due to the instrument limitations, most portable XRF instruments are not capable of detecting fluorine directly, but fluorochemicals may be combined with chemical taggants which are measurable. When properly calibrated, the taggant concentrations are a proxy for the fluorine level on carpet fibers, which in turn represents fluorochemical concentration.

Results in this research showed that when combining a proper chemical taggant with the fluorochemical solution, an accuracy of 150±50 ppm of fluorine can be achieved using a portable XRF instrument. This level and accuracy range is similar to that specified by manufacturers as an acceptable fluorine concentration on carpet fibers. Therefore, a portable XRF instrument can be used in place of the certified chemical burn test, thereby reducing the response time to obtain test results from hours for the chemical burn test to less than five minutes when using the portable XRF technology. This near-real-time measurement system for fluorochemical concentration can also be used as a practical means of determining fluorochemical distribution profiles across carpet samples.
New portable TXRF spectrometer with Ni/C multilayer, Si-PIN detector and rhodium anode low power x-ray tube

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A TXRF spectrometer was constructed using a Ni/C multilayer with 90% reflectivity for the rhodium K-alpha x-ray line, a low power x-ray tube with rhodium anode and a Si-PIN photodiode detector of 25 mm$^2$, 500 µm intrinsic area. A monocromathic excitation was achieved (20.165 keV), avoiding all the background due to the bremsstrahlung radiation. The multilayer used was designed with a central slit for collimation (width 50 µm, height 3 mm); this multilayer mirror was adjusted to the Bragg angle of 0.46° using three precision micrometers. The mirror acts both as a monochromator for the Rh K-alpha line of 20.165 keV so all other x-rays hitting the mirror with a different angle than the Bragg angle are reflected with less that 1% , it means not reflected and suppressed.

The sample carrier reflector of quartz was adjusted to the total reflection angle for 20.165 keV using a mechanism constructed with an aluminum plate and three precision micrometers. This mechanism was also used to hold the Si-PIN detector in such a way that the detector just follows the movement and final position of the sample carrier.

The x-ray spectrometer developed was used to analyze water, soil, fish, herbs, clams, air particles, fertilizers and rock samples with certain gold content. The results of such measurements will be presented here to prove the usefulness of the TXRF spectrometer developed. To obtain the sensitivity curve for the elements between Aluminum (Z=13) to Molybdenum (Z=42) a multi elemental solution was prepared with 5 mg/l of the following elements: Al, S, P, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr and Y. A volume of 20 µl was dried onto the surface of the quartz reflector previously siliconized. The measurements conditions were 35 kV, 0.5 mA, 300 seconds. Figure 1 shows the spectra collected for the sensitivity curve.

![Fig. 1. Rh anode, 35 kV, 0.5 mA, 300 sec, 20 ul, 5 ppm each.](image)
Optimization of a portable EDXRF-equipment for analysis of gold-alloys

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It is well known that an equipment for energy-dispersive X-ray Fluorescence (EDXRF) analysis must be optimized according to the sample under study. The optimization process mainly involves following components:

a. X-ray tube voltage, current, collimation and filtering;

b. X-ray detector collimation and filtering;

c. geometrical arrangement of source, sample and detector.

In this work the optimization is described for a portable EDXRF-equipment which analyses gold alloys; the equipment is composed of a X-ray tube working at 40 kV and 200 μA, and a Si-drift detector.

Gold alloys are generally composed of Au, Ag and Cu at various concentrations, and following main X-ray lines can be excited and detected: Au-M at 2.12 keV; Ag-Lα at 2.98 keV; Ag-Lβ at 3.2 keV; Cu-Kα at 8 keV; Cu-Kβ at 8.9 keV; Au-L1 at 8.5 keV; Au-Lα at 9.7 keV; Au-Lβ at 11.5 keV; Au-Lγ at 13.4 keV; Ag-Kα at 22.1 keV and Ag-Kβ at 24.9 keV.

It is impossible to optimize at same time the EDXRF-equipment for the low energy X-rays (from 2 to 10 keV) and for the medium energy X-rays (from 10 to 25 keV); In presence, for example, of a Au-alloy with a low Ag-content, the low-energy tail of the emitted bremsstrahlung (BS) beam must be strongly filtered. At the contrary, in presence of a Au-alloy with a low Cu-content, and/or when Au-M and Ag-L lines are important to differentiate an homogeneous gold sample from a gilded copper or a tumbaga sample, the X-ray tube should work at low voltages. Two different measurements must be carried out:

a. In the first case the X-ray tube should work at 35-40 kV, and the emitted beam collimated with (for example) Sn or Ag cylinders, and strongly filtered; also the detector entrance must be collimated and filtered. The result is a BS-beam practically extended from about 20 keV to 35-40 keV; the secondary XRF-spectrum of a gold alloy contains Cu-K, Au-L and Ag-K lines respectively.

b. In the second case the X-ray tube should work at about 10 kV; the output beam is collimated but not filtered; the detector entrance is collimated, but no filter is needed. The result is a beam extended from about 1 keV to 10 keV; the secondary XRF-spectrum of a gold alloy contains Au-M, Ag-L and Cu-K lines respectively.
The Roman wall paintings from Viminacium- analysis of the pigments

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Viminacium, the former capital of the Roman province Upper Moesia is located in the eastern Serbia, at the right bank of the Danube River. This archaeological site includes the remains of a Roman city, military camp and necropolises which date back to the period between the first and middle of the fifth century A.D. As an example of a protected archaeological site, Viminacium became the unique and significant Archaeological Park. Among the findings from this archaeological site, a very important role belongs to the wall paintings rendered in fresco technique. Generally, wall paintings of the ancient period in Serbia are not much preserved and this fact makes Viminacium as a more important site, because it has specially preserved wall paintings, as well as its fragments.

This paper presents the results obtained for the pigment analysis on wall paintings found in Viminacium tombs. The characteristic frescoes removed from four tombs were analyzed. Mobile EDXRF spectrometry technique was applied for the pigments analysis. The aim of the analysis was to establish the palette of pigments that were used, since the analytical examinations of the mentioned frescoes are rather obscure. Additional pigments analysis was performed on the wall paintings fragments excavated in termae, amphitheater, tombs and other buildings. The obtained results define the pigments palette that were used, which can be used for comparative studies of the Roman wall painting in numerous Roman towns on the territory of present day Serbia.
Validation of portable XRF measurements on corroded artistic bronzes by ion beam techniques

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One of the most often used non-destructive methods for elemental analysis when performing field measurements on bronze sculptures is X-ray fluorescence (XRF) analysis based on portable instrumentation. However, when performing routine in-situ XRF analysis on very corroded objects the obtained results are sometimes considerably influenced by the corrosion surface products.

Outdoor bronze sculptures are vulnerable to atmospheric corrosion environments – from acid rain containing sulfates and carbonates in urban-industrial environment, to chlorides in marine environmental exposure, which are main cause of “bronze disease”.

In this work artificially corroded bronze samples were analyzed by a portable XRF instrument using the same methodology and procedures as when performing in-situ analysis on real objects. The same samples were then further investigated using more sophisticated laboratory techniques (micro-PIXE and micro-RBS), in order to gain precise information on the formation of the corrosion product layers for different aging parameters. In this way a correlation was established between the portable XRF results and the results obtained with ion beam techniques, which yield additional and complementary information. Consequently, this knowledge helps in the future when interpreting the spectra obtained during regular field measurements on corroded bronze surfaces using a standard portable XRF with mentioned limitations.
Portable confocal micro X-ray fluorescence (CXRF) setup

for in situ analysis of paint layers

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A new portable confocal micro X-ray fluorescence (CXRF) setup based on polycapillary optics has been developed in the X-ray Fluorescence Laboratory of the Centro Nacional de Aceleradores (CNA). The system consists of a low power (30 W) air-cooled micro-focus X-ray source (Rh anode, 50 kV, 50 μm) [1,2], and a super silicon drift detector (25 mm² size, 500 μm thickness). In the excitation channel, a polycapillary mini-lens (25 μm at 10 keV) is used in confocal geometry with a polycapillary semi-lens (27 μm at 10 keV) in the detection channel. Scanning of the sample is performed by a computer controlled motorized x-y-z stage with submicrometric precision. The system is completed with illumination and imaging devices.

This setup is primarily designed to obtain in situ compositional depth profiles of artistic paintings, thus providing a non-invasive and non-destructive method suitable in cultural and historical heritage studies [3,4]. The design and preliminary results about the performance of the confocal system are presented in this work, together with the analysis of multilayered paint samples.

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Design Factors Affecting Performance of Portable and Handheld XRF Analyzers

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Portable and specifically handheld XRF analyzers are not miniaturized versions of large, laboratory instruments but are designed from ground up. Small overall size of these instruments creates unique challenges which need to be properly addressed. While manufacturers make every effort to design instruments easy to operate and rugged, it is beneficial for the user/operator to learn what to pay attention to as to obtain the best results.

For example, because of relatively short - on the order of millimeters - distances from x-ray source to sample and from sample to detector even small misplacement of sample may adversely affect the results. Similarly, selection of materials of construction close to sample support is critical for low analytical background. Even changes of air temperature contained between sample and detector may affect the results. Also critical is selection of materials inside detector capsule and precision of assembly of the detector itself.

These and many other factors specific to handheld analyzers are discussed and illustrated with real examples, followed with proposed solutions.
Portable X-Ray spectrometer for fast and high-resolution XRF analysis in cultural heritage applications

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A novel compact, portable and reconfigurable X-ray fluorescence spectrometer designed for high rate and high resolution spectroscopy will be presented and its performance will be discussed.

The spectrometer is based on a 25mm² active area Silicon Drift Detector (SDD) characterized by an energy resolution of 125-130 eV on the Mn-Kα line (5.895 keV) at 3-4 µs shaping time at -50°C (Peltier cooled), peak-to-background ratio of the order of 10,000 and silicon thickness of 500 µm. The excitation source is a low power 8W, 50kV, transmission X-Ray tube (Rh, Mo, W, Au or Ag anode) that can be equipped with several types of pin-hole collimators and filters to reach the best spatial resolution and excitation efficiency in different applications. The geometry of the source and detection system and the large solid angle of X-ray collection are optimized to obtain high counting-rate capability even if a low power X-ray tube is used. In order to fully exploit the high rate performances of the detector, the spectrometer is equipped with a fast read-out electronics and a high throughput Multi-Channel-Analyzer that can transfer spectra to a PC by USB2 port or by wireless Bluetooth connection. The compact detection head (Fig. 1) is completed by many other sensors as a video-camera, a sonar and lasers for fine positioning and other anti-shock controls. The main detection head can be installed into a shielded box and mounted on a five axis X-Y-Z-θ₁-θ₂ remote controlled motorized stage that is responsible of sample scanning for automatic 2D elemental maps on 3D-surfaces. The spatial resolution is limited to 500 µm by the X-ray spot obtained with pin-hole collimators.

Finally the data are processed by a dedicated software that performs an automatic analysis of the spectrum allowing the identification of the elements that are present in the sample, the fitting of the spectra, and an iterative Fundamental Parameters (FP) analysis to provide the user with the quantitative elemental composition of the sample, as well as the on-line images of elemental mapping acquisitions.

The project is developed in the framework of the POR FESR Lombardia 2007-2013 “Valorizzazione del patrimonio culturale” ID-14481639 for cultural heritage conservation in Italy, and several examples of analysis of prestigious works of art will be presented and described. Other applications in the field of industrial technology and materials analysis will be shown as well.

Fig.1. The compact detection head with inside the complete X-Ray SDD detection unit, X-Ray Tube, service sensors. Overall dimension 250x167x110mm, weight <2kg. The unit can operate simply with power connection (12V DC) and a PC with USB2 or Bluetooth connection.
For the fluorescent X-ray spectra excited with the energy near or around the absorption edge, the spectral change generally appears in the profile. One of the important phenomena under such excitation condition is the process that an inner shell electron is excited to any unoccupied orbital just below the valence band (resonance excitation) and the subsequent electron transition from an occupied orbital to inner shell is caused (RIXS). On the other hand, in the case that no resonance excitation occurs in the atom, the spectral change can be also observed in the excitation energy region just below the absorption edge (electron Raman scattering). This kind of change can be interpreted to the excitation of inner shell electron to the virtual level that is described as the partially unoccupied level. Thus, the emission spectrum profile appears in the form that is missing in the high energy side of the spectral profile in the fluorescence region. When the excitation energy goes just under the threshold for the ejection of the electron to the vacuum level, the profile and peak position of the x-ray spectrum begin to change. It is considerable that the point between the fluorescent X-ray region and electron Raman scattering region should correspond to the X-ray absorption edge, and this fact gives the practical and physical method to decide the energy value of absorption edge clearer than the direct measurement of the absorption edge.

The experiments were executed for the X-ray emission spectra in Fe and Co, respectively at SPring-8 BL14B1. The high resolution X-ray fluorescent spectra were measured using a RIGAKU system 3570EMF with double-crystal type spectrometer [1, 2].

The result of the measurement of Co $K\alpha_{1,2}$ of metallic Co is shown in Fig.1, for example. $K\alpha_{1,2}$ spectra show the clear edge at 7707.2eV. The energy position of this value can be defined as the absorption energy value of metallic Co $K$-edge.

Probing the Ba 5d states in BaTiO$_3$ and BaSO$_4$: A resonant x-ray emission study at the Ba-L$_3$ edge

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We have directly probed the Ba 5d states in the ferroelectric barium titanate BaTiO$_3$ using two bulk-sensitive spectroscopic probes, resonant x-ray emission spectroscopy (RXES) and x-ray absorption spectroscopy in the partial fluorescence mode (PFY-XAS) at the Ba-L$_3$ edge. The results are compared with those of the non-ferroelectric barium sulfate BaSO$_4$.

The experiments were carried out using synchrotron radiation at the BL-15XU beamline of SPring-8 [1]. It was found that while the RXES spectra point to a localized character for the Ba 5d states in both compounds, the main peak of the PFY-XAS spectrum, corresponding to the dipolar transitions from 2p to 5d, is found to be significantly broader for BaTiO$_3$ than for BaSO$_4$. On the basis of band structure calculations, this broadening is ascribed to strong hybridization between the unoccupied Ba 5d and O 2p states in the ferroelectric phase. This suggests that the hybridization between the conduction states of the Ba$^{2+}$ and O$^{2-}$ ions, and not only Ti$^{4+}$ and O$^{2-}$, plays a central role in determining the electronic structure of BaTiO$_3$, and is therefore likely to be indirectly correlated with the occurrence of ferroelectricity in this material.

L-edge for the 1st period transition elements

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It is needless to say that the 1st period transition metals are so important for the advance of human culture, and that the revelation of the behavior of these elements gives so necessary item for innovation of materials. Especially, the necessity of chemical state analysis for such element atom is very strong so that K-edge XAFS measurement has widely been applied as the powerful tool. However, the changes of spectrum of the K-edge are generally less obvious than L-edge. Based on these points, this group has executed XAFS measurement of L-edge of 1st transition metal element by the beamline BL05B at New SUBARU, Univ. of Hyogo[1], for establishing the base of practical analysis technique. In this report, some examples of measurement will be presented.

The XAFS spectra were measured by fluorescent X-ray yield method (FY) or total electron yield method (TEY). The high purity powdered reagents were used as the measured samples, except the metallic sample. The powdered samples were fixed on the In foil or double side adhesive conductive carbon tape.

Ti L-edge spectra of anatase type and rutile type TiO2 are shown in Fig.1. The difference of crystal field orbital (eg) can be just clearly observed by means of L-edge measurement.

In Fig.2, the difference between Cu2O and CuO is shown. In this figure, the peaks correspond to CuO appear on Cu2O spectrum, and the origin of these small peaks can be presumed the oxidized product by the moisture of the atmosphere during the preservation period.

More details will be discussed on our poster.

Fig.1 Ti L-edge spectra of Ti oxides (TEY). Fig.2 Cu L-edge spectra of Cu oxides (TEY).

Sulfur is one of the key elements for realizing useful properties of the advance materials, and is important element in the field of bio-materials or environment, etc. However, it is also well known that the chemical state analysis, especially oxidation state analysis, for sulfur is not so easy, even by the XAFS measurement. Because sulfur K-edge exists on the soft X-ray region (around 2.47keV), the example of practical analysis using K-edge XAFS has not been reported so frequently. In addition, the measurement of L-edge which one can expect to get the more close information about the chemical state is seldom reported. Based on these points, this group has tried XAFS measurement of K and L-edge of sulfur by the beamline BL05B at New SUBARU, Univ. of Hyogo[1], for establishing the base of practical analysis technique. The XAFS spectra were measured by fluorescent X-ray yield method for K-edge, and total electron yield method for L-edge. The high purity powdered reagents were used as the measured samples, and were diluted with the BN powder so that the concentration of S atoms may consist with 2% or less for the measurement of K-edge. The powdered samples were fixed on the holder with In foil or double side adhesive conductive carbon tape.

In Fig.1, the measured L-edge spectra of several sulfur compounds are shown. The changes of energy position and spectral shape corresponding to the environments of sulfur atom can be seen. The measured K-edge spectra and close discussion will be presented on our poster.

Fig.1 S L-edge spectra of several sulfur compounds.

In situ XANES and EXAFS analysis of Li$_2$NiTiO$_4$ cathode materials for Li-ion batteries

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Development of the high capacity cathode materials for Li-ion batteries represents significant challenge within the goal to increase energy density of cells. We have recently showed that so called “titanates” with a general formula Li$_2$MTiO$_4$ (M=Fe, Mn, V) could deliver high capacity in the battery [1,2]. The presence of Ti$^{4+}$ in the structure and its strong bond with O$^{2-}$ enables that transition metals can be easily oxidized. Recently we have synthesized another candidate for cathode material from the titanate family: Li$_2$NiTiO$_4$ with rock salt structure. The material showed good electrochemical activity.

Here we present in-situ Ni K-edge XANES and EXAFS analysis of the Li$_2$NiTiO$_4$ cathode material, which provides detailed information on the local symmetry and oxidation state as well as short-range order around Ni atoms during charging and discharging of the Li-ion battery, i.e. extraction/insertion of Li from/to the cathode material. The XAS spectra were measured initially on as-prepared battery and repeated continuously during the first cycle of charging (520 minutes) and discharging (535 minutes) of the battery with a current density corresponding to C/6. The measuring time for each spectrum was 30 minutes, so that 37 XANES and EXAFS spectra were collected. In Ni K-edge XANES analysis, using a high precision linear combination fit (LCF) method with XANES spectra of relevant reference compounds [1,2,3], we monitored gradual changes of oxidation state of Ni cations during lithium exchange. The information is complemented by simultaneous in situ Ni K-edge EXAFS analysis which provided information on deformations of the local structure around Ni cations, accompanying the change of their valence state. The degree of reversibility of the processes on atomic level in one cycle of battery charging and discharging are revealed.

XAS spectra were measured at C beamline of HASYLAB (project II-20080058 EC) and at XAFS beamline of ELETTRA, Trieste (project 20105073). The research was funded by the Slovenian Research Agency (program P1-0112), Centre of Excellence Low-Carbon Technologies (CO NOT) and by DESY and the EU FP7/2007-2013 Programme ELISA (agreement n° 226716).

Micro-Determination of Oxidation States by means of Confocal X-Ray Raman Spectroscopy

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Micro X-Ray Fluorescence (μXRF) analysis is one of the latest branches of XRF. This spectroscopic technique has been quickly developed over the last years, mainly due to the use of synchrotron facilities. Since nowadays 3D-mapping becomes viable in micrometer regime, μXRF is established as an analytical method in a variety of fields, such as material science and environmental sciences, geology, biology, archaeometry, etc. A remarkable field of application is the investigation of stratified materials. This technique was opened up by the arrival of new X-ray optics, especially by the improvement of capillary optics [1]. This optics is widely used in synchrotron beamline setups. In the last few years, quantification procedures reasonably accurate have been developed [1,2]. The most important problem in these quantification procedures is the existence of light elements in the sample from which no fluorescence is detected. This “dark matrix” problem is not yet solved and is now one of the most serious limitations of this technique [2].

Lately, it has been successfully employed X-ray Raman scattering spectroscopy to determine oxidation states of metals [3,4].

This work presents results concerning the possibility of determining the oxidation state of an element, in a three-dimensional regime, by resonant Raman scattering using an energy dispersive system combined with a confocal setup.

A depth scanning was carried out in multilayer samples in the XRF Beamline of the LNLS [5] (Brazil) using a confocal setup. The samples consisted of an arrangement of layers with different diluted transition metal oxides each, over a substrate. These samples were irradiated with monochromatic photons having energy close but lower than the K absorption edge of the elements of interest. The X-ray Raman peaks were analyzed with specific programs for fitting the experimental data to theoretical expressions. After that, residuals were determined in the low energy side of the RRS peaks. Finally, a FFT smoothing procedure, in order to take into account the instrument functions of the detecting system, was applied. The results show an oscillation pattern that depends on the oxidation state of the analyzed element.

The result allows the discrimination of the oxidation state of the elements present in a sample in a 3D-micrometer regime by means of X-ray Raman scattering combined with a confocal setup. In addition, this result could be used as a tool to determine the dark matrix present in a sample with the aim of establishing 3D-μXRF as a reliable and complete analytical tool.

Grazing-Incidence X-Ray Resonant Raman Scattering (GI-RRS)

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As the refractive index for x-rays is less than unity, external total reflection is possible if the glancing angle is less than a critical angle derived from the Snell’s law [1]. This fact gives origin to GIXRF, GEXRF and TXRF, largely proved spectroscopic techniques that allow the study of material surfaces and spectrochemical analysis. Using the GIXRF technique, different depths of a sample can be analyzed by means of the correct election of the incident radiation angle. In this way, analysis of the reflected intensity provide a method for studying surface properties, as variations of electron density with depth (e.g., corrosion, porosity, aging, etc.) with a resolution from Armstrong to hundred nanometers deep [2]. On the other hand, this technique presents a high signal/background ratio, allowing excellent detection limits.

X-ray Resonant Raman Scattering (RRS) is an inelastic scattering process which presents fundamental differences compared to other scattering interactions between X-rays and atoms; when the energy of the incident photon approaches from below to an absorption edge of the target element, a strong resonant behavior takes place. Recently, a spectroscopic technique in formation based in this process showed to be useful to distinguish surrounded chemical environments [3,4].

In this work both total reflection and resonant Raman scattering techniques are used in combination in order to discriminate oxidation states in three cases: a) oxidized nano-layers of stratified transition metal samples; b) pure Cu and Fe foils oxidized in water and salty water respectively and c) arsenic speciation. All of the samples were studied at the XRF Beamline [5] of the Brazilian synchrotron facility. The measurements were carried out in total reflection geometry with incident energy lower and close to the K absorption edge of the element of interest in order to study the RRS emissions. In cases a) and b) the incident radiation angle was scanning around the critical angle.

The RRS spectra were analyzed with specific programs for fitting the experimental data to theoretical expressions. Then, residuals were determined in the low energy side of the RRS peaks. These residuals were treated with FFT smoothing methods taking into account the instrument functions of the detecting system. The residuals show an oscillation pattern that depends of the observed nano-layer, i.e., the local oxidation state of the absorbing atom.

The results show the possibility to obtain detail structural information by means of X-ray Raman scattering in total reflection geometry using a low resolution system, allowing a depth study of the oxidation state with nano-metric resolution.

HPGe and Si-PiN characterization for measurement of continuous photonic emission ($E < 50$ keV) of medical X-ray tubes

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X-ray sources are widely used in medicine: radiodiagnosis, mammography and contact radiotherapy. However, the lack of knowledge on their emission spectra limits the accuracy of the dose delivery assessment. The Laboratoire National Henri Becquerel has launched an in-depth study of the emission of continuous and discrete X-ray sources used in dosimetry. Two semiconductors detectors are discussed: a High-Purity Germanium (CANBERRA Ultra LeGe), and a Silicon PiN (AMPTEK XR-100CR), both cooled and working with dedicated electronics and software (LYNX + GENIE 2000 and PX4 + ADMCA). In the low energy range ($E < 50$ keV), those spectrometers are complementary:

On the one hand, the germanium efficiency is close to one in this range, thanks to its thicker crystal (140 mm$^2$ x 1 cm) and higher Z, but spectrum analysis is complicated by escape peaks of various intensities (area up to 18% of the total absorption peak after K absorption edge).

On the other hand, even though escape peaks can be disregarded in silicon, its efficiency drops after 10 keV (only 3 % at 50 keV) and there is a lot of backscattering in the detector surroundings due to its small size (13 mm$^2$ x 500 µm).

As a result, both detectors were characterized in terms of spectral response and efficiency using a tuneable monochromatic X-ray source (SOLEX at CEA Saclay) in the 3-20 keV range and various radionuclides [1, 2]. The characterization methods and results, as well as the first measured spectra of medical X-ray tubes (High voltage < 50 keV) are presented in this work.

The end of the project aims first at knowing the emission spectra independently of the detector choice in order to reduce dose delivery uncertainty. Then a beam quality criterion could be deduced and compared to actual beam quality indices (HVL) used in dosimetry of medium and low energy X-rays.

Titanium local structure in blue sapphires probed by

X-ray absorption spectroscopy

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Blue sapphire is a variety of gem corundum ($\alpha$-Al$_2$O$_3$) in which its blue color is resulted from the presence of transition metal impurities, i.e. (Fe-Ti) pairs. The local crystallographic structure around these trace elements is therefore essential to understand their influence on the physical and optical properties of blue sapphires. In the present work, two natural blue sapphires, occurred in geological environments related to basaltic and metamorphic rocks, have been investigated by Ti K-edge X-ray absorption spectroscopy (XANES and EXAFS). From X-ray absorption near edge structure (XANES) spectra, in which the edge energy position and the pre-peak feature are similar to those of rutile and anatase, it was possible to conclude that Ti$^{4+}$ ions in both sapphires occupy slightly distorted octahedral sites. A complete picture of Ti local structure was given by X-ray absorption fine structure (EXAFS) analysis. In a basaltic sapphire, Ti$^{4+}$ was found to be localized at Al site in $\alpha$-Al$_2$O$_3$ structure. The mean Ti-O distance in Ti substituted $\alpha$-Al$_2$O$_3$ is 1.95 Å, which is different to the Al-O distances in $\alpha$-Al$_2$O$_3$ (1.86 and 1.97 Å). This study reveals that the substitution of Ti ion in the structure leads to a local relaxation in a host structure. For a metamorphic sapphire, the Ti ions were found in two structures. Linear combination fitting (LCF) results of EXAFS spectra suggest that Ti ions are located at Al site in $\alpha$-Al$_2$O$_3$ structure and in TiO$_2$ rutile.

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Synchrotron based micro-XRF study to assess the uniformity in solid pellets

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Synchrotron based micro-XRF is a useful tool to check for the uniform distribution of the constituent elements in any solid matrix. The micro-XRF beam line BL-16 at Raja Ramanna Centre for Advanced Technology, Indore was used to assess the uniformity of the mixed natural uranium and thorium oxide pellets. These pellets were produced by conventional Powder Metallurgical (PM) Process and Coated Agglomerate pelletization (CAP) process.

Monochromatic x-ray beam of 17.30 keV, selected using a double crystal monochromator, capable to efficiently excite \( L_\alpha \) lines of the two elements was used. A microprobe beam of size ~ 4 x 7 microns at the sample was obtained using Kirkpatrick Baez focusing optics. The pellets produced by the two different routes were measured at both the sides in EDXRF geometry using beam size of 1mm x 1mm. A calibration plot was obtained by plotting average intensity ratios of \( L_\alpha \) lines against the corresponding mass ratios of U and Th in the pellets produced by PM routes. Using this calibration plot, pellets produced from both the routes were analyzed using micro-XRF geometry at five different spots. It was found that the pellets prepared by PM routes showed EDXRF determined values of the two elements very close to the corresponding expected concentrations (on the basis of their preparations) whereas those produced by CAP process showed large differences with respect to the expected concentrations. In addition, the variation in the data obtained from different spots was very large compared to that obtained with the samples produced by PM route. Subsequently, the micro fluorescence measurements performed on the pellets prepared by PM route, in an area of 0.5 x 0.5 mm\(^2\), revealed that the pellets having 20% expected uranium concentration gave values in the range of 8.75% to 18.9% and showed thorium concentrations in the range of 81-91 %, with a positive correlation in the concentrations of the two elements. For the similar samples prepared by CAP process, the Th concentration varied in the range of 22.8 to 83.4 % whereas the U concentration varied from 16.6 to 77.2% and the two elements showed a negative correlation. It was also observed that the samples of lower uranium amounts showed a larger variation in uranium and thorium distribution compared to the pellets having higher uranium percentage. The study demonstrates the usefulness of micro-XRF facility to check the uniformity of the samples prepared by different routes.
New Possibilities for the IAEA Developing Member States for Advanced X-Ray Spectrometry Applications using Synchrotron Light and Charged Particle Beams


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The Physics Section (PS) of the International Atomic Energy Agency (IAEA) supports and fosters through its programmatic activities the development of interdisciplinary applications of laboratory and accelerator based X-ray spectrometry techniques. With support from Technical Cooperation projects the IAEA builds and strengthens the capacity of researchers from IAEA Member states to utilize frontline Synchrotron Radiation (SR) and Ion Beam Analysis (IBA) techniques. However, in the highly competitive research environment of large-scale facilities, beam time can be obtained only on the basis of scientific merit of proposals, selected by review panels, providing limited opportunities for hand’s on training.

The PS-IAEA has initiated in 2011 a research and development project to construct a novel transportable experimental facility to be installed and operated at SR (Sincrotrone Trieste-Elettra) and IBA (Ruđer Bošković Institute, Zagreb) beamlines, accessible through the IAEA for training and research. The IAEA experimental set-up is based on a prototype developed by the Physikalisch-Technische Bundesanstalt and the Technical University of Berlin [1]. It is mainly composed of an Ultra High Vacuum Chamber (UHVC) equipped with an ultra-thin window silicon drift detector, photodiodes and a motorized 7-axis sample manipulator (with four linear stages and three (3) goniometers). This makes possible to move the sample to be investigated in various orientations with respect to the exciting probe (Grazing Incidence - GI analysis mode) or/and the x-ray detectors (Grazing Exit - GE analysis mode).

The UHVC is scheduled to be operational at the new X-ray Fluorescence beam line at Elettra in 2013. The advanced sample handling options in conjunction with the optimized beamline properties (2-13.5 keV energy range, <0.15 mrad beam divergence and spot size at the exit slits ~ 250(hor)X 50(vert) microns) will allow the application of GI-XRF, GE-XRF, Total Reflection XRF techniques and X-Ray Reflectometry (XRR) measurements for nanoanalytics. At the IBA beamline at Zagreb, the UHVC will allow for further exploration of the promising capabilities of the GI-PIXE/GE-PIXE techniques [2, 3]. Targeted analytical applications include the characterization of environmental samples, nanoparticles, energy storage and conversion related micro- and nano-scaled materials [4, 5].

Mineral localisation and complexation in ferritin-expressing wheat grain

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A Synchrotron X-Ray Fluorescence Microprobe has been used to study two types of wheat grain in an effort to access the causes of reduced content of essential micronutrients in the parts of the grain that enter food production. The experiments took place at I18, the Microfocus Spectroscopy beamline at the Diamond Light Source, where two types of grain were studied, a strain over-expressing ferritin and wild type grains.

High resolution distributions of a number of essential minerals were acquired revealing specific sites of accumulation for Fe, Zn, K, Mn and Cu. Of particular interest are Fe and Zn because of their direct involvement in diet related diseases in countries where diets are substantially grain-based.

In principle the modified grain should promote mineral accumulation however the produced metal maps reveal that the elements are not transported into the endosperm but accumulate in the outer crease region therefore constituting them bio-unavailable. This observation suggests that it is not a lack of minerals that is responsible for poor bioavailability but rather their complexation to the surrounding atoms (phosphorus being of great importance) that impedes the transport of the minerals to the inner regions of the grain.

This hypothesis is investigated using spatially resolved X-Ray Absorption Near-Edge Structure (XANES) and EXAFS (Extended X-ray Absorption Fine Structure) spectroscopy in an effort to determine the molecular form of iron and zinc. Modelling of spectra acquired from similar regions of the two grain types suggests differences in the complexation of both metals mainly to phosphorus which could be the link to obstructed transportation and bioavailability.
X-ray absorption near edge structure of Al$_2$O$_3$-Cr$_2$O$_3$ series

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The red color of ruby is caused by Cr$^{3+}$ impurities substituting Al$^{3+}$ in Al$_2$O$_3$ structure. The complete substitution of Al$^{3+}$ by Cr$^{3+}$ produces Cr$_2$O$_3$ which is green color. A series of Al$_2$O$_3$-Cr$_2$O$_3$ samples was prepared, by mixing fine powders of Al$_2$O$_3$ and Cr$_2$O$_3$ chemicals in various ratios, ground together and recrystallized. The samples were ground again for X-ray absorption near edge structure (XANES) measurements to avoid polarization dependent [1]. The measurements were carried out at the Cr K-edge absorption energy of the fluorescence mode using 13-element Ge detector [2]. The XANES spectra showed line-shape transitions with varying Cr$_2$O$_3$ concentrations of 0.125, 0.5, 1, 5, 10, 20, 40 and 100 wt%. There were small transitions between 0.125% and 20% of Cr$_2$O$_3$. The significant transition marked at the Cr$_2$O$_3$ content between 20 and 40 wt%, i.e. possibly at around 30% of Cr$_2$O$_3$. The sample colors apparently turned from pink to dark green with the increasing Cr$_2$O$_3$ variations [3]. The color variations of Al$_2$O$_3$-Cr$_2$O$_3$ were caused by the differences of Cr$^{3+}$ local environment, which were confirmed by the first principle calculation method. This XAS study could be applied on the research in mineral sciences, i.e., the solid solution between corundum and eskolaite mineral series.

The application of mosaic prism lenses for wide band-pass X-ray monochromatisation

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The strong photon energy dependence of the refractive index of materials is applied for wide band-pass monochromatisation of high energy X-rays. For this purpose we employed a refractive mosaic lens, which has reduced passive material compared to a continuous parabolic profile resulting in a larger physical and numerical aperture. Through an appropriate pinhole in the focal plane photons with matching energies pass with few losses whereas photons of deviating energy can be efficiently suppressed. The average energy of the transmitted photons can be tuned by translating the pinhole along the optical axis and even the bandwidth can be changed by selecting an appropriate pinhole aperture and central beam stop. This method of monochromatisation was realized at the ANKA FLUO beamline using a mosaic lens together with a pinhole and beam stop. A photon energy resolution of 2.0% at 16 keV has been achieved.

Oxidation State Analysis of Fe in Volcanic Rocks

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In the field of volcanology, the chemical state, especially oxidation state of Fe which is the major element of the earth, is one of the key points for precise discussion about the mode of eruption. Previously, wet chemical analysis technique or Mössbauer spectroscopy has been used for the decision of the oxidation state of Fe. However, in the case of volcanic rock, obtaining correct result has been difficult in general due to the influences of coexistence elements or technical hardness. In contrast, the author group applied high-resolution X-ray fluorescence spectroscopy (HRXRF) to volcanic rocks for this aim.

The equipment used for HRXRF measurement was RIGAKU 3580E3 of which monochromator was double-crystal type [1]. All the samples were powdered, and were fixed with wax on the Al plate. The standard of oxidation state was \( \alpha-\text{Fe}_2\text{O}_3 \) for Fe\(^{3+} \) and FeTiO\(_3\) for Fe\(^{2+} \), both minerals were synthesized by Prof. T. Fujii, Okayama Univ. FeO is not adequate for standard because it is metastable. All the high-resolution Fe K\( \alpha \) spectra were analyzed by non-linear least square curve fit technique with the measured spectra as the component profiles for the decision of the existence ratio of Fe\(^{2+} \) and Fe\(^{3+} \).

As an example, the results of volcanic rocks of Asama Volcano in Japan are shown in Fig.1. The difference between Onioshidashi lava and the others (pyroclastic fall) is clear. When we will compare with the ratios of Fe\(^{2+} \) and Fe\(^{3+} \), Onioshidashi lava is lower than other pyroclastic falls. The authors will suggest that this difference would be caused by the mode of eruption. The other results and discussion will be presented at the poster. Thus, HRXRF will bring new knowledge for volcanology.

Electron structure and valence state of the new ternary intermetallic compounds: experimental and theory

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High-energy spectroscopy has been used to study the electron structure and valence state of new ternary intermetallic compounds, which crystallize in the CeNiSi₂, ThMn₁₂, ThCr₂Si₂ and HfFe₂Si₂ types. The calculations of electron energy bands E(k) and partial DOS for compounds were performed by the semi relativistic linear muffin-tin orbital method (LMTO) without considerations of spin-orbit interactions. Effective filling numbers of electrons in different bands of components in R.E.M₂X₂ (R.E = Sc, Y, Ce, Yb; M= Fe, Co, Ni, Cu, Pd, Rh; X= P, Si) compounds have been calculated. On the basis of the obtained, photoelectron, X-ray emission spectra and calculation of density of total and partial electron states in R.E.M₂X₂ compounds, the localization of electron of s- and p-states of Si (P) has been established within the energy ranges 14-7 eV and 7-2 eV, respectively. These states of Si (P) are hybridized with 4p-states of M atoms. The electron occupation of the d-states of the M atoms has a dominant influence on the degree of their hybridization. Between the experimental and calculated X-ray emission spectra R.E.M₂X₂ good agreement has been obtained.

The crystal structure of new representatives of the CeNi₈.₅Si₄.₅ structure type (substructure of NaZn₁₃ type) and RM₅Si₃ (UC₅Si₃ and YNi₅Si₃ structure types) was determinate. X-ray phase and structure analyses were used to specify the composition of the samples. The elemental composition of the compounds was confirmed using the scanning electron microscopy. Magnetic and electrical properties of these compounds were measured. High values of the Curie points were observed in RM₅Si₄ compounds in spite of the low magnetic moments per atom (~0.4 μB).

LIII - absorption spectra Ce and Yb in ternary YbNi₄In, YbNiIn₄, Ce(Yb)M₂X₂ and Ce(Yb)M₄X₈ compounds were obtained at 78K and 300K using a tube spectrometer equipped with an RKD-01 co-ordinate detector. The mixed valence state of Ce and Yb was obtained in the YbNiIn₄, Ce(Yb)M₂X₂ and Ce(Yb)M₄Al₈ compounds.

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Quantitative Determination of the Oxidation state of Fe in Fe₃O₄ by High-resolution X-ray Fluorescence Spectroscopy


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The oxidation state analysis of Fe in several kinds of compounds or materials has strongly been requested, because this information is so important to reveal the expression mechanism of the property of Fe contained materials. In addition, any technique for this aim should be non-destructive in practical. On the basis of this point, this group has been investigated for the application of the combination of High-Resolution X-ray Fluorescence Spectroscopy (HRXRF) and non-linear least square curve fitting analysis using measured spectra [1] as the component profiles. The x-ray spectral measurement was executed for using RIGAKU 3570EKI system. This system had the double-crystal monochromator with (+, +) setting [2,3], and two Si(220) crystals were used as analyzer.

High-resolution Fe Kα₁,₂ spectrum of Fe₃O₄ and the result of the curve fitting analysis are shown in Fig.1. The result of the analysis shows that about 90% of Fe in Fe₃O₄ should be Fe³⁺. The similar result was obtained from the experiment using the same type spectrometer in the SPring-8 BL14B1. In contrast, the case using Fe Kβ was shown in Fig.2, and the result of the analysis show the reasonable conclusion as Fe²⁺:Fe³⁺ = 1:2. Thus, it can be concluded that using Fe Kβ is suitable for the quantitative oxidation state analysis in practical. The result of the oxidation analysis of Fe in RuFeO₃ will also be presented in the poster. The difference between Kα₁,₂ and Kβ₁,₃ spectra has been investigated on the basis of the considerations.

Fig.1 The result of the analysis using Fe Kα.  Fig.2 The result of the analysis using Fe Kβ.

The Observation of The Profile Change of Fe $K\alpha_{1,2}$ spectra using excitation energy around $K$-absorption Edge

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When the oxidation state analysis of Fe using high-resolution X-ray florescence spectroscopy is carried out, it has often been observed that Fe$^{2+}$ state is almost covered by Fe$^{3+}$ state using W or Rh target, sufficiently higher excitation energy than Fe$K$-absorption edge. One of the typical examples is the case of Fe$_3$O$_4$. For investigation about this phenomenon by means of RIXS, the observation of the spectral change of Fe $K\alpha_{1,2}$ emission lines was executed for in the Fe oxides changing the excitation energy around Fe $K$ threshold.

The high-resolution Fe $K\alpha$ measurement was executed using RIGAKU 3570EMF system in BL46XU in SPring-8, which had the double-crystal type monochromator [1,2] with two Ge(111) crystals.

Fig.1 shows the measurement result of Fe $K\alpha_{1,2}$ spectra in Fe$_3$O$_4$ with the excitation energies. All the spectra shown in this figure were analyzed with non-linear least square curve fitting method with measured spectra as the component profiles [3] for the decision of the existence ratio between Fe$^{2+}$ and Fe$^{3+}$. The result of the analysis and the changes of the peak top intensity of Fe $K\alpha$ in proportion to the excitation energy was shown in Fig.2. It is so interesting that the spectrum of Fe$_3$O$_4$ excited with 7117eV shows the almost same profile of FeTiO$_3$ (Fe$^{2+}$). And, the investigation about this phenomenon has been discussed at present.

Oxidation State Analysis of Sulfur in Glass Samples by high-resolution X-ray Fluorescence spectroscopy

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Sulfur is one of the important elements for the several properties of several kinds of glasses. Especially, revelation of the oxidation state of sulfur is important for understanding the mechanism in which the property of glass occurs. This information about the oxidation state should be obtained as the average information of sample bulk, not from the surface or near surface region. Thus, high-resolution X-ray fluorescence spectroscopy (HRXRF) is more adequate than X-ray photoelectron spectroscopy or any other surface analysis technique for this aim. In this report, the example of the application of the combination of HRXRF and non-linear least square curve filling technique using the measurement spectra as the component profiles \(^{[1]}\) is reported.

The HRXRF measurement was executed for using RIGAKU 3570EKI system. This system had the double-crystal monochromator with (+, +) setting \(^{[2]}\), and two Ge(111) crystals were used as analyzer.

Fig.1 shows the typical changes (peak shifts) of the S K\(\alpha\) due to the oxidation state. The energy difference between S\(^{6+}\) and S\(^{2-}\) is 1.2eV or more, and width of S\(^{6+}\) peak is slightly narrower than S\(^{2-}\). Using these spectral changes and the curve fitting analysis, the existence ratio between S\(^{6+}\) and S\(^{2-}\) can be decided from S K\(\alpha\) of sample spectrum. In Fig.2, three components were assumed for the curve fitting analysis, and the almost same result was obtained shown in the result which obtained with two components. This result means the two points; one is that the number of component, corresponding to the number of chemical state, can be decided objectively by this combination method. Another is that the curve fitting analysis is also practical in the case of low statistic measurement, because both curve fitting method and smoothing method depend on the same base, least square principle.

The other results of glass samples will be presented on the poster.

Chemical speciation by laboratory based X-ray spectroscopy with a newly developed HAPG von-Hamos spectrometer

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We present a new laboratory spectrometer for chemical speciation by means of high resolution X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES). This wavelength-dispersive spectrometer is designed in von-Hamos geometry. Key component is a sagittally bent HAPG (Highly Annealed Pyrolytic Graphite) crystal which is used as the dispersive element. This recently developed type of pyrolytic graphite delivers high energy resolution (E/ΔE=2000 in the first order of reflection) in combination with high integral reflectivity and facilitates a transfer of typically synchrotron based methods like XAS and XES to a laboratory scaled instrument.

In a series of experiments in the transmission mode (XAS) the performance of the spectrometer for chemical speciation was tested. The determination of the chemical species can be carried out by comparing the obtained absorption spectra to spectra of reference materials which show characteristic features in the XANES and EXAFS region. The main advantage of this setup is that a micro-focus X-ray tube can be used as source and, thus, greatly increases the accessibility of this method. On the other hand the samples have to be well prepared because of the transmission geometry. A comparison of the acquired spectra to synchrotron XAS spectra shows that the performance in terms of energy resolution is reduced. However it’s still sufficient to distinguish between different chemical species. This is demonstrated by means of a set of iron samples and mixtures of them.

Another method for chemical speciation which is complementary to X-ray absorption spectroscopy (XAS) is X-ray emission spectroscopy (XES). The main experimental advantages of this method compared to XAS in the transmission mode are the possibility of microanalysis due to the use of polycapillary lenses and the elimination of the sample preparation by operating in the emission mode. After a test with low power micro-focus X-ray tubes we could demonstrate the feasibility of chemical speciation by XES with a table top setup with rather high data acquisition times. To overcome this we developed a spectrometer concept with an improved efficiency and are currently building a new prototype which will facilitate XES measurements within less than one hour.
X-ray transition lineshapes on material characterization, using flat crystal spectrometer

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X-ray transition lineshapes measured using high resolution energy spectroscopy have been extensively applied for the elemental analysis in all fields of materials science. Identification of the variations of X-Ray line profiles and spectral positions give information concerning the chemical environment and the local chemical bonding. Usually, high energy resolution demands intense excitation beams (e.g. synchrotron) and either curved crystal or double crystal spectrometers. However, these sophisticated studies are implemented in demanding experimental environments (microscopes or synchrotron); it is therefore of great technological importance to extract comparable information using conventional, lab-scale instrumentation for the colloquial analysis of materials chemistry.

In the present work we show that a conventional flat crystal X-ray fluorescence spectrometer (Bruker, S4-Explorer), with the appropriate configuration, can achieve this goal. The necessity for the highest possible energy resolution and sufficient measuring statistics demands optimization of geometrical aberrations, diffraction crystal characteristics and measuring Bragg angles.

Characteristic case studies are discussed. Aluminum K\(\alpha\) and K\(\beta\) X-rays are used as probe to investigate the oxidation of AlN thin films and the electronic properties and bonding characteristics of AlN-Ag nanocomposite protective and decorative coatings. Carbon K\(\alpha\) X-rays are used for the determination of the sp\(^2\)/sp\(^3\) ratio in polymers. Si K\(\beta\) X-rays allows to verify the adsorption of [3-(2-Aminoethylamino)propyl]trimethoxysilane on expanded perlite (a SiO\(_2\) based volcanic glass) and the growth of poly(dimethylsiloxane) (PDMS) thin films. Phosphorus K\(\beta\) are used as a short range structural probe for the relative fractions of Q\(^n\) (n corresponding to the number of bridging oxygens) tetrahedral units of phosphate glasses with high magnesium content.
The study of Eu(III) sorption to MnOOH by using a high-resolution X-ray fluorescence spectrometer

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A X-ray fluorescence spectrometer based on Rowland circle geometry in the beamline BL14W1 of Shanghai Synchrotron Radiation Facility was developed. The high-resolution X-ray fluorescence spectrometer is composed by a spherically curved silicon crystal (or crystal array), detector and sample holder. The analyzing plane is horizontal, the bent crystal, the sample and the detector just beside the sample are located on the Rowland circle. The crystal was bent to a radius of 100 cm or 18.2 cm on a glass substrate with 4 inch diameter. The size and radius of curvature directly affect the solid angle to detect the fluorescence. At entrance angles close to back scattering the energy resolution can reach about smaller than 1 and 3 eV respectively for the two kinds of crystals. The applications in the fields of X-ray emission spectroscopy (XES) and high-resolution X-ray absorption near edge spectroscopy (XANES) can be carried out by using this technique.

To assess the potential pollution of the natural environment, we need knowledge of the sorption mechanisms and speciation of radionuclides on natural minerals. This method was used to study Eu(III) retention on MnOOH as a function of various environmental factors. The fluorescence peak Lα of Eu(III) and the fluorescence peak Kα of Mn is discriminated which is difficult to be discriminated using conventional XAFS technique with solid-state detector. The high-resolution X-ray fluorescence spectrometer mentioned above and the detail experimental results will be presented in this paper.
Kα, X – ray satellites of the elements in the Z range 32 - 38

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Data on Kα X-ray satellites beyond Z=32 are scarce. The energies and relative intensities of KαL\(^1\) and KαL\(^2\) X-ray satellites of Ge, As, Se, Br and Sr, which fall in the Z range 32-38, are measured in the present study by photon excitation using a crystal spectrometer with Lif 420, a crystal with 2d= 1.8 Å, optimum for these X-rays. The experimental values of the energy shifts and relative intensities of these satellites with respect to the Kα diagram line are compared with the theoretical estimates for the cases available. Their Z dependence is studied and Z systematics valid up to Z=38 are evolved supplementing the present results with the previous data available up to Z= 32.

The theoretical values of KαL\(^1\) relative intensity based on the combined (1s 2s\(^-\))\(^{-1}\) and (1s 2p\(^-\))\(^{-1}\) multi-vacancy production probabilities calculated by Mukoyama and Taniguchi [1] using non-relativistic Hartree Fock Slater formalism with sudden approximation, reported for Ge, As, Se and Br are found to be higher than the present experimental values. No theoretical values of KαL\(^2\) relative intensity are available for comparison.

The KαL\(^1\) relative intensity is found vary as Z\(_{\text{eff}}\)^{-4.837}, where Z\(_{\text{eff}}\) = Z - σ, where σ is the Slater’s screening constant taken as 6.828 for the L shell [2]. Similarly the KαL\(^2\) relative intensity is found vary as Z\(_{\text{eff}}\)^{-4.301}.

Following the procedure adopted by Torok et al [2] in evolving a semi-empirical formula for the prediction of KαL\(^n\) satellite energy shifts, we arrived at the following relations which are based on experimental values available till to date including the present experimental values,

\[ \Delta E (K\alpha L^1) = 1.9359 Z_{\text{eff}} - 2.4935 \text{ eV}, \quad \Delta E (K\alpha L^2) = 2.99606 Z_{\text{eff}} - 4.449 \text{ eV}, \]

which are in good agreement with the experimental values over the Z range 11- 38.

The above energy shifts are with respect to the composite energy of the Kα\(_{1,2}\) peak. This peak is well resolved in to its constituent lines Kα\(_1\) and Kα\(_2\) in the present work and when the energy shifts of KαL\(^1\) and KαL\(^2\) separately with respect to Kα\(_1\) and Kα\(_2\) are plotted versus Z\(_{\text{eff}}\) for these five elements, linearity is maintained but with altered slopes.

Crystallite size and strain study of nickel oxide nanoparticles by X-ray diffraction profile analysis

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We have synthesized nickel oxide nanoparticles by chemical method using four different concentrations of cetyltrimethylammonium bromide (CTAB). The X-ray diffraction patterns were obtained on a Rigaku X-ray diffractometer using Cu Kα radiations. The diffraction peaks of NiO were clearly observed, which are in agreement with those of standard NiO of cubic structure. The presence of peaks at (111), (200), (220), (311) and diffraction pattern confirm the formation of face centered cubic (fcc) structure. All the synthesized samples of NiO show a single phase formation. The lattice parameter, crystallite size and of the nanostructured nickel oxide have determined by Scherrer formula. The crystallite size found to be 10 nm, 12 nm, 20 nm and 23 nm for these nanoparticles. When nanoparticles are not perfect crystals, microstrain contributes to the line broadening of diffraction peaks. The microstrain for nickel oxide nanoparticles have been calculated by using the Williamson–Hall plotting. CTAB is playing an important role to control the size of the nanoparticles. The crystallite size is found to increase while strain reduces by decreasing the concentration of CTAB. The decrease in crystal size as an increase in surfactant concentration is related to the selected adsorption of ions and their respective counter ions on the crystal faces during the growth of nanoparticles. The broadening of different peaks in diffraction pattern is due to the change in particle size, which occurs when a sample is made up of very small crystallites. It is observed from the Transmission Electron Microscopy (TEM) images that the particle size possesses a small and narrow size distribution in the range of 5 nm to 25 nm, and the mean diameter (taken as average particle diameter) is about 18 nm. We have noticed that the mean particle size determined by TEM is in good agreement with the average crystallite size calculated by Scherer formula from the XRD patterns.
Crystallographic behavior and determination of stacking order of bi- and trilayer graphene

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Few layer graphene has been shown to exist in various crystallographic sequences that can strongly modify their electronic behavior. Here, we present X-ray diffraction, Raman analysis and electron diffraction analysis of bi and tri-layer graphene sheets synthesized through modified Hummers method. X-ray diffraction pattern of as synthesized graphene reveals a shoulder around 10.29° and a peak at 26.32° with inter-planer spacing of 0.856 Å and 0.337 Å respectively. Raman spectral analysis shows the presence of G band at 1583 cm\(^{-1}\) without any defect caused due to oxygen derivative functionalities. A distinction is made between bi and tri-layer graphene sheets on the nature of 2D band in Raman spectra positioned around 2715 cm\(^{-1}\) that have accordingly shown fourth order and third order Gaussian fitting. Apart from that, 2D peak also reveals the presence of rhombohedral (ABC) stacking order in tri-layer graphene sheets. The intensity of electron diffraction spots in consequent hexagonal rings of graphene further validates the finding of Raman analysis about its number of layers and stacking order that extends up to 5-7 μm in length.

Keywords: X-ray Diffraction, Graphene, Raman
The Change of high-resolution Nb Lα spectra of LiNbO3

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LiNbO3 is the most popular ferroelectric material and is used a lot of industrial field. However, almost of close property or behavior, relation between stoichiometry and crystal structure for example, has not be understood [1]. It can be said that most of production process was established by trial and error. Thus, the establishment of practical characterization technique is strongly requested. On the other hand, it is well known that the change of characteristic X-ray obtained by high energy resolution measurement shows the good correspondence to the chemical state. In this report, the energy change of Nb Lα between stoichiometric and congruent LiNbO3 measured by high-resolution X-ray fluorescence spectroscopy is presented.

All the measurement was executed with RUGAKU 3580EKI system which had the double crystal type monochromator [2]. The (001) plane of all the LiNbO3 samples was measured as the analysis surface. In addition, metallic Nb and Nb2O5 were also measured. For the investigation about the energy change of Nb Lα, the cluster calculation with DV-Xα was performed.

The measurement result of the peak sift of Nb Lα is shown in Table1. The Nb Lα peak of Nb2O5, stoichiometric LiNbO3 (SLN) and congruent LiNbO3 (CLN) appear at the almost same energy position. In contrast, Mg doped CLN shows small shift to low energy side. It can be assumed that Mg doping process should make Nb move to Li site. Thus, the cluster calculation was executed using the models of NbO6 7- of which spatial arrangement were same as Nb site or Li site. The result of the calculation is shown in Table.2, and it can be seen that the energy of Nb Lα from Li site is smaller than that of Nb site. This calculation result means that Nb Lα peak shifts to low energy side as substitution quantity to the Li site increases. And, this might be one of the possible reason about the shift of Nb Lα of Mg doped CLN.

<table>
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<th>Nb foil</th>
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<th>NbO6 at Li site</th>
<th>NbO6 at Nb site</th>
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<td>calculated energy</td>
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<td>2160.216</td>
<td>2160.153</td>
<td>2160.222</td>
</tr>
<tr>
<td>shift (from metal)</td>
<td>0.000</td>
<td>0.255</td>
<td>0.193</td>
<td>0.262</td>
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In-situ XPS study of ultra-thin TiN$_x$O$_y$ films
grown by ion beam sputtering

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The important task in the formation of ultra-thin films of titanium nitride is precise control both the N / Ti ratio in formed structures and the content of oxygen impurity. This is due to the fact that the presence of oxygen in titanium nitride films strongly affects the number of properties including conductivity, microhardness, adhesion, diffusion coefficients. Monitoring the oxygen content is extremely important also because the formation of titanium oxide is thermodynamically more favorable than the nitride and a number of undesirable titanium oxides can be formed even with a small amount of oxygen impurity. This is especially important in the formation of titanium nitride films by ion-plasma methods, in particular by ion-beam sputtering. In this case, additional source of oxygen in the film is a gas (nitrogen, argon), which is used in the preparation of TiN films by reactive sputtering. On the other hand, the presence of oxygen in titanium nitride films leads to a large range of functional materials TiN$_x$O$_y$, whose properties are strongly dependent on the N / O ratio. Thereby, X-ray photoelectron spectroscopy (XPS) due to its high surface sensitivity and excellent elemental sensitivity is an indispensable tool in the study of ultra-thin films of titanium nitride and oxynitride obtained by ion-plasma methods.

The current work presents in-situ study by high-resolution X-ray photoelectron spectroscopy of TiN$_x$O$_y$ films with about 5 nm thickness obtained on silicon by low-current ion beam sputtering of titanium target in nitrogen atmosphere. Titanium of 99.99% purity was sputtered by argon ions with the 5 keV energy and 10 $\mu$A/cm$^2$ ion current density. The influence of substrate temperature during ion beam synthesis and thermal annealing on the chemical state of TiN$_x$O$_y$ films was studied in details. It is shown that after deposition there is more nitrogen and less oxygen in the films formed at growth temperature 350°C, than in the films obtained without substrate heating. After thermal annealing at 750°C oxide content in the films grown at low temperature is significantly reduced, but remains in comparison with films formed at 350°C, where oxygen disappears completely. XPS shows formation of different amounts of saturated and unsaturated N-Ti bonds at different growth temperatures that influences on changing of chemical composition of the films during annealing. Analysis of the film-substrate interface after annealing at 750°C shows a greater diffusion of silicon atoms in the films with higher oxygen content. Thus, changing the substrate temperature during ion beam sputtering it is possible to affect the oxygen content in deposited films forming both oxygen free TiN films for use, for example, as diffusion barriers and TiN$_x$O$_y$ films for applications in optoelectronics.
Confocal micro X-ray fluorescence (CMXRF) is a nondestructive and three dimensional method capable of analyzing a defined volume of the sample material laterally and in depth. This is enabled by using two X-ray optics that are limiting a) the area of excitation and b) the origin of the fluorescence signal. Combined with a crystal monochromator and high brilliance source available at synchrotron facilities it is possible to measure XANES (X-ray absorption near edge structure) spectra elucidating the chemical species of an element at the surface and with restrictions also in depth. Therefore this technique is suited for three-dimensional research of inclusions, as well as for layered structures and surface areas. This is especially interesting for precious or limited sample materials or time resolved (in situ) analysis.

With the demand for energy storage ever increasing, a very interesting sample material for three dimensional analyses are electrode materials of Li-ion batteries. They have been the subject of intensive research in recent years, because they offer the highest energy density. A high energy density is needed for the use in electronic vehicles or the storage of the only partly predictable power sources wind and sunlight. Improving the cathode material is essential, since it primarily sets the energy density, rate capability and cost of Li-ion batteries. One promising cathode materials is the high voltage spinel LiNi0.5Mn1.5O4. It displays a remarkable discharge voltage plateau at around 4.7 V and the material is inexpensive and environmentally benign.

The oxidation state of manganese (and nickel) is crucial for the high voltage capacity and the stability against corrosion. The oxidation of Mn3+ to Mn4+ signs responsible for the 4.1 V plateau, the capacity at 4.7 V is attributed to the Ni2+/Ni4+ couple. Consequently, when there is more Mn4+ in the LiMn1.5Ni0.5O4 spinel, more Ni2+ will be oxidized and the capacity at 4.7 V is improved.

However at this high voltage a possible corrosion between the electrolyte and the cathode surface is a major concern, especially at elevated temperatures (60°C). The electrolytic salt LiPF6, most commonly used, can readily decompose reacting with trace amounts of water and form HF that is continuously attacking the cathode material. This leads to the disproportionation 2 Mn3+ solid -> Mn4+ solid + Mn2+ solution. The Mn2+-ions are readily dissolved in the electrolyte and are found to deposit on and in the SEI layer of the anode. This process causes a huge increase in charge-transfer impedance and is mainly responsible for cell deterioration. Studies using Raman-Spectroscopy show that the formation of λ-MnO2 out of Mn4+ on the cathode surface occurs locally. Therefore a detailed, three dimensional knowledge of the oxidation states of the included metal ions is of great interest.

The combination of CMXRF and XANES allows to probe exclusively the surface and if absorption can be treated properly also deeper layers of the electrode. The text of your abstract should be entered here. This is the standard font (Times New Roman 12) and layout for the individual paragraphs. To use this template, replace the text in this template with your text. The "Enter" key will take you to a new paragraph. This paragraph represents the standard font and layout for individual paragraphs.
Development of calibration samples for TXRF and XRF by means of multilayer production technology

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Both the increasing demand for lower uncertainties of analytical results in XRF and the increasing sensitivity of TXRF instruments are requiring improved calibration standards and reference samples of very low mass fractions in the range of ng/mm² or less with homogeneous distribution of the element(s) over the sample. In this range standard droplet samples reach their limits due to agglomeration and crystallization in the drying process of the droplet [1]. Therefore, we developed free-standing thin films (FSTF) into functional reference materials and produced test samples by physical vapor deposition (PVD) techniques common in multilayer production. This deposition technique assures very homogeneous layers and a large degree of flexibility regarding the choice of elements and mass densities [2]. In a similar way, TXRF reference samples with layer type depositions in the atomic monolayer and sub-monolayer range (< 10\(^{15}\) Ni atoms/cm\(^2\)) were developed and tested to meet the demands of the decreasing lower limits of detection of TXRF in terms of technical feasibility. It could be shown by grazing incidence X-ray fluorescence analysis in combination with a fundamental parameters approach that layer-like structures with a mass deposition below the monolayer range can be fabricated [3].

WDXRF determination of iron and lead distribution in roadside soil

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The pollution of roadside soil by heavy metals in account of a constant increase of the number of auto cars became a considerable part of a common problem of the environmental aggravation. This leads to the death of roadside trees and the erosion of roadside bents. Heavy metals enter the roadside soil mainly as a result of transport work. When engine barrels and other inner parts have abrasing iron enters the air. The combustion of ethylated fuel is the main source of lead. Iron, manganese, lead, titanium and other elements enter the roadside soil as a result of tire abrasion. When some of the above mentioned pollutants enter the soil they can keep there for many decades. They can be accumulated by plants and reach people soon moving by food chains, causing serious diseases.

In this paper the wave-dispersive X-ray fluorescence (WDXRF) determination of technogenic metal pollution of Moscow soil near two highways with heavy traffic was fulfilled. Sampling was conducted parallel the leeward side of the road with heavy traffic moving aside. Ten samples of soil from the ground surface on the equal distance to the highway and the distance 5 m from each other were collected. Samples were thoroughly mixed and by the method of quartatitation the representative samples were prepared. The first series of samples was collected aside the Moscow circle highway and the second one – aside the Minskaya Street. The soil samples were dried in the desiccator and thoroughly milled. Analysis of soil samples was conducted by a portable WDXRF spectrometer “Spectroscan” (“Spectron”, Russia). X-ray tube of the spectrometer was completed by molybdenum anode, working voltage – 40 kV. Quantitative analysis was conducted by the method of external standard using Fe Kα, Mn Kα, Ti Kα and Pb Lα spectral lines.

It was found that as a result of vehicle running the macro- and microelement composition of Moscow roadside soil substantially differs from the composition of both soddy podzolic soil (typical for Moscow region) and any other soil of temperate climatic region of Russia. The average Fe, Mn and Ti contents in soil were found exceeding the usual background level by 2-5 times, maximum Pb content – by 10-15 times.

The lateral and depth distribution of Fe and Pb contents in soil near the highways was studied. It was shown that the lateral pollutant distribution in soil has no specific exponential shape. Moreover it has the fine structure with the local extremuma and strongly depends on the metal nature and the roadside terrain topography. For Pb – one of the most dangerous pollutants – the mechanism of chemical transformations was proposed and the interrelation of the pollutant chemical form, its molecular weight, the dwelling time in atmosphere and the distance to the highway was discussed.
WDXRF as a nuclear analytical technique for the studies of argentinean cultural heritage

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This work represents an application of X-Ray Fluorescence Wavelength Dispersive (WDXRF) in the field of Archaeometry, as part of several archeological research lines about argentine cultural heritage materials [1].

WDXRF was used in order to obtain relevant information. Samples involved were the followings:

- A group of english wares (19th century) rescued from archaeological excavations in Buenos Aires city
- Stains on bones of animals eaten by hunter-gatherers in selected archaeological sites.
- Beads (llancas) from the site of Cipreses, north area of Traful lake (Neuquén Argentina)
- Obsidian of archaeological north sites of Traful lake
- Paints, ceramics and pigments of archaeological sites in Nahuel Huapi National Park (Patagonia, Argentina)

Samples were analyzed using WDXRF with a VENUS 200 MiniLab equipment of PANalytical. The results provided information on the elemental composition drawing conclusions on:

- Kinds of weathering have undergone the english wares, as well as to know composition of pastes, glazes and pigments. Glazes showed lead as major constituent. The presence of tin revealed the use of cerulean blue for pigments
- In the composition of beads were observed copper minerals
- Inferences about the origin, with the purpose of grouping artifacts identifying the sources of supply [2]. Three potential sources of supply were identified
- Composition of pigments used in archaeological sites of Traful Lake: painted pottery as used in cave paintings and geochemical characterization of coating paint. The red color is most common in all sites. This color was obtained from hematite (iron oxides). On all surfaces painted ceramic were observed mainly Fe and some minor elements that could be related to the different shades observed (Y, Rb, Zr, Sr, Ni, Cu and Zn). Part of these findings provides important information to discuss degrees of mobility of prehistoric and historic inhabitants in the area of Lake Traful.

Intensity Correction of WD-XRF Spectra from 2θ to Energy Scale

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Spectra measured by WD-XRF spectrometers are often displayed as a function of energy to assign the characteristic X-ray peaks easily using the following equation,

\[ E = \frac{hc}{2d \sin \theta}, \]  

where \( E \) is the energy of X-rays, \( h \) the Plank’s constant, \( c \) the velocity of light, \( d \) the diffracted lattice spacing, \( \theta \) the diffracted angle. However, the intensity correction is not considered in this equation.

WD-XRF spectra are usually measured by step scan or continuous scan method using equal 2θ interval. But the interval of energy is not equal in the converted energy scale. Therefore, intensity should be corrected by,

\[ I(E) = I(\theta) \tan \theta / E. \]  

An example of intensity correction is shown in Fig. 1.

Fig. 1 XRF spectra of an acrylic plate measured at 50 kV X-ray tube voltage without a filter, (a) converted by Eq. (1) (b) corrected by Eqs. (1) and (2). 30 channels in 2θ steps are indicated in low and high energy region. (inset) Same spectrum indicated in 2θ axis.
Main ways of planar X-ray waveguide-resonators modification

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Planar X-ray waveguide-resonator (PXWR) is the base device of X-ray Nanophotonics. It functions in result of the uniform interference field of X-ray standing wave appearance in all space of a narrow radiation transporting channel formed by planar extended reflectors. The distance between reflectors can not exceed half value of the quasi-monochromatic radiation coherence length transported by PXWR [1]. The planar waveguide-resonator is destined for formation of thread X-ray fluxes with nanosize width and enhanced radiation density exceeding this parameter for the fluxes formed by conventional slit-cut former on 2-3 orders. Moreover, PXWR is characterized by very high radiation transporting efficiency. But this device has real shortages. Its emergent beam demonstrates not very reasonable integral intensity and visible angular divergence, which is usually equal to 0.1 degree. These shortages can be compensated in result of the waveguide-resonator construction complication.

This work presents results of investigations devoted to methods elaboration for decreasing of PXWR emergent beam angular divergence at conservation of its integral intensity. Simplest manner of the emergent beam angular divergence decreasing is the constitution of planar waveguide-resonator by nonequivalent length reflectors. Such approach allows to reduce the emergent beam angular divergence by half. But the cardinal decreasing of its angular divergence is connected with conception of the composite planar X-ray waveguide-resonator (CPXWR) [2]. One had showed by experimentally that the application two waveguide-resonators deposited one after another on distance falling into the interval “L” (0<L<P=λ₀³/4Δλ) leads to reduce of angular divergence for the resulting emergent beam. P is the parameter describing the protrusion of interference field of X-ray standing wave from the radiation transporting channel. λ₀ and Δλ are the respective average wavelength of quasi-monochromatic X-ray radiation and degree of its monochromatization. There are discussed the experimental dependence of CPXWR emergent beam divergence dependence on L distance for the classical composite waveguide-resonance construction. There are presented results characterizing of emergent beams formed by CPXWR with original design. The effect of the partial angular tunneling of X-ray flux in gap between waveguide-resonators forming CPXWR is introduced for explanation of the composite waveguide-resonator function.

A quasi-monochromatic X-ray source is constructed as part of the IAP NASU microanalytical facility [1, 2] based on 2 MeV electrostatic accelerator. X-ray radiation in the source is generated from interaction of an ion beam, passing through the ion-optical system, with a water-cooled target. Focusing of the proton beam in the source is performed by doublet of electrostatic quadrupole lenses. Ion optics modeling was carried using PROBFORM [3] software. A polycapillary optics was chosen as an X-ray optical system for the source. Measurements of X-ray spectra and K-line yield calculations shows that the constructed source provides K-line yield identical to that obtained with 30 - 50 keV electron beams [4] with the bremsstrahlung background being reduced by two orders of magnitude. Thus, filters or monochromators are practically unnecessary. The X-ray quasi-monochromatic source is intended to be used in the investigation of radiation effects on biological samples, and to implement high sensitivity XRF method.

A soft X-ray beam monitor made by thin-film CVD single crystal diamond

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Synchrotron light is an important tool available for many types of research applications. Due to its low atomic number, high thermal conductivity, high electric resistivity and excellent charge transport properties, diamond is an ideal candidate for the fabrication of radiation hard, permanent on-line X-ray beam monitors. Furthermore, due to low absorption coefficient for X-rays in the energy range 5–25 keV, diamond is a very promising semi-transparent material for in situ beam monitoring. The use of simple electrode geometries allows for high resolution beam position sensitivity with little intensity perturbation downstream.

A new beam position monitor based on artificial single crystal diamond for use under intense synchrotron soft X-ray beams was produced at Rome “Tor Vergata” University. The detector is based on a multi-layered Schottky diode structure. A conductive boron-doped diamond homoepitaxial layer (~2 μm thick), used as a backing contact, is deposited, at first, by Microwave Plasma Enhanced Chemical Vapour Deposition (MWPECVD) on a commercial low-cost synthetic High Temperature High Pressure single crystal diamond (SCD) substrate, 4 × 4 × 0.3 mm³ in size. After that, a high purity intrinsic single crystal diamond (~2 μm thick), which operates as detecting region, is homoepitaxially grown on the doped one. Finally, four-quadrant rectifying low atomic number aluminium electrodes were deposited by standard lift-off photolithography technique on the CVD intrinsic diamond. A photo of the device is shown in Fig. 1(a).

To minimize beam perturbation, the thickness of the HTHP diamond substrate was reduced by a reactive ion etching (RIE) technique under CF₄/O₂ gas mix. As reported in Fig. 1(b) the total thickness of the diamond thin-film beam monitor (DBM) resulted of about 60 microns.

The detector was inserted in the B16 beam line of the Diamond Light Source synchrotron in Harwell (UK). The device was thus characterized under monochromatic high flux X-ray beams from 6 to 20 keV and a micro-focused 10 keV beam with a spot size of ~3 μm. Time response and position sensitivity were investigated. The device response uniformity was measured by a raster scan of the diamond surface with the micro-focused beam, as shown in Fig. 1(c). Transmissivity and spectral responsivity versus beam energy were also measured as well as long term time stability, showing excellent performance of the new thin film SCD beam monitor.

Fig. 1a  Fig. 1b  Fig. 1c
VERDI-3: new improvements in multi-detector readout ASIC


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The availability of Application Specific Integrated Circuits (ASICs) for the readout of radiation detectors represents a valuable resource for the development of compact, low-power detection systems with multiple readout channels. A limitation often encountered in the development of ASICs for radiation detectors is their specificity to a given detector application.

In this work we present the circuit VERDI-3 (Versatile Readout for Detector Integration -3), an integrated circuit developed to provide a unique readout solution for different families of radiation detectors, from nitrogen-cooled Ge and Si(Li) detectors, to silicon drift detectors (SDDs), to scintillation detectors, to photomultipliers tubes and others. The detectors can have an output capacitance from 0.1pF to 39pF, while the energy range spreads from 300eV to 3MeV with both signal polarities, positive and negative. The readout scheme can be pulsed-reset or continuous-reset with an optional external zero-network. The new VERDI chip is characterized by a revised programmable shaping amplifier and baseline holder, a new embedded biasing network and a revised SPI communication with added functions.

The circuit includes 8 channels, each one composed by a hybrid charge preamplifier, a shaping amplifier, a baseline holder, a peak stretcher, an output power buffer and an RC integrator for external digital processing. The output of each channel may alternatively be multiplexed on a single output for low-speed, low-power random readout. Different settings, like gain, shaping time, preamplifier compensation, “gamma” or “x ray” readout mode and many others can be externally programmed by SPI for the specific detector to be readout. Only the input JFET, the feedback capacitor and the reset device are left external to the ASIC, to be chosen specifically for each detector as shown fin Fig.1.

In the work, we will present the experimental results obtained with different kinds of detectors, like Ge, Si(Li), SDD and SSDD detectors, demonstrating the versatility of the VERDI chip.
The BLiX Laser-Produced Plasma Source for the soft X-ray 1 keV-region

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There are two basic source requirements for applications in soft x-ray spectroscopy: a high spectral brightness and a high average photon flux. Both of these requirements are fulfilled by synchrotron radiation sources. Another possibility is to utilize x-ray sources based on laser-produced plasmas (LPP). The advantage compared to the use of synchrotron radiation is the realization on a laboratory scale, which makes investigations possible independent of beam-times. However, to meet both demands high brightness and high average power dedicated optimized pump laser systems are required. Our goal is a reliable LPP source for routine spectroscopic measurements in the soft X-ray region with operating times of up to 8 hours per day.

We are presenting a compact LPP source, which emits soft X-ray radiation in the range between 80 and 1200 eV. The radiation emission relies on the formation of a hot localized plasma on a target through the focusing of a short laser pulse. At present the source is featured with a solid copper target. The plasma is generated using a Yb:YAG-thin disk laser system (TRUMPF Laser Technology). The laser system has been equipped with a diode-laser seed with adjustable pulse duration. In normal operation the pulse duration of a single laser pulse and thus the X-ray pulse is about 1 ns with a repetition rate of >100 Hz. With this configuration the source has a diameter of < 35 µm for the soft X-ray region. Depending on the target and the used spectral range the source gives the possibility to use characteristic line emission for fluorescence spectroscopy as well as to use the whole spectrum for absorption spectroscopy. The source is constructed as such that flexible measurements can be arranged on two beamlines, thus, rendering different measurements feasible simultaneously.

On the current poster characterization results of the LPP source are presented. Wavelength dispersive spectra, measurements concerning the source size as well as information about the source stability are shown. Furthermore first applications are presented.
Advanced synchrotron radiation based XRS
instrumentation and a continuative design study for an
analytical platform for 450 mm wafers

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Keywords: XRS instrumentation, UHV, grazing incidence, nanotechnology, 450 mm wafer

In the PTB laboratory at BESSY II [1] an advanced UHV instrumentation for synchrotron radiation based X-ray spectrometry (XRS) [2] was developed. The new instrumentation enhances the measurement options for up to 100 mm large sample systems. All translational and rotational degrees of freedom of the sample are realized by means of a 9-axes manipulator. It enables total-reflection, grazing-incidence and conventional regimes in XRS including access to polarization-dependent detection channels. Furthermore, rotational and linear movements of several photodiodes as well as the introduction of a rigid aperture system are integrated, that allows for X-ray reflectometry measurements and for reference-free X-ray fluorescence analysis respectively. These complementary techniques provide access to sample characteristics such as thickness, mass deposition and species of surface contamination, depth profile of matrix elements or of implants, composition and speciation of nanolayers or of interfaces as well as the molecular orientation of bonds.

In addition, an advanced metrology chamber for a 450 mm wafer analytical platform has been designed within the framework of European project EEMI450. For the 450 mm wafer applications including optical ellipsometry and VUV reflectometry in spectral ranges complementary to XRS the concept of the current instrumentation of the PTB has been transferred and extended.

Pyroelectric X-ray tube using quick release couplings

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We developed an electron probe microanalyzer (EPMA) with a palm-top size chamber including the electron source and the sample stage using pyroelectric crystal as the electron source [1]. It is easy to exchange samples for the palm-top EPMA because detachable vacuum joints were used for the sample chamber and samples were attached with carbon tape. Applying this feature, we developed a pyroelectric X-ray tube using quick release couplings [2]. The name of quick release coupling is defined by ISO, and the quick release coupling consists of several parts such as flange, center ring which consists of stainless steel ring and rubber O-ring, clamp, flexible tube, and so on. It is quite easy to assemble a vacuum line using the quick release couplings. Figure 1 shows the schematic view of the pyroelectric X-ray tube we developed by using quick release couplings. When silver and titanium plates with the area of 10 mm² were attached on the brass stage of the pyroelectric X-ray tube, strong intensities of Ag Lα and Ti K lines were detected for 90 seconds measurement. This result indicated that the area of 10 mm² is enough size for target metals of the pyroelectric X-ray tube. Cr, Fe, Ni, Cu, and Zn K lines were additionally detected. Cr, Fe, and Ni came from the stainless steel vacuum flange. Cu and Zn Kα lines originated from the brass rods and the brass stage. These characteristic X-rays other than target metals were removed by replacing the stainless steel flange and brass stage with glass tube and carbon stage, respectively.


Figure 1. Schematic view of the pyroelectric X-ray tube we developed.
Specialised capillary optics –
from small spot focusing to large fullfield

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Glass capillary optics can be used for numerous different X-ray analytical methods such as XRF or XRD, or, recently, full field X-ray fluorescence. Improvements in the technology to produce polycapillary optics made it also possible to reach spot sizes of about 10 µm in a broad energy interval at distances between source and sample of 400 mm and more. These lenses are used for XRF application in scanning electron microscopes.

For applications in micro X-ray fluorescence analysis a new generation of polycapillary optics was produced with improved physical parameters such as spot sizes of about 10 µm for MoKα and intensity gains of more than 10 000. Furthermore, new lenses for a high efficiency in the energy region 1 – 30 keV were especially designed.

For the full-field color X-ray camera (SLcam[1]), one needs new types of optics. These large exchangeable polycapillary (12x12) mm in front of the entrance window of the camera conduct X-ray photons from the probe to energy dispersive pixels on a pnCCD. The transport of X-ray photons inside the capillary channels realise a correct imaging of the sample on the pixels and avoid cross views. A real-time visualization of the element distribution in a sample, without scanning system, becomes possible. The straight polycapillary optics allow for 1:1 imaging with a spatial resolution of 50 µm and no limited depth of sharpness, ideal to map uneven objects. Using conically shaped optics, a magnification of 6 times was achieved with a spatial resolution of 10 µm.

The development in capillary optics is directed to a further decrease of focal spot sizes and an increase of brilliance. Such parameters can be realised if corresponding high brilliant microfocus sources are available and a high quality of the capillary optics is guaranteed. An important task is the realisation of a small focal spot independent of the working distance. To achieve such a result several technological and physical problems must be solved. New developments were carried out for capillary optics by changing the capillary diameters as well as using new glass types to improve the transmission qualities.

It is shown that a polycapillary optics can be flexible adapted to concrete applications.

Influence of K-edge absorption on Kβ x-rays of Ti, V, Cr and selected compounds induced by the proton impact

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Recently we performed simple parametrization of Kβ'' and Kβ2,5 x-rays’ relative positions and intensities over the range of 3d metal compounds [1]. The parametrization was based on high resolution spectra from thick targets measured by two wavelength dispersive x-ray spectrometers (WDS) capable to resolve Kβ x-ray band into several visible components, including the main Kβ1,3 line and second order contributions Kβ’, Kβ'', Kβ2,5, and Kβ/L1 [2,3,4]. As excitation, 2 and 3 MeV protons were used. We hope that the parametrization obtained could be useful for improved interpretation of K x-ray spectra of 3d transition metal compounds measured by solid state detectors, since reliable Kβ/Kα intensity ratios are essential for x-ray spectroscopy methods, PIXE being the one where proton beams are used as excitation source.

The measured high-resolution WDS spectra from thick metallic targets showed asymmetric Kβ2,5 lines with sharper (narrower) high-energy wing. This could be due to their location very close to the K-shell absorption edge. Kβ2,5 peaks in measured oxides did not show visible asymmetric behavior, although compounds with tetrahedral coordination have strong absorption pre-peaks in related XANES spectra close to the Kβ2,5 peaks. In order to estimate the influence of K-edge Kβ self-absorption to thick-to-thin target yield ratios, we used experimental XANES data of Ti, V, Cr and related compounds to estimate absorption coefficients very close to the absorption edge. Comparison of published XANES spectra showed differences in energy calibrations which lead to uncertainties in calculated thick-to-thin target yield ratios for Kβ2,5 emission line, especially for metallic and tetrahedraly coordinated compounds.

In order to resolve these uncertainties and investigate the influence of the K-edge on self-absorption of Kβ x-ray band components more precisely, we measured K x-rays from Ti, V, Cr, and their selected compounds with and without Ti, V, Cr absorber foils of appropriate and well known thickness. Corresponding K x-ray spectra were also measured with standard Si(Li) detector with and without absorbers. Having in mind that the intensity of the strongly absorbed multiple-ionization satellite Kβ/L1 is proportional to the ionization cross section for simultaneous ionization of K- and L-shells, which depends on the proton beam energy, the measurements have been performed by proton beams at several selected energies. The measured spectra have been analyzed and the results discussed.

Understanding the diffraction properties and the complex mosaicity structure of HAPG mosaic crystals

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Highly Annealed Pyrolytic Graphite (HAPG) is a novel type of mosaic crystal which can be employed in various fields of X-ray spectroscopy. Its high integral reflectivity and low mosaicity, i.e. in comparison to Highly Oriented Pyrolytic Graphite (HOPG), are mainly responsible for its possible application in high spectral resolution experiments like XANES and HRXES at synchrotron sources as well as laboratory sources.

To investigate the mosaicity of HAPG, angle dependent measurements were performed at the electron storage ring BESSY II using monochromatized synchrotron radiation at a 7 T wavelength shifter beamline (BAMline). The rocking curves, that were measured in first and second order of reflection in a wide photon energy range from 8.4 keV up to 60 keV, also allowed for the experimental determination of the integrated reflectivity and the reflecting power, an energy and order of reflection dependent material parameter.

These measurements revealed that the HAPG crystals have a rather complex structure. The determined mosaicity depends on the thickness. Moreover, the results indicate that the mosaicity varies with depth. This structure will have to be well-understood for the design of HAPG X-ray optics. A first approach to model the thickness and depth dependency of the mosaicity was made. This approach is validated by means of its capability to predict the measured rocking curves in a consistent way.
A new method to characterize the diffraction properties of HAPG mosaic crystals with a laboratory von-Hamos setup

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Highly Annealed Pyrolytic Graphite (HAPG) is a mosaic crystal, which has various advantages for X-ray applications. In comparison to other PG crystals, such as Highly Oriented Pyrolytic Graphite (HOPG), HAPG crystals have a more narrow angular crystallite distribution, which is called mosaicity. This characteristic leads to a much better achievable energy resolution, which is in ideal cases only limited by the intrinsic reflection broadening (IRB). The IRB can be compared with the Darwin width of ideal crystals. The mosaicity is also responsible for a high integral reflectivity because reflections can take place in a large solid angle. Because of these two characteristics, HAPG is very well suited for setups requiring high spectral resolving power in combination with high efficiency. These setups may be at synchrotron sources as well as in the laboratory. X-ray tube based X-ray absorption spectroscopy or X-ray emission spectroscopy are examples for the latter.

For the usage as X-ray optics in high spectral resolution applications, there are several requirements for the quality of the crystals, such as a narrow and lateral homogenous mosaicity. Hence it is necessary to develop methods to characterize the diffraction properties by means of a quality control. Preferably this characterization method should be available in the laboratory for routine measurements.

We present a new laboratory method for the investigation and characterization of these HAPG mosaic crystals in the von-Hamos geometry with a low power X-ray tube as a source. With this method it is possible to determine the mosaic spread (full width at half maximum of the mosaicity) for flat as well as for sagittally bent crystals. With a second crystal of the same material and of different thickness it is also possible to determine the reflecting power, which depends on the energy and the order of reflection. The method presented is based on a simplified and adaptable reflection model for mosaic crystals.
Measuring Temperature Dependent Ti K-edge XANES Using a 100 mm$^2$ Silicon Drift Detector

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X-ray absorption spectroscopy has become increasingly important in materials and chemical research applications. EXAFS (extended x-ray absorption fine structure) spectroscopy, XANES (x-ray absorption near-edge spectroscopy) and their associated techniques require a high performance x-ray detector to detect subtle changes in the spectra associated with phase transitions and other chemical information. We have developed a large area 100 mm$^2$ silicon drift detector (SDD), with excellent energy resolution and high peak-to-background (P/B), to maximize the sensitivity of these types of x-ray fluorescence measurements.

An un-collimated 100 mm$^2$ SDD Vortex$^\text{TM}$ spectrometer was evaluated in response to $^{55}$Fe $^{[1]}$. Figure 1 shows an energy resolution of 135 eV, at 5.9 keV and 6 µs peaking time, with a P/B >1800:1. The 100 mm$^2$ SDD was then evaluated at the National Synchrotron Light Source at Brookhaven National Laboratory, by investigating the temperature dependent Ti K-edge XANES spectra from a EuTiO$_3$ film deposited on a DyScO$_3$ substrate $^{[2]}$. The measurement was done in grazing incidence with the SDD inserted into a low-temperature displex with the x-ray polarization vector parallel to the [110] direction of the EuTiO$_3$. Figure 2 shows the enhancement of the pre-edge $e_g$ feature at 15 K, which indicates that the film undergoes a transition to a ferroelectric phase. The data demonstrates the ability of the SDD to detect subtle changes in the XANES spectra associated with phase transitions in materials.

Fig. 1 - $^{55}$Fe spectrum from 100mm$^2$ SDD; FWHM is 135eV at 5.9keV, 6µs peaking time, with P/B > 1800:1 on uncollimated detector.

Fig. 2 - XANES spectra from a EuTiO$_3$ thin film sample, showing intensity of Ti x-ray fluorescence signal as a function of x-ray excitation energy, and as a function of temperature at 15 and 300 K.


During the last 10 years the Energy Dispersive Spectrometer (EDS), based on the Silicon Drift detector (SDD) has been most often used for x-ray microanalysis, x-ray fluorescence (XRF), total reflection XRF (TXRF), XRF imaging and x-ray absorption spectroscopy (XAS). Due to its high-count rate capability, high energy resolution and convenience of use SDD spectrometers are also very popular in synchrotron based experiments such as XAFS (x-ray absorption fine-structure) and XANES (x-ray absorption near-edge structure) especially because of the increasing flux provided by current and next generation synchrotron sources.

We have developed the Vortex® SDD with a large active area of ~ 50 mm$^2$ and a variety of a high performance single-element SDD spectrometers based on the Vortex® SDD. Despite the high count rate capability of the SDD its performance is limited by signal processing electronics. Therefore to get a further increase in count rate capability, we have developed a four-element version, Vortex-ME4 SDD spectrometer. The Vortex-ME4 spectrometer has several design configurations widely used on different synchrotron beam lines [1, 2]. Recent advancements in the Vortex® SDD and in the Vortex-ME4 spectrometer design have significantly enhanced the energy resolution performance at short peaking times and have enabled a difference reduction in the performance between the spectrometer channels. Table 1 shows the resolution (FWHM at 5.9 keV) typically achieved now with the Vortex-ME4 spectrometer as a function of processor peaking times (PT). Another improvement in the Vortex-ME4 performance is achieved by the implementation of precise synchronized channel reset with very short reset time of ~ 0.5 µs (presented in the Figure 1) that ensures that there is no cross-talk between channels. More detailed data will be presented including the preliminary results achieved with a novel monolithic multi-element SDD arrays.

Table 1. FWHM vs. PT

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<th>PT, µs</th>
<th>FWHM, eV</th>
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Figure 1. Vortex-ME4 common reset

Performance Evaluation of High Rate High Throughput Pulse Processing Algorithms

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X-ray absorption spectroscopy (XAS) is a popular technique with a diverse range of applications as it enables the determination of both geometric and electronic structure of matter. However, for many XAS applications the rate that data can be collected is limited by the performance of the detectors. Thus measurement of individual samples such as dilute material systems or biological tissues can take considerable time.

Consequently there is strong interest in new techniques for improving detector efficiency and resolution at high input count rates. In this poster we present a performance comparison of SITORO\(^{\circledR}\) (a novel model-based signal processing algorithms) versus more traditional approaches to detector pulse processing. By harnessing a priori information about the expected detector pulse shape, model-based signal processing algorithms demonstrate a significant increase in detector throughput and an improvement in resolution.

The model based digital pulse processing algorithm has been implemented in real time on a Spartan-VI FPGA from Xilinx. Detector data is digitised at 120 MHz with 16-bit resolution and the SITORO\(^{\circledR}\) digital pulse processing algorithm is capable of output count rates in excess of 1 million counts per second.
Implementation of a truncated cusp filter for real-time digital pulse processing in nuclear spectrometry

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In this work the transfer function for a truncated cusp infinite impulse response (IIR) filter has been derived. Truncated cusp filter, when given an exponential pulse in the presence of white noise, outputs a truncated cusp pulse which is optimum pulse shape under the constraint of finite pulse duration. The filter features a pole outside of the unit-circle, therefore it is inherently unstable. To overcome it a switching algorithm with two alternating poles was applied. The filter has been simulated with MATLAB and Simulink and implemented in FPGA. The pulses from waveform generator and silicon drift detector (SDD) have been also processed by the filter and results compared with theory.

Simulation and measurements were in agreement with theory and show that energy resolution due to electronic noise can be improved up to 7.5\% by using truncated cusp instead of triangular filter. An improvement of up to 2.8\% in overall energy resolution was measured with a typical X – ray spectrometer based on SDD detector with nominal energy resolution of around 150 eV at energies of MnK\textsubscript{α} line. Also it has been experimentally verified that, when using a simple noise whitening filter, energy resolution monotonically increases with increasing of peaking time.
How to determine experimentally the Fano factor in semiconductors

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The fundamental limit of energy resolution, also referred to as intrinsic resolution, is determined by variance in the number of charge carriers produced by X-rays in semiconductor detector. Materials for semiconductor detectors are characterized by the Fano factor, very important parameter that determines the intrinsic variance of semiconductor detector. Now, all existing methods of experimental determination of the Fano factor in semiconductors are based on the subtraction of electronic noise from the signal variance. In this work, the method of experimental determination of the Fano factor based on dependence of energy resolution on the electric field in semiconductor detector is proposed. By using of the theory of branching cascade processes formalism, the generating function for the process of X-rays registration by semiconductor detector was obtained. It was shown, that power serial expansion of detector variance in terms of the inverse electric field allows determining the Fano factor, electron mobility lifetime product, relative variance of electron lifetime due to inhomogeneous charge transport in semiconductor material. The important advantage of proposed method is its independence on detector electronic noise.
Improved High Performance Silicon Drift Detectors

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Silicon Drift Detectors are the state of art detectors for X-ray fluorescence analysis and SEM/TEM energy dispersive X-ray analysis. We will present recent developments of KETEK’s VITUS series of Silicon Drift Detectors:

- The spectroscopic performance of KETEK SDDs has been improved over the last years by advanced semiconductor processes. Today’s KETEK detectors achieve energy resolutions close to the theoretical limit to less than 121 eV and Peak to Background values of >20,000.
- The low capacitance of the latest VITUS SDD generation allows very high count rates compared to other detectors. By introducing a new low capacitance FET KETEK has improved to count rate capability even more. At ≤1 µs peaking time the energy resolution is improved by more than 10 eV with the new FET, allowing a FHWM of ≤149 eV at count rates of up to 200 kcps input count rate.
- To achieve very good spectroscopic performance the detectors only need to be cooled to operating temperatures below -20°C with the integrated thermoelectric cooler. Especially in mobile applications the power consumption of the TEC needs to be very low. KETEK has introduced a new TEC with 30% lower power consumption to allow for longer operating times in mobile applications. The new TEC is also RoHS conform.
- VITUS SDDs can measure X-ray photons with energies down to 100 eV. To measure such low energy photons the chip entrance window has been optimized to avoid tailing effects and absorption within the entrance window. KETEK has developed a completely new entrance window that shows no tailing effects and allows energy resolutions of the Carbon line <41 eV and even the detection of Beryllium.
- SDDs typically are collimated to improve the peak to background ratio. The material of the collimator can be seen in the spectrum and needs to be selected very carefully, dependent on the application. KETEK has developed a new multilayer collimator that is invisible in the spectrum and is therefore suited for any application.
- Materials used in the module itself can be excited by incoming radiation and can be seen in the spectrum. Careful selection of materials used in the VITUS modules reduces any undesired lines in the spectrum. In addition KETEK has developed a special filter layer located between the TEC and the detector to absorb any x-ray photons excited within the TEC.
- In high count rate applications the radiation hardness of SDDs is of great importance. KETEK has improved the radiation hardness again and guarantees total doses of >10^{12} photons without any loss in spectroscopic performance. Measurements will be presented that show the stability of the KETEK detectors with radiation dose.
New Measurements of Large Area, Multichannel SDDs for Synchrotron and Particle Physics Applications

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The Silicon Drift Detector (SDD) represents the state-of-the-art detector for an increasing number of X-ray industrial applications, as well as in many research areas. Featuring the monolithic integration of the FE-FET onto the detector, the SDDs manufactured by PNSensor and PNDetector have established themselves as high resolution, high throughput energy dispersive detectors for many X-ray spectroscopy applications.

Very large area detectors with large solid angle coverage are often mandatory for many synchrotron applications. Whereas single cell SDD modules are available up to an active area of 100mm², for significantly larger active areas, monolithic arrays of SDDs are the first choice. Moreover, multichannel SDD arrays can also cope with much higher count rates than the single devices, which again make them very attractive for synchrotron applications where the count rate values can be driven very high.

In this contribution we will present new results obtained with 3x100 mm² monolithic SDD arrays built in various configurations. Mounting two such structures in a twin configuration inside a compact package with Peltier cooler, leads to a 6-cell SDD detector with a total area of 600 mm². This detector configuration is very attractive for high count rate EXAFS or XRF applications at synchrotron beam lines. Manufactured in an ultra-clean planar process, the detectors feature extremely low leakage current levels (e.g. 100 pA/cm²), leading to very good energy resolution at moderates cooling temperatures (e.g 136 eV at -20°C). Results of recent measurements performed with this detector array will be presented.

A different application field for large area SDD detectors is the detection of charged particles such as low energy protons in particle physics experiments. A detector configuration consisting of an arrangement of 3x3x100mm² SDD arrays has been developed for the aSPECT experiment. Details on the experimental setup, as well as spectroscopic results obtained with this detector configuration will be reported.

Another detector configuration also very interesting for synchrotron applications is the compact 7-cell detector configuration with 70 mm² total active area. This detector combines the advantage of a very compact packaging with the huge count rate potential of up to 7x10⁶cps. New measurements with this special detector structure will be shown and the results will be discussed.
New developments toward a table-top device for laboratory and synchrotron X-ray imaging

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A new compact device, a Color X-ray Camera, capable of energy-resolved X-ray imaging at high readout rates has been developed. A high-resolution pnCCD detector with an image area of 12.7 x 12.7 mm², 264x264 pixels and 48 μm pixel size is integrated into a vacuum-sealed housing. The split frame, frame store operation along with a full column parallel readout allows for high readout speed of up to 1000 fps. At this rate, the statistical RMS noise per pixel is about 4 e⁻ ENC. The detector has a fully depleted volume of 450 μm thickness and shows very high quantum efficiency approaching 100 % in the 1 keV-10 keV energy range and amounting to 35 % for 20 keV photons. The CCD-chip is thermoelectrically cooled and the camera housing is evacuated to a pressure below 1 mbar by a fore pump in regular intervals to avoid condensation on the chip. For applications outside the vacuum the device can be used as a standalone instrument with a 50 μm thick Beryllium entrance window. Since the camera head is compatible with high-vacuum environment, it is possible to directly attach the housing to a UHV-measurement chamber. In this case a windowless operation is also possible, pushing the lower detection limit down to about 200 eV.

Polycapillary optics acting as an angular filter for the X-rays can be attached directly in front of the detector entrance window. This allows full-field imaging of fluorescence photons emitted by the specimen to be performed. This is a valuable alternative to probe scanning methods e.g. to quickly determine region of interest on a specimen. In this regard we will present results of measurements at synchrotron facilities as well as results from experiments carried out with laboratory X-ray tubes.

Further developments regard the detector capability to reach sub-pixel resolution. In single photon counting mode, by combining the charge splitting and center of gravity reconstruction, the impact position of single photons can be obtained with a precision far below the pixel size. Without any optics, the detector intrinsic theoretical limit for 5 keV photons gives a RMS precision of the position reconstruction of few micrometers. Dedicated experiments along with better algorithms which aim at this resolution have been carried out at synchrotron facilities and will also be presented. Relevant design and performance features of this improved X-ray imager will be outlined as well as measurement results of its enhanced capabilities presented.
KETEK has developed a new product family of discrete electronic components, engineered specifically for operation with VITUS Silicon Drift Detectors. The new VICO Electronics offers OEM customers fast time-to-market. The additional available VICO evaluation board is a tailored OEM development platform for customized OEM spectrometer designs.

- **VICO Electronics** are packaged in flat and minute, standard DIL housings and can therefore be easily adapted by using standard 2.54 mm sockets.
- **VICO Electronics** are designed and tested to fulfill European CE regulations regarding electromagnetic emission and immunity.
- **Magnetic shielding** of the VICO components ensures maximum operating margin even in the case of electromagnetic interference generated by neighboring X-ray sources or switch-mode power supplies.

The new VICO family consists of:

- **Preamplifier** designed for the optimal performance of VITUS detectors. It generates a ramped output signal of positive polarity with very low peak shift (<2eV) over the whole specified temperature range of -10° to +50°C at free air convection. FWHM below 127 eV and P/B in the range of 20000 are achievable.

- **High Voltage Supply** which provides the detector bias voltage (typically -165V ±0.03% line regulation). It is characterized by a minimal output ripple down to 30mV_{p-p} despite the module’s high efficiency. The module comes with a continuous output short-circuit protection, available on request at different output voltages.

- **TEC temperature controller** provides a 3.6V/700mA output stage for peltier elements which may be extended by an external booster transistor. At full load, a maximum thermal dissipation loss of 1.2W is offered. Due to the optimized thermal design, no active cooling is required for operation. The non-switched linear regulator guarantees minimum noise insertion in the SDD’s signal path. An analogue PI algorithm leads to very quick and stable temperature settings (±0.5°C), adjustable by a potentiometer in the range of 0°C to -60°C.

- The state of the art **Digital Pulse Processor** board contains a high performance A/D-converter with 16 bit and a sample frequency of up to 65 MHz. Two interfaces are provided, USB2.0 and Ethernet. Configuration allows the input of either exponential or ramped signals while the input stage is capable of handling single ended and even fully differential signals.

- The **evaluation board** has a spectroscopic and EMC approved design. It can be used by OEMs as a reliable reference for evaluating own designs. Apart from an SDD, VICO-EV is equipped with sockets for the preamplifier, temperature controller and HV supply.
Re-Configurable Digital Pulse Processor for High-Rate High-Resolution X-Ray Spectroscopy

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A Digital Pulse Processor (DPP) developed for high resolution and fast X-Ray Spectroscopy will be presented. The system is principally suitable for spectrometers based on last generation Silicon Drift Detector (SDD) used in application with high speed elemental mapping. The analog input signal, typically from a preamplifier (in pulsed reset mode or RC feedback mode) cascaded with an analog conditioning stage, is digitized by a high performance 150 MHz 16-bit analog-to-digital converter (ADC). The bitstream is driven into the digital processing section of the module, which is based on a digital Field Programmable Gate Array (FPGA) device that plays the roles of main processor, control logic and digital communication interface. The choice of a FPGA instead of a DSP device, for instance, stems from spatial computing improvements in hardware resource availability and in operation frequency. The design of the digital processor has been carried out bearing in foreground linearity, noise immunity, i.e. active and passive electromagnetic (EMI) compatibility, and processing data rate that the specific application requires. This in addition to the (re)configurability of the processing hardware that the configurable FPGA device offers. A user friendly firmware and interface both for configuration and use of the instrument have been realized. The FPGA operates slightly above 100 MHz of clock frequency and controls the whole process. The on-chip RAM stores the acquired spectrum. The spectra are sent to the host PC via USB2.0 interface. Custom made control software provides data visualization and analysis.

The DPP can implement following outstanding:
1. Fast processing: the fast filtering peaking time (less than 0.1 usec) allows processing of an Input Count Rate of 2Mcps.
2. High performances pile up rejection recovery thanks to an Automatic Adaptive Filtering Mode: the processor in real time changes the filtering parameters in order to recovery the maximum number of piled up events maintaining best performance in resolution with constraints preset by the user.
3. Optimum filter synthesis that is addressed by taking into account the specific characteristics of both signal and noise, plus any other desired filter constrain according to the Digital Penalized LMS method.

The characterization and some XRF application of the proposed DPP coupled with a complete X-ray spectrometers based on a Silicon Drift Detector will be presented showing high spectroscopic resolution, high peak stability and high data throughput in high count-rates regime.
Miniature X-ray Source for Hand Held and Portable XRF

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Sanjay Kamtekar, Charles Jensen

Moxtek, Inc., 452 W 1260 N, Orem, Utah 84057, U.S.A.

Portable and handheld XRF instruments become tools of choice for rapid material identification in the field. For these applications, small size, light weight, long battery life, and performance of the x-ray source are critical. We will present the current status of the miniature x-ray source technology as well as a novel approach to testing their performance. In particular the spot size, spot stability, flux stability, turn on speed, power consumption, power efficiency, and other key metrics for miniature x-ray sources will be presented. We will also present the metrology tools and methodology used in the development and subsequently in production testing of the high voltage power supplies and x-ray tubes.
Multilayered samples studied with energy dispersive X-ray fluorescence analysis using $K_\alpha/K_\beta$ or $L_\alpha/L_\beta$ - ratios

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When a multi layered material is analyzed by means of energy-dispersive X-ray fluorescence (EDXRF), then one of the most important problems consists in identifying for each element the correct layer, and to determine the thickness of the various layers. These questions may be solved in many cases by using the internal ratio of each element, i.e. the $K_\alpha/K_\beta$ or $L_\alpha/L_\beta$ – ratio. These – ratios are tabulated and can be measured; anomalous values for a given element may depend on the position and thickness of the layer in which the element is located, and on the thickness and composition of the superimposed layer (or layers).

Multilayered materials are common in the field of archaeometry (in the case of paintings, frescos, enamels, illuminated manuscripts and so on, where many layers are generally present) and in the industrial field (for example zinc-plating, nickel-plating, gilding, silvering and so on).

In this paper the ratios $K_\alpha/K_\beta$ and $L_\alpha/L_\beta$ are calculated as a function of a useful element in the layer material and corresponding thickness, and as a function of the superimposed material and thickness. It will also be shown how X-ray spectra should be processed in order to determine in the best manner the $K_\alpha/K_\beta$ or $L_\alpha/L_\beta$-ratios. Then, several examples will be given of using these ratios to identify layers and corresponding thicknesses in the field of archaeometry (ancient pre-Columbian and iranian object on gilded copper, on gilded silver or on tumbaga) and in the industrial field (zinc and nickel plating).
Limits of detection of $\mu$-XRF with the SEM/EDS for RoHS relevant elements

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For determination of elemental compositions of specimens, most modern Scanning Electron Microscopes (SEM) are equipped with an energy dispersive X-ray spectrometer (EDS). Based on the technological improvement of low-power X-ray tubes and X-ray polycapillary optics in the last few years, a new analytical tool for SEM has been developed: micro-focus X-ray fluorescence $\mu$-XRF. The excitation with polychromatic photons up to $50 \text{ keV}$ is a valuable completion of the analysis capabilities at a SEM, where excitation with an electron beam is used. The most “attractive” figure of merit of $\mu$-XRF with SEM/EDS is the low limits of detection (LoD), which are one or two orders of magnitude lower than in the case of the “conventional” excitation with electrons. A typical application of $\mu$-XRF is the detection of high-Z trace elements in low-Z matrices.

In order to evaluate the performance of the new $\mu$-XRF with SEM/EDS systematically, the trace element concentration of a set of ten plastic reference materials were under examination [1,2]. The interest for this kind of samples has its roots in the European Directive 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipment, RoHS [3]. Especially the presence and concentrations of a number of additives and fillers or the presence of certain elements is of special interest for legislation and the national assistance for health. The reference material utilized here consists of acrylonitrile-butadiene-styrene terpolymer (ABS) and has been doped with different contents of the elements Br, Cd, Cr, Hg, and Pb. The material is available in form of granulate or in form of solid discs with a diameter of 40 mm and a thickness of 1 mm, 2 mm or 6 mm. The LOD’s for the elements under study have been determined from the calibration curves.

Additionally, the LoD under defined conditions can also be predicted by means of forward calculations of $\mu$-XRF spectra based on a physical model. The model assumes a synthetic tube spectrum, the real transmission of the X-ray optics, interactions of the X-rays with the specimen atoms, the knowledge of the X-ray spectrometer and the knowledge exact measurement geometry.

DETERMINATION OF IRON VALENCE STATE IN PICOILMENITES USING X-RAY SPECTRA

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As a satellite of diamond, picroilmenite contains genetic information about condition of kimberlite forming, used for deposit finding. Picroilmenite related with diamond contains no significant amounts of hematite Fe$_2$O$_3$. X-ray spectra can be used for simultaneous determination of the concentration and speciation of iron [1]. Iron valence state in minerals can be evaluated by an electron microprobe analyzer (EPMA) from the ratio of FeL$\alpha_{1,2}$ and FeL$\beta_1$ line intensities [2]. The X-ray fluorescence (XRF) determination of iron valences state in rocks and ores is preferential using ratio of the FeK$\beta_5$ and FeK$\beta_{1,3}$ line intensities as an analytical parameter [3].

This study was performed to search for the possibility of iron valence state determination in picroilmenites using K- and L-series of X-ray spectrum. The samples of kimberlite pipes (Udachnaya, Mir and others) have been analyzed by wet chemistry technique. The measurements have been implemented by XRF spectrometer S4 Pioneer and EPMA JXA-8200. Dependence of ratio $R^c$ of FeO content using EPMA for the ratio range of FeO content 20-26%. The FeL$\beta_1$/FeL$\alpha_{1,2}$ ratio is preferred in EPMA. Precision of XRF analysis of picroilmenites using FeL$\beta_1$/FeL$\alpha_{1,2}$ ratio is the same as with FeK$\beta_5$/FeK$\beta_{1,3}$ ratio. Both ratios can be applied as analytical signals in XRF analysis. The relative standard deviation of FeO content using XRF was about 5.5%. For estimation of accuracy of determination of iron valence state, samples of picroilmenites were analyzed by EPMA, XRF and wet chemistry technique. Content of FeO was also estimated using stochiometric calculation. The relative standard deviation of FeO content was about 2-8%.

The XRF method is preferred for iron valence state determination in the sample mass over 1 g., as it is faster and more convenient for sample preparation than the wet chemistry analysis. The EPMA method allows the iron valence state to be determined in local areas of 1-10 A with precision comparable with XRF analysis.

Calibration of the X-ray fluorescence based system of in vivo bone strontium quantification

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Radioisotope induced (I-125) K X-ray fluorescence spectrometry has been applied to the problem of quantifying strontium in bone tissue in vivo. The current calibration protocol is based heavily on the calibration procedure which has been applied with great success to the in vivo K XRF system of bone lead quantification. Calibration is based on the use of solid-state plaster of Paris (calcium sulphate) bone calibrators (phantoms), doped with exogenous strontium, where these solid state phantoms are intended to mimic bone. A signal normalization regime, based on the coherently scattered source radiation, is also employed, intended to correct for variations in bone volume, bone size and overlaying soft-tissue attenuation of the characteristic X-ray signal. This work evaluates the current calibration procedure for the I-125 induced K XRF based system of bone strontium quantification at a theoretical level with the aid of Monte Carlo simulation. Particular emphasis is placed on the effect of known intra-subject compositional variations in wet bone tissue and the gross compositional variation between the sample bone matrix (calcium phosphate) and the calibrators (calcium sulphate). It has been found that coherent normalization, in the case of strontium analysis, is only valid if concentrations are quoted on a per mass of calcium basis and only if calibration is performed against calcium phosphate-based calibrators. Absolute quantification is not possible through the current calibration procedure. The design, synthesis and implementation of a new generation series of calcium phosphate (hydroxyapatite) calibrators is discussed as a means of improving the current calibration protocol.
Monte Carlo simulation and PLS regression based XRF spectroscopy quantification method

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Partial least squares (PLS) regression based methods have been proved to be a good alternative to the conventional ones for quantification in X-ray fluorescence (XRF) spectroscopy. These methods are in fact fast and easy to use though giving satisfactory results if some conditions are fulfilled. One of these conditions is the necessity of having a great number of spectra to build the model (training set). Besides, good predictions can be achieved if elements of interest concentration ranges in these training samples contain the concentrations in the sample to be measured (unknown samples).
In the present work, Monte Carlo (MC) simulated spectra are used to form the training set. An iterative approach is used to have concentration range that contains the unknown concentration. The method is used to predict some standard materials from BAM (Berlin, Germany). The samples are measured using synchrotron radiation at the BAMline at BESSY II (Berlin, Germany). Both versions of PLS regression PLS1 and PLS2 are used. Obtained results allow to investigate which PLS version is appropriate depending on the sample characteristics and the measurements to be carried on.
Reconstruction of layered specimen by means of marker energies

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3D Micro X-ray fluorescence (3D Micro-XRF) spectroscopy enables three-dimensional resolved, nondestructive investigations in the micrometer regime [1,2]. A nondestructive investigation of the electronic structure of atoms (e.g. oxidation state) and their local geometric environment (e.g. distance to neighbors) is possible by the use of X-ray absorption spectroscopy (XAS). With a combination of 3D Micro-XRF and XAS it is possible to carry out chemical speciation of layered specimen in a depth-resolved and non-destructive manner [3].

For some scientific questions, for example the investigation of corrosion processes, the elemental composition does not change with layers, but the chemical bonding of an analyte does. Such layered specimen (e.g. Figure 1 left) can not be reconstructed with 3D Micro-XRF (Figure 1 right, grey). But with depth scans at energies, where the corresponding XANES-spectra of the chemical bonding differ significantly, so called marker energies (ME) (Figure 1 middle), it is possible to visualise the layered system (Figure 1 right black).

We adopted the use of marker energies to the reconstruction procedure of 3D Micro-XRF. With this procedure it is now possible to reconstruct such layered specimen.

**Figure 1**: Left: Cross section of layered structure with identical elemental composition in each layer but varying Cu compounds (CuO and Cu\textsubscript{2}O); middle: XANES-spectra of CuO and Cu\textsubscript{2}O (dashed); right: Depth scans at marker energies ME1 and ME2 (dashed) and a normal 3D Micro-XRF depth scan (grey)

Examples of relief imaging with X-ray fluorescence microanalysis

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Scanning of an investigated sample with X-ray fluorescence analysis can provide surface distribution of present elements. When untreated objects are analyzed, and not prepared samples, several disturbing effects can come to light in a quantitative evaluation. Especially rough and curved surfaces are a serious problem because the intensities of the characteristic X-rays are significantly modified due to the presence of surface irregularities, even if the chemical composition of the object is constant. It is therefore difficult to distinguish whether the decreases or increases in the X-ray intensities are due to changes in elemental concentrations or due to the topology of the object.

A special method of data evaluation has been proposed and described in the paper [1]. Its main purpose is to separate compositional and topographical image of scanned infinite thick samples. The simplified description of these calculations consists in adding another parameter to the equations for intensities of characteristic X-rays. This parameter represents basically a shape of a surface in an analyzed spot. When a surface of a sample is scanned with X-ray fluorescence microanalysis and data for each spot are evaluated quantitatively including the additional parameter, the drawing of their values represents the relief image of the sample surface. In addition, element concentrations are determined precisely because surface effects are partially reduced this way.

Several examples of relief imaging are presented in this contribution. The best results were obtained for metallic objects.

Novel Utility of Scatter Spectra in Energy Dispersive X-Ray Fluorescence Analysis

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X-ray fluorescence (XRF) spectrometry is an established method for material characterization. Although the method involves elucidation of the chemical composition of materials only based on the fluorescence, additional analytical utility is realizable from the scattered radiation as small Raman scatter alterations occur around the Compton and Rayleigh peaks based on the significant contribution of the light elements to the backscattered X-rays. We exploited the scatter spectra from a $^{109}$Cd radioisotope-excited XRF spectrometer utilizing the power of multivariate chemometrics to determine anionic components and low-Z elements; to correct for matrix effect in analysis of heavy trace elements following multivariate calibration using the full spectrum (fluorescence and scatter); and to realize material property modeling and prediction rapidly (200 sec) and non-invasively from undigested liquid and solid powder pellet samples of complex matrix materials held in a propylene dish. Partial least squares (PLS) and artificial neural networks (ANN) techniques were used to develop calibration and prediction models relating the materials parameter of interest to the scatter spectra. Principal components analysis (PCA) was used for spectral modelling of the scatter in a reduced multidimensional space for an interpretable overview and to perform exploratory analysis for material property modeling. We present selected results from problem-specific applications in rapid soil quality assessment (SQA); and elemental analysis, brand differentiation and authentification as well as viscosity prediction in lubricating oils. We further demonstrate the potential to utilize the X-ray scatter to estimate and model the ‘dark matrix’ of the analyzed materials, a problem whose solution is required in order to realize non-destructive quantitative analysis of a variety of important but complex light element matrices such as glasses, ceramics, etc. The case studies demonstrate the novel utility and potential of scatter beyond its classical use in XRF analysis to calculate the average atomic number, mass thickness, and mass absorption coefficient of materials; and to distinguish between materials of different chemical formulae, or tightly and loosely packed atomic networks. The results further show that XRF analysis via the scatter approach utilizing multivariate chemometrics is very suitable for, among others, applications that place demand on accurate, direct (non-invasive), rapid, multi-elemental analysis and characterization of materials.
Minimizing uncertainties in the XRF analysis of atmospheric particulate matter (PM) through calibration with standards that mimic PM samples

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X-ray fluorescence (XRF) analysis is used to measure elemental mass for 24 elements with atomic numbers between 11 to 40 (Na-Zr) and also for Pb with atomic number 82 in ambient particulate matter (PM) samples collected in the Interagency Monitoring of Protected Visual Environments (IMPROVE) network across the US. Historically, commercially available standards made by vacuum depositing uniform deposits of elements onto either a Mylar or nuclepore substrate have been used to calibrate the energy-dispersive (ED) XRF instruments used in PM analysis. Typically one standard per element, i.e. single-point linear calibrations have been used to be able to report masses of elements. In this work, we have prepared reference materials that are more ideal for use in the quantification of element masses in PM samples. Our reference materials aim to minimize uncertainties in the XRF analysis of PM through limiting the need to account for differences in geometry, matrix and substrates between ambient samples and standards. Overall, they bring improved transparency and credibility to our XRF calibrations.

The reference materials resemble the chemical composition of the sampled particulate matter, replicate the unique geometry of IMPROVE samples, and span the mass encountered in the network samples providing multi-point data sets for linear regressions used in calibrations. By using many standards that bracket the whole range of mass measured, we can improve the precision of the calibration response factor, and although using additional standards for calibration requires considerable more time on the XRF instrument than does a single standard, we consider this a reasonable option since the expense of making many reference materials is fairly small. Furthermore, when a standard has a larger deposit area compared to the ambient sample, which is the case for some commercial standards, the deposit area of the IMPROVE sample must be known to obtain mass per filter. Hence, by using reference materials that mimic the geometry of the sample we can report mass on a mass per filter basis and minimize uncertainty associated with sample deposit area measurements.

We will show the preparation of [1] and data from about 20 sulfur, chlorine and sodium reference materials in the measurement range of each element that have been implemented into the calibration of commercial EDXRF instruments (PANalytical Epsilon 5) used for analyzing IMPROVE samples.

[1] Indresand et al, Preparation of sulfur reference materials that mimic atmospheric particulate matter samples for XRF calibration, X-ray spectrometry, 2012 (Submitted)
Calibration test of the ARTAX™ 200


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XRF is a multi-elemental analytical technique, which is fast, low cost, and easy to operate. The physical principles of XRF, its advantages and limitations are well known and accepted in the environmental research. In this work we present the results of the preliminary tests of the ARTAX™ 200 machine from Bruker Microanalysis GmbH as a tool for XRF analysis of some typical liquid environmental samples: water, vine and honey. The aim of this work was to determine the limitations and calibrate the equipment.

Two types of samples were prepared, both within the same methodology of pre-concentration using APDC with further filtration on thin membranes [1]. The first one was composed of ordinary substances, and the second one was represented by the same substances but pre-contaminated with known quantities of Cu, Fe, Pb, and Zn. Two kinds of membranes were tested: with 22μm and 45μm cells.

As the main result the absolute concentration of some elements in non-contaminated samples were determined based on the calibration with pre-contaminated ones.

Quantitative elemental analysis of historical paper with a portable EDXRF spectrometer

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Characterization of paper documents has shown to be extremely useful for forensic purposes, manuscripts identification and paper conservation\(^{1}\). Paper composition is one of the most important issues in all the characterization processes. In energy dispersive x-ray fluorescence spectrometry (EDXRF), 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\(^{2}\). In this work we make use of a paper standards database\(^{3}\) to proceed with elemental quantification of historical documents analyzed with a portable EDXRF spectrometer. Quantitative analysis of x-ray fluorescence data was accomplished using WinFund comparative mode which is based on fundamental parameters approach and does not take into account x-ray attenuation and enhancement effects. Comparative mode can only be used as paper standards and historical documents have a very similar matrix composition.

Quantitative EDXRF analysis using Monte Carlo simulation

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An important feature of EDXRF techniques is the possibility to predict elemental concentrations from experimentally measured spectral intensities using well established mathematical relations. The Fundamental Parameters Method (FPM) \cite{1} has been, for many years, very useful on predicting concentrations of unknown samples. Two ways are possible in using the FPM: the standard-less approach, where additional information about the geometrical and physical quantities of the spectrometer and experimental setup are needed, or using standards, of known elemental concentrations, to calibrate the measured intensities. The later approach has the advantage of cancelling out unknown factors in the fundamental equations and eliminates, in first approach, dependences on the experimental setup parameters.

The need of standards is however a practical limitation for doing quantitative EDXRF analysis. Standards are expensive or simply they are not available with adequate compositions for the type of samples to be measured. To overcome this drawback we propose to implement a Monte Carlo (MC) simulation of the full setup, including the radiation source, sample and detector \cite{2}. The state-of-the-art MC package PENELOPE \cite{3} for the transport of electrons and photons is used. The package is capable to simulate electrons and photons with energies as low as 250 eV and includes all the relaxation processes relevant to EDXRF.

The accurate simulation of both radiation source and detector is of primordial importance to the final result, since the sample elemental composition must be the sole unknown to be sorted out. Our approach is to obtain EDXRF spectra of a few known pure samples using a well known \textsuperscript{241}Am radiation source. The data is then used to make the energy calibration and obtain the detector energy resolution. The MC simulation of this test setup is made and the detector characteristics tuned in an iterative process so that the best overall agreement between experimental and simulated spectra is obtained. After establishing the detector's parameters the simulation can continue with the X-ray tube characterization. At this point two different approaches can be made. Either the X-ray spectrum is obtained from an available library or is simulated using a program. The first option is easiest but limits the choice of X-ray tube parameters. The second approach might give extra freedom on the parameters choice in particular if the MC simulation of the X-ray production in the tube is made. The downside is the large computation time this option requires since a very large number of primary electrons are required to obtain a meaningful bremsstrahlung spectrum.

To benchmark the overall procedure experimental measurements of an available standard was made with the \textsuperscript{241}Am source and the MC simulation of the full set-up made. A good agreement between data and MC simulation is obtained proving the procedure concept.

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A fast GPU-based Monte Carlo code for XRF simulation

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Monte Carlo techniques are powerful tools for the simulation of X-Ray interaction with matter. They usually are used off-line in order to simulate a measurement to be performed and so to test the experimental setup chosen. A standard Monte Carlo code usually requires a long time of simulation in order to give a good statistic result. The time depends on the complexity of the simulation and it can last up to several days. However, in order to overcome this problem, several techniques and algorithmic procedures have been developed and they usually fall inside the definition of “variance reduction” techniques. In this case a good quality simulation can require several minutes up to one hour. However, even this shorter computational time can be too long if the Monte Carlo code must be used online, for example iteratively for quantification aim. A new opportunity for speeding up Monte Carlo can be found in the use of GPU cards. They are graphical cards with high parallelization degree. Moreover, being one of them usually included in every computer, it can be used to speed up the calculation and so for shortening the simulation time. In this work preliminary results obtained with NVIDIA cards are presented and discussed.

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Three dimensional Miro-XAFS method at SSRF and its applications in analysis of ancient paints in Forbidden City

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Confocal Micro-XAFS equipment have been constructed at Miro-XRF beamline in SSRF by the combination of KB mirror and polycapillary half-lens. This method is very suitable for nondestructive three-dimensional element and chemical speciation analysis of archaeology samples, especially for the ancient paints with a multilayer structures. Recently, several paints in Forbidden City have been analyzed, their elements depth profile and chemical speciation have been obtained from the depth profile resolved XRF and depth profile resolved XANES. The multilayer structure of the paints and the pigments in each layer will be discussed.
Assessment of spatial variability of heavy metals in metropolitan zone of Toluca Valley, Mexico using the biomonitoring technique in mosses and TXRF Analysis

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This study is aimed at assessing atmospheric deposition of heavy metals using the moss genera \textit{Fabriona ciliaris} collected from six urban sites during August 2010 in the metropolitan zone of the Toluca Valley in Mexico. The concentrations of 13 elements (K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr and Pb) were determined in mosses samples by instrumental total reflection X ray fluorescence analysis. A TXRF spectrometer “TX-2000 Ital Structures” with a Si(Li) detector and a resolution of 140 eV (FWHM) at Mn Ka and a Mo tube (40 kV, 30 mA) with 17.4 KeV excitation energy, was used for elemental analysis with a counting time of 500 s. Results show that the average metal concentration in the mosses decrease in the following order: Fe (8207 mg/Kg) > Ca (7315 mg/Kg) > K (3842 mg/Kg) > Ti (387 mg/Kg) > Mn, Zn (191 mg/Kg) > Sr (71 mg/Kg) > Pb (59 mg/Kg) > Cu, V (32 mg/Kg) > Cr (24 mg/Kg) > Rb (13 mg/Kg) > Ni (10 mg/Kg). High enrichment factors for Cr, Ni, Cu, Zn and Pb were obtained using the soils from the same sampling sites. These high enrichment factors provide an evidence of anthropogenic impact in the industrial and urban areas, mainly due to the intense vehicular traffic and the fossil fuel combustion. Monitoring techniques in mosses have proved to be a powerful tool for determining the deposition of heavy metals coming from diverse point sources of pollution.

Keywords: Heavy metals, TXRF, Moss biomonitoring, Air pollution
Determination of Fifteen Elements in Nickel-Chromium Alloy by X-ray Fluorescence Spectrometry

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Fifteen Elements including Ni, Cr, Mo etc. in Nickel-Chromium alloy were determined by X-ray fluorescence spectrometry. In order to obtain line overlap correction coefficients, the binary samples of high pure metal were prepared by using re-melting technique with centrifugal casting. The influence on analysis results by different polishing medium (Al₂O₃, ZrO₂, SiC) and graininess was shown and discussed. The absorption and enhancement effects among elements were corrected by using theoretical Alpha coefficients. X-Ray fluorescence spectrometer (ARL9900) was used. Voltage and current of X-Ray tube (Rh) was 40kV, 70mA. The same sample was polished eleven times, and then its content was determined respectively. When the average contents of Ni, Cr, Mo, Si, Mn, P, S, Cu, Al, Nb, Ti, Co, Fe, W were 36.06%, 25.83%, 4.47%, 0.47%, 0.13%, 0.045%, 0.004%, 0.13%, 0.13%, 0.22%, 0.067%, 0.082%, 4.34%, 26.54%, 1.53%, the relative standard deviations were 0.16%, 0.16%, 0.09%, 0.43%, 0.77%, 2.22%, 5.00%, 0.77%, 0.31%, 1.36%, 1.49%, 1.22%, 0.28%, 0.19%, 0.65% respectively. Precision was good. Standard samples and control samples as unknown samples were determined, and the results were in good agreement with their certified chemical values. The accuracy was satisfactory for routine analysis.
Coating analysis independent from spot size and working distance

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XRF is a powerful non-destructive method for analysis of coating systems in electronic industry for example for Printed Circuit Board (PCB), contact pins or Lead Frames for metal finishing in automotive industry or jewellery. The always higher integration in micro-electronics requires more and more coating structures that are very small. Than for quality control very small spots are necessary which generates also very small measurement signal. For a sufficient accuracy it is necessary to use long measurement time or to concentrate high excitation intensity to the sample. But this would require special x-ray optics which are expensive.

Usual quantification models use the emission signal of the layers only. But this is sensitive for working distance and the size of the sample area that covers the excitation spot. Correct quantification results require the same focus distance both for the measurement and the calibration procedure. Unfortunately that cannot always be guaranteed especially on the production lines. So the accurate in-line measurement poses a vast challenge for manufacturers of measuring systems.

To solve this situation it is possible to perform quantification using both the signal of layer emission and but also from the substrate which is absorbed in the layer. This so called relative mode delivers quantification results that do not depend on working distance or on the content which is covered by the analyzing spot. Normally the relative mode works very well for single layer but has difficulties by the quantification of multilayer coatings.

The last developments by Bruker open the new possibility to use the relative mode for the analysis of multilayer independent from the working distance or from the size of the measuring spot, which can be larger as a sample itself. For that analysis no new calibration is necessary.

The comparison of results calculated using the “normal” emission mode and the relative mode for different layered systems and different sizes of samples such as with Ni and Au plated pins, Sn(Pb), Au and Ni coating on PCB, very fine contacts on Lead Frames or ZnNi coating by different working distances measured with a relatively large spot will be presented.

<table>
<thead>
<tr>
<th>Collimator</th>
<th>Mode</th>
<th>Ni, µm</th>
<th>StD</th>
<th>Au, µm</th>
<th>StD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,1x0,3 mm</td>
<td>emis.</td>
<td>2,17</td>
<td>0,05</td>
<td>0,238</td>
<td>0,004</td>
</tr>
<tr>
<td></td>
<td>relative</td>
<td>2,47</td>
<td>0,03</td>
<td>0,256</td>
<td>0,006</td>
</tr>
<tr>
<td>0,2x0,2 mm</td>
<td>emis.</td>
<td>1,92</td>
<td>0,03</td>
<td>0,208</td>
<td>0,008</td>
</tr>
<tr>
<td></td>
<td>relative</td>
<td>2,52</td>
<td>0,04</td>
<td>0,261</td>
<td>0,004</td>
</tr>
<tr>
<td>0,5x0,5 mm</td>
<td>emis.</td>
<td>1,39</td>
<td>0,02</td>
<td>0,171</td>
<td>0,003</td>
</tr>
<tr>
<td></td>
<td>relative</td>
<td>2,51</td>
<td>0,05</td>
<td>0,309</td>
<td>0,005</td>
</tr>
<tr>
<td>0,7 mm</td>
<td>emis.</td>
<td>1,31</td>
<td>0,01</td>
<td>0,156</td>
<td>0,001</td>
</tr>
<tr>
<td></td>
<td>relative</td>
<td>2,49</td>
<td>0,04</td>
<td>0,312</td>
<td>0,003</td>
</tr>
</tbody>
</table>

Au/Ni/Cu-pin measured with different collimators: A–0.1x0.3 mm, B–0.7 mm.
A liquid phase microextraction strategy combined with benchtop TXRF for ultratrace cadmium determination in environmental water samples

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Cadmium is one of the most ecotoxic metals as it exhibits highly adverse effects on soil biological activity, plant metabolism, and on the health of humans and animals. The World Health Organization (WHO) established as 3 µg/L the maximum permissible in drinking water while 5 µg/L is the limit established by the US Environmental Protection Agency (EPA).

The determination of Cd at trace levels in aqueous samples by TXRF has been mostly restricted due to the inherent use of L-series spectral lines measured to quantify this element when using Mo-target X-ray tubes or the limited excitation conditions when using W-target X-ray tubes. For this reason, a sample pretreatment is usually necessary to extract, isolate and concentrate Cd prior the TXRF analysis.

In the present contribution, the feasibility of a liquid-phase microextraction approach (LPME) combined with TXRF for Cd determination in different type of environmental waters is shown. LPME is a solvent-minimized sample pretreatment procedure of the conventional liquid-liquid extraction, in which only several µL of solvent are required to concentrate analytes. Therefore, taking into account the micro-analytical capability of TXRF spectrometry, the combination with LPME procedures is an interesting approach [1].

Parameters affecting the extraction procedure and TXRF measurement conditions have been carefully evaluated to ensure the best sensitivity for Cd determination. Using the best analytical conditions, it was found that the minimum cadmium content that can be detected in an aqueous solution was 0.1 µg/L. The precision of the methodology was evaluated in terms of relative standard deviation of five replicate analysis of a standard solution containing 3 µg/L and it was less than 10%. In order to test the suitability of the method when dealing with complex matrices as well as the influence of interfering ions, the determination of Cd in spiked water samples (sea water, estuarine water, natural water and tap water,) at the levels of 1 µg/L and 5 µg/L, was undertaken and Cd added to the samples was quantitatively determined.

Our results give insight into the possibilities of the combination of LPME and TXRF for ultratrace Cd determination in aqueous samples.

Improvement approaches for trace metal determination in aqueous samples by benchtop TXRF systems: Preconcentration using multiwalled carbon nanotubes

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(2) Institute of Earth Sciences “Jaume Almera”, CSIC, Solé Sabarís s/n, 08028 Barcelona, Spain
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In the last decades, most of the published TXRF analyses were performed using large-scaled instruments with high-power X-ray tubes, demanding water-cooling systems and liquid-nitrogen cooled detectors. However, in recent years, the development and commercialization of bench top TXRF instrumentation, which offer extreme simplicity of operation in a low-cost compact design, have promoted its application in industry as well as in research activities for elemental analysis. Despite the fact that the limits of detection using such instrumentation are suitable for some applications, an improvement of the limits of detection by using sample preparation or preconcentration strategies prior the TXRF is usually necessary in environmental applications.

Taking into account the micro-analytical capability of TXRF and the possibility to analyze suspensions, the use of multiwalled carbon nanotubes (MWCNTs) as solid sorbents is an interesting preconcentration strategy to improve the analytical performance of trace metal analysis when using benchtop TXRF systems. MWCNTs have desired characteristics as solid-phase extraction sorbents because of their large specific sorbing surface area, their well-defined structure at atomic scale and very small particle size.

In the present study, a precocentration strategy based on the used of MWCNTs has been developed for determination of Cr, Fe, Co, Ni, Cu, Zn, Se, Cd and Pb at trace levels in aqueous samples. The proposed sample preparation is quite simple and economic. After the adsorption processes of the metals on the MWCNTs, the aqueous sample is separated by centrifugation and the metal loaded MWCNTs are suspended using a small volume of an internal standard solution and analyzed directly by TXRF. Parameters affecting the extraction process (complexing agent, pH of the aqueous sample, amount of MWCNTs) and TXRF analysis (volume of deposited suspension on the reflector, drying mode, and instrumental parameters) have been carefully evaluated to test the real capability of the developed methodology for the intended purpose.
Possibilities of liquid-phase microextraction strategies for trace and speciation antimony analysis by low power W-target tube TXRF instrumentation

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Antimony (Sb), which can have both acute and chronic toxicity effects, is an emerging contaminant regulated in drinking water in different countries at action levels ranging from 2 to 6 µg/L. Sb contamination can result from metal smelting, petroleum refineries but new studies have shown that it can also leach from polyethylene terephthalate (PET) plastic bottles. In the present study, the possibilities of two liquid-phase microextraction procedures (LPME) combined with low power W-target tube TXRF instrumentation have been evaluated for trace Sb determination in aqueous samples.

LPME is a solvent-minimized sample pretreatment procedure of the conventional liquid-liquid extraction, in which only several µL of solvent are required to concentrate analytes. Recently, different LPME modes have been developed including the named “Hollow fiber liquid-phase microextraction” (HF-LPME) and the “Dispersive liquid-liquid microextraction” (DLLME). In the former case, a hydrophobic hollowfiber is used to protect and expose a certain volume (few µL) of the extractant to the sample. The extraction process occurs in the pores of the hollow fiber where the solvent is immobilized. DLLME is based on the cloudy solution formed when an appropriate mixture of an extraction solvent and a disperser solvent is quickly injected into the aqueous sample. The fine droplets of extraction solvent are dispersed through the aqueous sample, allowing its interaction with the analyte. In both cases, after the extraction procedure, only few µL of organic solvent (containing the extracted metal) are obtained and thus, a microanalytical technique (TXRF) is mandatory to determine the target metal.

For each of the LPME configuration aforementioned, several experimental parameters affecting Sb extraction from the aqueous sample and also the measuring conditions for the subsequent TXRF analysis were carefully evaluated. Using the best analytical conditions the determination of Sb in the low µg/L range was feasible. Moreover, selecting the optimal pH of the aqueous phase it was possible to get information on inorganic Sb speciation (Sb(III) and Sb(V)) in the solution in a simple and inexpensive way, which is crucial to study the bioavailability, toxicity and transport of this metal in the environment.
Determination of selenium by X-ray fluorescence spectrometry using preconcentration with multiwalled carbon nanotubes as solid sorbent

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Selenium is an element of environmental, biological and toxicological importance due to its narrow range between the nutritious requirement as essential element and toxic effects upon exposure. Therefore the determination of trace selenium concentrations in water, biological and food samples is required.

Method of determination of selenium using multiwalled carbon nanotubes (MWCNTs) as solid sorbent and ammonium pyrrolidinedithiocarbamate (APDC) as chelating agent was developed. In the proposed procedure, Se(IV)-APDC complex is adsorbed on MWCNTs dispersed in aqueous samples. Such analytical strategy promotes the immediate interaction between the Se(IV)-APDC complex and MWCNTs. After adsorption process the aqueous samples are filtered and MWCNTs with selenium chelate are collected onto a cellulose filter. The loaded filters are directly measured using X-ray fluorescence spectrometry (XRF). The MWCNTs are ideal solid sorbent which can be applied in preconcentration procedures prior to XRF analysis. It results from their well-defined structure at atomic scale, large surface area and very small particle size.

In order to obtain the high recovery of selenium ions on MWCNTs, the proposed procedure was optimized for various analytical parameters such as pH of the aqueous sample, the amounts of MWCNTs and complexing agent (APDC), the sample volume and the time of sorption process. Under optimized conditions selenium ions can be determined with very good recovery (97±3 %). Moreover, using acidic solution (pH=2) makes possible separation of Se(IV) from Fe(III), Mn(II) and Zn(II) which can be present in natural samples at high concentrations. To obtain the best sensitivities and detection limits (DLs) the conditions of XRF measurement were optimized (DLs ranged from 0.06 to 0.23 ng mL⁻¹, depending on counting time and XRF equipment: EDXRF and WDXRF). The proposed method was applied to the determination of selenium in mineral water and biological samples.
Determination of heavy metal ions by EDXRF spectrometry using dried-spot technique and dispersive liquid-liquid microextraction with APDC and DDTC as chelating agents

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The application of dispersive liquid–liquid microextraction (DLLME) for multielement determination of trace elements using energy-dispersive X-ray fluorescence spectrometry (EDXRF) is proposed. The goal of the presented research is to show that combining DLLME with EDXRF spectrometry allows obtaining very low detection limits in simple, non-time consuming and low-cost way.

Two nonspecific chelating agents, ammonium pyrrolidine dithiocarbamate (APDC) and sodium diethyldithiocarbamate (DDTC) were applied as chelating agents. The procedure was performed using 5 mL of the sample, 100 μL of 0.5% solution of APDC or DDTC, 30 μL of carbon tetrachloride (extraction phase) and 500 μL of methanol (disperser agent). The organic phase containing preconcentrated elements was deposited onto a Millipore filter with the use of spray-on technique. After that EDXRF measurement was performed. Because DLLME was combined with dried spot technique the repeatabilities of various stages of the proposed procedure were evaluated. The experiment shows that Fe, Co, Cu, Zn, Ga, Se and Pb can be simultaneously extracted with very good recoveries (92-101%). For all analytes, the linear range was observed up to 0.4 μg mL⁻¹. If Fe and Zn are present in concentration 10 times higher than the other analytes, then the linearity is observed up to 0.2 μg mL⁻¹. Obtained detection limits were 2.8, 1.5, 2.0, 2.3, 2.5, 1.7, 2.1 and 4.0 ng mL⁻¹ for Fe, Co, Ni, Cu, Zn, Ga, Se and Pb, respectively, for 5 mL samples.

Such a combination of DLLME and dried-spot technique can be very promising for multielement analysis using X-ray spectroscopy techniques.
Energy-dispersive X-ray fluorescence spectrometry combined with directly suspended droplet microextraction in determination of trace amounts of phosphate in water

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Phosphorus is one of the essential mineral required for normal growth of every living system. It plays an important role in energy production, and transmission of genetic information. Orthophosphate is usually present at submicromolar concentration in surface water due to the limited solubility of various phosphorus-containing minerals. Nevertheless, phosphate export from industrial and agriculture activities as well as domestic sewage to water can result in increased primary production and eutrophication, with the potential for seasonal development of toxic algal blooms, which can have a major impact on global water quality. Therefore, control of phosphate in the aquatic environment is very important.

Determination of trace elements with low atomic number such as phosphorus by X-ray fluorescence spectrometry (XRF) is hampered because of the low fluorescence yield and relatively low energy of characteristic radiation (strong absorption by the sample matrix). However, to improve sensitivity and detection limits for determination of $PO_4^{3-}$, the indirect methods have been usually applied [1-3]. In our work, energy-dispersive X-ray fluorescence spectrometry (EDXRF) combined with directly suspended droplet microextraction (DSDME) for determination of trace concentration of phosphate is proposed. The method is based on the determination of phosphate through molybdenum in the phosphomolybdenum blue complex. Because phosphorus is determined indirectly via molybdenum fluorescent radiation the difficulties resulted from low fluorescent yield and low energy of phosphorus radiation are successfully overcome. Under the optimized conditions, the detection limit of 2.8 ng mL$^{-1}$ for the sample of 1.5 mL was achieved. The developed method was used to determine the concentration of phosphorus in surface waters.

Interpretation of eventual anomalous results in Iron determination by the XRF (borate pearl) method.

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The X-Ray Fluorescence Areas at the Faculty of Chemistry of UNAM apply several methods and techniques of elemental analysis: EDXRF and ADXRF to samples in powder, pellets and borated pearls forms, chosen accordingly to the sample type and project requirements. A local inter comparison is performed in order to assure the precision of results. The yield has been usually satisfactory since the variations fall in the range of +/- 2% in repetibility and +/- 10% in the comparison between angular and energy dispersive techniques. However, in that concerning the comparison of powder or pellet techniques with the borated pearl sample, the results are sometimes disappointing since differences higher than 50% occur eventually in the Fe determination.

This paper presents some examples of the above mentioned comparisons and a possible explanation for the irregular case of Fe, based on the mineralogic effect¹ originated by the different crystal structures remnant of the element and its compounds at high temperatures.

Total Reflection X-ray Fluorescence analysis (TXRF) is widely used in semiconductor industry for the analysis of silicon wafer surfaces. Typically an external standard is used for the calibration of the spectrometer. This is sensitive to errors in quantification. For small sample amounts the thin film approximation is valid, absorption effects of the exciting and the detected radiation are neglected and the relation between sample amount and fluorescence intensity is linear. For higher total sample amounts deviations from linearity have been observed (saturation effect). These deviations are one of the difficulties for external standard quantification.

Content of the presented work is the determination and production of the ideal TXRF sample to improve external standard quantification. The element nickel (Ni) was chosen for these investigations because it is usually used as reference standard for calibration of TXRF Wafer analyzers in the semiconductor industry.

A comparison of theoretical samples with different shapes shows that the ring shape matches the ideal TXRF sample shape best and exhibits the lowest saturation effect. After theoretically determining the ideal TXRF sample it was investigated if there is a simple method for the realization of a ring shaped sample. A possibility for the production of samples with ring shape is the use of a nanodispensing system combined with a positioning device. Therewith it is possible to produce ring shaped samples in a controlled way with the ring consisting of individual picodroplets, so that the wanted diameter of the ring can be chosen. A comparison of the fluorescence intensities emitted by contracted and ring shaped samples shows that the ring shape is not only theoretically the best TXRF shape but also experimentally. It could be proven that for contracted samples the saturation effect occurs at a lower sample mass than for samples with ring shape.
Effects of plasma cleaning on the spectral shape and resolution of carbon containing materials

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It is a well-known fact, that samples observed by SEM are covered by coating of hydrocarbons originating in vacuum system, contamination during contamination etc [1]. These hydrocarbons are even polymerized under the beam of electrons giving to arise to adherent layer usually observable after de-magnifying as a dark rectangle [2]. Although these layers are very thin, when observing the WDS spectra of carbon containing material it may be very undesirable since it convolutes with the signal of intrinsic material.

One possibility to avoid this is use of plasma cleaning. Principle of the method is oxidation of hydrocarbon contamination to gaseous compounds that are then removed by vacuum system.

Description of the effect of plasma cleaning parameters on WDS spectra of graphite and carbonate materials is presented work.

Application of Radioisotope EDXRF for throwing power
determination in aluminium electrolytic coloring.

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Electrolytic coloring of anodized Aluminium is one of the most important ways for aluminium protection and decoration. Nickel (Ni) and Tin (Sn) are the most common metals that are used for this process, by their deposition at the bottom (5-20 µm depth) of the aluminium oxide pores; color hue is directly related with the deposited metal surface density [1]. The even metal distribution in complicated form objects is an important property of the coloring, called Throwing Power. The well-known advantages of the EDXRF (possibility of solid analysis, no destructivity, fast analysis) as well as easy Ni and Sn detection, makes it a suitable tool for TP determination.

Fe-55 (for Sn L-lines), Cd-109 (for Ni) and Am-241(for Sn K-lines) annular radioactive sources were used for sample excitation, and thin NIST and Micomatter standards for surface density calibration. The results were represented by the exponential function:

\[ \text{Surface Density} = A + B \cdot \exp\left(-\text{distance}/C\right) \]

where distance measures the aluminium specimen - counter electrode distance. The parameters A, B and C were used for the TP estimation and color intensity. Parameter A dominated the surface density values at long distances (the long distance limit), while parameter B regulates the surface density at the positions near the counter electrode. The sulphosalicylic acid (SSA) addition in tin baths improved these factors in most cases, while piperidine-3-carboxylic acid and piperidine-4-carboxylic acid addition in nickel baths usually improved mainly the B parameter. The variations of these factors with the time of treatment are correlated with the kinetic of coloring as well as with the mode of action of these additives.

Dendrochemical analysis of tree cores from Shoubra El-Kheima, Cairo, Egypt

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This is the first time Synchrotron Radiation micro X-Ray Fluorescence (SR µ-XRF) have been used to study the elemental composition of the tropical tree Royal Poinciana (Delonix regia (Boj. ex Hook.) Raf.). Trees can be seen as natural archives of the changing conditions in the region in which they grow. By studying the elemental composition of growth increments, extracts from this archive can be obtained.

The species Royal Poinciana (Delonix regia) is a tree that can be found in tropical regions all over the world. The trees in this study were growing in Shoubra El-Kheima, Cairo, a heavily polluted industrial district dominated by chemical industries, ferrous and nonferrous metallurgical work, ceramics and plastics industries. There are also two big power plants in the district [1]. Cairo itself is one of the largest cities in Africa with a population estimated to 20 million in the greater Cairo area.

Samples were taken with an increment borer from the stems at ca. 1.5 meters height, yielding cross section cores, 0.5 cm in diameter. The diameters of the sampled tree stem varied between 30 and 51 cm. The tree cores were cut in half and the flat surface of the cores was used for analysis at the FLUO beam line in ANKA, Karlsruhe, Germany. A length of 20 cm was analyzed a total of five times in each of the three tree cores. The elemental values presented are averages of all five runs. A monochromatic beam with an energy of 20 keV was used and the spot size approximately 100 times 100 µm with a scan step of 200 µm.

The results show clear trends of increased pollution of elements like Cu, but a decreasing trend in Pb. The decrease in Pb is a reflection of the use of unleaded fuel after 1997 and the closing down of a Pb smelter in the area [2, 3]. Sturchio et al. estimated that the high concentration of Pb in the urban air caused 15 – 20,000 deaths each year in greater Cairo [4]. This preliminary study shows that tree rings are highly useful in providing information about the pollution history of urban environments.

[4] N. Sturchio, M. Sultan, M.E. Sharkaway., A.E. Maghraby., A. Taher, Concentration and Isotopic composition of lead in Urban particulate air, Cairo, Egypt; Argonne National Laboratory, Argonne, IL and Center for Environmental Hazard Mitigation, Cairo University, Cairo, Egypt, 1996.

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Characterization of soils and sediments in the delta of the river Neretva, Croatia

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The area of river Neretva delta is approximately 170 km\textsuperscript{2} with 70\% of it (i.e. 120 km\textsuperscript{2}) within Republic of Croatia. In this survey of this area 18 chemical elements (K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Br, Rb, Sr, Y, Zr and Pb) were analyzed by the Energy Dispersive X-ray Fluorescence (EDXRF) method for 390 soil and 116 sediment samples collected in the area. Each sampling point was characterized by its GPS coordinates enabling the production of concentration maps for the measured elements by using the “Spatial Analyzer – Inverse Distance Weighted Method”, Arc View 9.3 software. Several «hot-spots» resulting from the applied agricultural practices have been identified and classified according to the newly developed classification scheme.

The human intervention into the delta of river Neretva started in 1880-ies when the flow of river was regulated. The soil melioration started by transfer of river sediments into swamp zones. Additional reduction of swamp area has been accomplished by channels digging and using the resulting material for the generation of fields. Therefore, we decided to treat data on the soil and sediment concentration levels as a unique data base.

The multivariate statistic approaches (Principal Component Analysis and Between Group Analysis) were adopted for data treatment, allowing identification of nine environmental and anthropogenic factors controlling the variability of elements in soils and sediments. The geological factor (containing positively correlated variables: Ti, V, Mn, Fe, Ga, Rb, and Zr) is the most dominant describing 34.5\% of total variance.

Obtained environmental and statistical data were integrated with the geographical, geologic, pedologic, land use and administrative databases using GIS software. GIS presented spatial variations allowed refinement of results obtained by multivariate statistics.
Measuring sodium concentrations in London winter aerosols with Synchrotron Radiation induced X-Ray Fluorescence Spectrometry

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Detecting trace elements in small quantities in ambient aerosols can be done using Synchrotron Radiation induced X-Ray Fluorescence Spectrometry (SR-XRF) [1]. This technique has been successfully applied to samples of many field campaigns in recent years. Elements from silicon (Si) to zinc (Zn) could be determined in this way when a He atmosphere was used to reduce absorption at the lower energies. Conventional silicon drift detectors (SDD) with a 12 micron Be window can detect Si as lightest element, because the detector efficiency decreases and absorption effects increase for lower fluorescence energies. We tested the possibilities of measuring sodium (Na) concentrations with a similar setup [1], but modified with the possibility to measure in vacuum. Furthermore, we used a detector with an AP3.3 ultra-thin polymer window which ensures the highest transmission of low energy X-rays, and a sensor with 30 mm² area. The detector has a lower energy threshold of 200 eV. This is low enough to detect the Na-Kα line at 1.04 keV.

Na is environmentally important as a tracer for sea salt. During reaction involving reactions with HNO₃, chloride is lost by release of HCl while sodium remains in the particulate phase. The aerosol samples were collected during the winter campaign of the ClearfLo project (www.clearflo.ac.uk), that took place in London, UK, in January and February 2012. Our measurements show that with the described setup Na measurements are feasible with good accuracy. The time series of Na concentrations obtained in this way will finally be used together with other concentration time series of trace elements and organic aerosols for refined source apportionment studies [2].

Investigation of soil evolving from Municipal Solid Waste using Energy Dispersive X-ray Fluorescence

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Municipal Solid Waste (MSW) generated in the city of Kolkata [1], India has been dumped at a site known as “Dhapa”, situated in the eastern fringes of the city, since the middle of 19\(^{th}\) century. The soil in this area is expected to be evolving from several layers of dumped MSW through several decades. It becomes primary environmental prerogative to investigate the bulk-elemental composition of the soil at various depths. Samples from three different layers had been collected from six selected spots spanning a length of around 2 km, starting from the present core dumping area to a bypass highway dividing the rest of the city from Dhapa [2]. Samples at each location are divided into surface soil, Middle (1.5-2 m depth), and Lower (2.5-3 m depth). In all 15 surface (including four near the highway), 12 middle, and 12 lower layer samples were collected. Pure thick pellets of each sample were analyzed using an EDXRF set-up [3], comprising a \(^{109}\)Cd disc source and a Si(Li) detector [2], with detection range of 3-20 keV. The AXIL code and Back Scatter Fundamental Parameter (BFP) code of the QXAS package [4] were used for spectrum analysis and quantification respectively. The Fluorescence, Coherent and Incoherent scattering instrumental constants were determined using pure foils and pellets of pure compounds. The average constant values were 784, 629, and 762 with standard deviations of 29, 36, and 14 respectively. NIST SRM 2586 comprising Pb contaminated soil was used for quality control. The relative deviations of the EDXRF estimated elemental mass fractions were generally within 15\% except for Y and Nb.

The Geometric Mean (GM) of the EDXRF estimated concentrations of a few heavy metals with respect to depth has been plotted in Fig.1.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{geom_mean.png}
\caption{Plot for Geometric Mean of concentrations of Cr, Cu, Zn and Pb in soil at surface, middle and lower layers.}
\end{figure}

Cu, Zn, and Pb concentrations are found to be high in all the samples. Pb has higher accumulation in the lowest layers whereas that of Cr is low. Pb concentrations in two of the four surface soils collected from near the highway were exceptionally high (2300 and 4500 mg/kg).

Elemental imaging of actinides in human tissues using LA-ICP-MS and SR micro-XRF

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The aim of this study was to evaluate the capabilities and limitations of two state-of-the-art approaches for elemental imaging of the distribution of actinides in human tissues in both a qualitative and a semi-quantitative manner. Human tissues were provided by the United States Transuranium & Uranium Registries (USTUR), which studies the uptake, the translocation and the biokinetics of actinides in humans [1]. Tissue sections from different USTUR cases (Registrants), which were occupationally exposed to certain actinides (U, Pu, Am), were investigated. Two highly sensitive analytical techniques were applied: Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) and Synchrotron Radiation (SR) micro X-Ray Fluorescence (micro-XRF) spectrometry. The latter was combined with complementary laboratory scanning micro-XRF measurements.

One of the investigated subjects (Case 1060) was occupationally exposed via inhalation to uranium. From this Registrant, parabronchial lymph node sections were made available by the USTUR. The LA-ICP-MS study showed that uranium is not homogenously distributed within the areas investigated, but is present under the form of micrometer-sized hot spots. Similar results were obtained from the SR micro-XRF experiments at beamline L, DESY, Hamburg. A semi-quantitative study of the LA-ICP-MS and SR micro-XRF elemental maps using a standard-based calibration curve revealed that the concentration of the uranium hot spots is within a similar range (up to ≈ 30 µg/g). In this case, detectable amounts of zirconium were found as well, also present in the form of microscopic aggregates.

Paratracheal lymph node sections from a second subject (Case 0407) were analysed for the presence of plutonium and americium. The LA-ICP-MS study revealed an inhomogeneous presence of plutonium under the form of microscopic hot spots. In addition, one ablated area possibly exhibited the presence of americium. The SR micro-XRF experiments confirmed that plutonium is present under the form of micrometer-sized heterogeneities. In addition, also amounts of zirconium and uranium were found, which were again distributed under the form of microscopic aggregates.

From the experiments performed in this study, it can be confirmed that both LA-ICP-MS and SR micro-XRF are very useful complementary techniques to study the distribution of actinides in tissue sections. LA-ICP-MS however, causes considerable damage to the sample, precluding a second measurement to be performed on the same sample area, which is not the case for (SR) micro-XRF experiments.

Intercomperission of EDXRF, TXRF, AAS, PIXE and ICP methods for analysis of medical plants

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A long term monitoring program has been carried out in INRNE for more than 10 years. The subject of the program is “Investigation of different element concentration in herbs and plants”. Three different spectrometric systems, covered the whole energy range from 1 to 32keV, are available for determination of 32 elements in plant samples. In order to improve the calibration procedures for each spectrometer, typical sample from each species was selected and measured by different analytical methods in order to check the calibration curves. In such way an additional internal standards were obtained. Five different methods – EDXRF, Total reflection XRFA, PIXE, AAS, ICP-MS were used to analyze ten typical species. This work shows the results from the inter comparison test between the methods. The main problems came out for the analysis of major elements – K, Ca. Significant differences were found also for Ba and Pb. The results will help for improvement of calibration procedures for the available spectrometers and for receiving more reliable results.
Great Smoky Mountains National Park – Long Term

Reproducibility of IMPROVE Elemental Concentrations

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The IMPROVE network has collected 24h PM$_{2.5}$ samples for elemental and light-absorption analyses continuously since 1988, at a sustained frequency of twice a week or every third day. The network today includes about 170 sites, about 70 of these having operated continuously since 1995. The same size selective inlets and filter media have been used throughout the measurements, and all analyses have been performed at Crocker Nuclear Laboratory of the University of California in Davis. All original sample filters collected since 1995 are archived on the Davis campus.

The elements from Na to Zr and Pb have been reported throughout the program, but significant changes have been made in the analytical methods used over the years. For example, from 1994 to November 30, 2001, Na – Mn were determined by Proton Induced X-ray Emission (PIXE) and Fe – Pb were determined by XRF analysis using a Mo excitation in EDXRF system. Currently, Na – Fe have been determined by Cu-anode EDXRF analysis in vacuum environment, while from December 2001 to December 2004 these elements were reported based on analysis by Cu-anode EDXRF system in helium flushed atmosphere.

Because the analytical methods used in previous years were non-destructive, the IMPROVE sample archives can be reanalyzed with the current analytical method. Therefore, the impacts of historical changes in instrumentation can be evaluated by reanalyzing the sample archive in a single analytical batch on the current instrumentation. The 15-year sample archive from Great Smoky Mountains National Park was recently selected to generate such an analytically homogeneous data set.

This presentation examines trends in the relationships between reanalyzed and originally-reported elemental composition data and assesses the implications of the analytical changes for long-term trends analysis at Great Smoky Mountains National Park.
Energy Dispersive X-ray fluorescence analysis of total bromine in soils

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Bromide ion is widely used as a tracer to study water and solute transport because it does not absorb to negatively charged soil minerals. Tracking \(\text{Br}^-\) movement through the vadose zone by taking undisturbed core samples and using ion chromatographic techniques based on soil-water extracts is difficult and time consuming. Previous results demonstrate the usefulness of wavelength dispersive X-ray fluorescence for total bromine tracking in agricultural soils [1]. The bromine content in soils varies considerably ranging from as small as 0.5 up to 850 mg·kg\(^{-1}\). Larger concentrations are found in coastal soils and the content seems also to be positively correlated with the organic matter [2]. The four major manmade releases of \(\text{Br}\) and \(\text{Br}^-\) into the environment are from K mining, from emissions of 1,2-dibromoethane, a scavenger in leaded fuel, from the irrigation with salty water and from the use of pesticides in agriculture, mainly from the use of methyl bromide.

Methyl bromide (MB) is a broad-spectrum, highly toxic pesticide. Under the EU Plant Protection Products Directive (PPPD) all authorizations for MB were cancelled by 18 March 2009, and the use of remaining stocks must cease by 18 March 2010 [3] due to unacceptable levels of risk to operators, bystanders and consumers.

In the present work we check the use of benchtop EDXRF instrumentation for the study of the total bromine accumulation in agricultural soils that were treated with MB for long time and also in soils of recreational areas that were irrigated with reclaimed water.

Geochemical features of a coastal Mediterranean watershed affected by metal mining activities determined from X-ray fluorescence analysis data

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The main objective of the study is the application of different sampling strategies and the use of different X-ray fluorescence instrumentation for the study of the environmental effects of metal dispersion around metal mining zones. The content and extent of heavy metals was investigated at the highlands, at mid-bed course and at the alluvial plain near sea coast. At the natural heavy metal sources placed in highlands the study was mainly addressed to the transfer from mineralized rocks to soils, water and vegetation.

In the middle course the research target was the study of settlement and remobilization of overbank and mid-bed sediments and its role in the transport of heavy metals to watershed lowlands. Sedimentary deposits and soils existing at lowlands were investigated by incremental in-depth sampling, to verify the extent of metal pollution and post-depositional processes affecting metal dispersal to water bodies.

Three different X-ray equipments were employed (EDXRF with triaxial geometry, micro-EDXRF and WDXRF) for the study of rocks, soils and mining wastes. Other complementary non-invasive on-site geophysical technique such as electrical tomography was applied in order to determine the in-depth extension of pollution in sedimentary record.

Noticeable heavy metals’ leaching was proven, sometimes even at basic pH. The remobilization of overbank sediments implies a serious environmental risk in the case of the typical Mediterranean heavy rainstorms. The additional use of electrical tomography to define the extension of metal mining wastes in the alluvial plain was especially helpful for the assessment of the environmental impact of metal-bearing sediments.
Distribution of trace elements on leaves of roadside trees exposed to traffic generated dust pollution in and around Kolkata, India

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Abstract:

Plants have extensively been used worldwide as filters of air particulate matters. They act as efficient absorber and adsorber of gaseous pollutants and particulates including trace elements and heavy metals, respectively. This work describes the specificity of leaves of different road side plants towards adsorbtion of trace elements present in the dusts. In the present work Energy Dispersive X-ray Fluorescenc (EDXRF) technique was used for elemental analysis. The results indicate that the samples from sites are burdened with elements such as Si, V, Cr, Mn, Cu, Zn and Pb. More over some plants have shown specificity for adsorbtion of heavy metals like Zn, Cu, Cr and Pb. Such information can be utilized for air pollution monitoring and developing policies for air pollution management.
Calibration method for confocal x-ray microanalysis with polychromatic excitation

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The confocal setup consists of x-ray lenses in the excitation as well as in the detection channel. In this configuration, a probing volume defined by the overlap of the foci of both x-ray lenses is analyzed. Scanning the sample through this micro volume, 1-3 dimensional studies can be performed. For depth profiling studies, only the scan of the probing volume in the normal direction to the sample is required. An elemental analysis is obtained by the detection of the x-ray fluorescence produced in the micro volume.

During the last years, experiments with confocally aligned x-ray lenses have been performed at various synchrotron radiation sources. This setup proved to be capable to supply three-dimensional or depth-sensitive information on the elemental composition of a sample with a spatial resolution of around 10 to 20 micrometers.

The quantitative reconstruction of the composition of stratified material by means of confocal micro-XRF with monochromatic excitation relies on a three-dimensional model for the probing volume [1]. The model has been implemented into analysis software and recently validated for monochromatic excitation [2]. In contrast to most of the confocal setups at synchrotron sources using monochromatic excitation radiation, a quantification scheme for polychromatic excitation, like with x-ray tubes or polychromatic synchrotron radiation, has not a development accord to the potential of the technique.

In this work, the three dimensional model for the probing volume is applied for the calibration of the confocal setup implemented in the Brazilian Synchrotron Radiation Source (LNLS) using white beam. The experimental parameters of the theoretical model were obtained by means of the depth profile analysis of several thin films (Micromatters\textsuperscript{TM}). The calibrated confocal setup was used to quantify reference standards in order to validate the calibration procedure. Our results for elemental concentrations had good match with the nominal values of light matrix reference standards.

Analysis of natural water with low and high mineral content by total reflection X-ray fluorescence

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Application of total reflection X-ray fluorescence analysis (TXRF) for the determination of elements in different water samples, e.g. drinking water, mineral water, rainwater, river water, wastewater, is one of the traditional tasks [1, 2]. The progress achieved in this field over recent years is discussed in the brief review. The main attention is given to the possibilities of TXRF without preconcentration procedures prior to the analysis of water samples.

In the present work all measurements were performed using the benchtop TXRF spectrometer S2 PICOFOX (Bruker Nano GmbH) equipped X-ray microfocus tube with Mo-target (50 kV, 750 µA), a multilayer monochromator and XFlash® silicon drift detector. Specificities of the analysis of natural water samples with different salinity such as fresh waters (1 g/L), brackish waters (1-10 g/L), saline waters (10-50 g/L) and brines (>50 g/L) are described. Gallium was used as internal standard for the determination of P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Ba and Pb.

Different sample preparation procedures were compared. For fresh water the influence of the repeating sample volume pipetted onto the quartz glass carrier (10, 10×2, 10×3, 10×4, 10×5 µL) on TXRF results was performed. For water samples with high salt content dilution (from 1:1 till 1:10) using bidistilled water or 1% solution of a surface-active substance Triton X-100 were tested. The hydrophobisation of sample carrier surface by silicone solution in isopropanol (Serva) significantly reduced the sample preparation error especially for elements with atomic number \(Z\leq20\).

The critical thickness of “infinitely” thin films for different water samples with varying concentrations of matrix ions (Cl\(^-\), HCO\(_3\)\(^-\), SO\(_4^{2-}\), Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\)) was calculated. For water with high salt matrix, when condition of thin layer is broken, absorption effects and their influence on TXRF quantification by internal standardization were estimated.

The effect of matrix contents on the detection limit of trace elements was experimentally investigated using a set of multi-element standard solutions with different amounts of matrix ions. The results showed increasing the detection limits with increasing the sample salinity. The minimal values of detection limits were 0.5-1.5 µg/L for Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr and Pb; 2-4 µg/L for Cl, K, Ca, Ti, V and Ba.

The data obtained by direct TXRF analysis of natural water samples has been compared to that obtained by methods of “wet” chemistry and ICP-MS.

Measurement control and data acquisition system for scanning micro-beam X-ray fluorescence spectrometer

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The main aim of this work was to create a user friendly software interface for a tabletop confocal micro-beam X-ray fluorescence microscope (confocal \(\mu\)-XRF). The main area of application of the spectrometer is two and three-dimensional (2D/3D) mapping of elemental distributions in environmental, biological and geological samples. The spatial resolution of the spectrometer for 2D elemental imaging is equal to 16.5\(\mu\)m and for 3D imaging it is in the range from 23\(\mu\)m to 40\(\mu\)m, depending on the energy of the registered radiation.

The spectrometer was assembled by using commercially available components: Mo-anode X-ray tube (maximum power 50W) with polycapillary X-ray optics (nominal focal spot diameter of 13 \(\mu\)m at Mo-\(K\alpha\)), 10 mm\(^2\) active area silicon drift detector (SDD) with 8\(\mu\)m Be window and two sets of motorized XYZ stages, one for positioning the detector and the other for positioning the sample during a scan. Optical microscope with video camera is utilized for on-line sample preview and selection of the analyzed region. The detector can be also equipped with polycapillary conical collimator (nominal focal spot size of 28\(\mu\)m at Fe-\(K\alpha\)) for 3D measurements in confocal geometry. A triangulation laser distance sensor is used for accurate positioning of the analyzed sample spot.

The National Instruments’ LabVIEW graphical programming language was used to create complete measurement control and data acquisition software integrating various elements of the spectrometer system. The modular feature of the LabVIEW together with the so-called virtual instrument (VI) blocks provided by the component suppliers enable controlling variety of different hardware components with simultaneous data processing [1-2]. Moreover it makes the process of exchanging/upgrading and eventual further expansion of the system relatively easy.

The developed LabVIEW software consists of two main modules. The first module controls the video camera and handles sample positioning. A live camera image allows the user to define spatial regions and program \(\mu\)-XRF scans. The second module executes the programmed scan(s) controlling the measurement and data acquisition. This module handles sample stage movement, X-ray spectra acquisition, simple data preprocessing, and data storage. Several user-defined spatial regions (either 2D or 3D) can be scanned this way.

The reliability of the spectrometer and its control software was examined. Preliminary measurements in 2D/3D mode were carried out [3].

X-ray imaging of inorganic pigments by micro-beam X-ray fluorescence and energy dispersive X-ray radiography


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X-ray fluorescence (XRF) spectrometry is a well-established and frequently used technique for noninvasive in situ identification of inorganic pigments in historical paintings. One of the disadvantages of XRF analysis is a long measurement time required to map the pigments in a larger region of a painting. Therefore, XRF technique is usually applied to selected spots of interest. However, these spots of interest can be difficult to pinpoint in the background of an old historical painting. It may also happen that the original painting background is overpainted with another layer of inorganic pigment, e.g. carbon black, hiding the underpainting and making the selection of regions for local XRF analysis even more difficult. In such cases conservators usually perform X-ray radiography of the whole painting to eventually reveal the presence of a hidden underpainting as well as to identify the features not detectable by visible/ultraviolet/infrared light spectroscopy. Unfortunately, if white lead pigment covers large areas of the painting and due to the way the radiography is performed (X-ray tube operated at about 80 kV equipped with a few millimeters thick Al window, the radiographic image collected by a flat panel detector (FPD)) the contrast in the radiographic image is dominated by the distribution of white lead. In such conditions X-ray radiography becomes insensitive to the presence of other inorganic pigments, e.g. azurite (Cu-rich) or earth pigments (Fe-, Ca-rich). In our work we demonstrate the use of dual energy X-ray radiographic imaging for in situ identification of different types of inorganic pigments in oil paintings. The method has been implemented using a custom built imaging system based on a laboratory X-ray source and a custom designed position sensitive and energy dispersive detector. The obtained energy dispersive X-ray radiographic images of a sample painting are compared with results achieved by micro-beam XRF mapping and conventional X-ray radiography. The advantages and limitations of the three techniques are discussed.
Calibrations for measurement of manganese and zinc
in nail clippings using portable XRF

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A calibration method was developed to assess elemental concentrations in nail clippings, using a portable x-ray fluorescence (XRF) device. Specifically, manganese and zinc were investigated in this study. Two sets of phantom nail clipping samples were prepared, one set containing manganese and one set containing zinc. In both sets, elemental concentrations in the phantom clippings were varied from 10 µg/g to 50 µg/g, in increments of 10 µg/g. Additionally, for each concentration, five distinct masses of sample were prepared ranging from 20 mg to 100 mg. XRF spectrometry was performed with the various samples using a portable x-ray tube and detector system.

Kα characteristic x-rays were detected for both manganese and zinc. Intensities of detection were plotted against added concentration, resulting in linear relationships for both manganese and zinc. The slopes of these calibration lines were then examined as a function of sample mass. An empirical function was fit to the slope-mass relationship and compared to those obtained previously from other elements [1]. Using this XRF calibration approach, it is possible to estimate elemental concentrations in human nail clippings for a variety of elements of medical interest.

Drinking Water Analysis by EDXRF

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In this survey 90 samples of water used in households were randomly collected from the wider area of the Neretva delta, southern Croatia. Samples of 100 mL were preconcentrated with APDC as a chelating agent and analyzed as thin targets for chemical elements Ca, V, Fe, Ni, Cu, Zn, As, Hg and Pb, by using Energy Dispersive X-ray Fluorescence method. The aim of the study was to determine the possible exposure of local population to elevated concentrations of heavy metals. Great number of households in the Neretva delta use rain water or water from private wells for drinking, cooking and hygiene. Since the delta of the Neretva River is one of the main agrarian regions of Croatia with intensive agrarian practice during all the year, the possibility of the water contamination is increased.

**Key words:** heavy metals, EDXRF, drinking water; APDC preconcentration

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Recycling of mining waste has become more important since global market prizes of metals have increased. Optimization of extraction procedures needs careful determination of elemental amounts in the waste, the extracts and the residue. Inductively-coupled plasma optical emission spectrometry (ICP-OES) and (total-reflection X-ray fluorescence spectrometry) TXRF were used to determine metals leached by sulfuric acid extraction. Comparison showed good agreement of both methods. Nonetheless, efficiency of continuous extraction is ideally determined by loss of metals in the solid residue comparing it to the original content. A determination directly from the solid sample is favorable to ensure a quick determination and prevent from digestion procedures involving concentrated HF. Here we present the optimization of determination of elements in suspensions of mining waste with TXRF. Special focus was on the determination of Si, because if Si can be determined probably the leaching of other elements can be determined by their decreased relative content to Si, assuming Si is not leached to the extract. The optimization was done by using acrylic glass reflectors (usually quartz reflectors are used) and using different certified reference material. The results show, determination of Si can be successfully done using P as internal standard.
Ag nanoparticles are commonly used for an increasing amount of a variety of products due to their antibacterial effects. These effects are caused by silver ions on the particle surface and therefore increased with increasing surface area. However, toxic effects on animals have been reported and harmful effects on human health are possible. Ag nanoparticles are also environmentally accumulated.

One pathway of mobilization of Ag is in form of air borne particles. Since harmful effects are always depending on concentrations and particle size a detailed knowledge about the amounts and size of Ag nanoparticles coming from fabrics is crucial. Therefore, aerosols from fabrics coated with Ag nanoparticles were collected from a test control unit were fabrics are tested for galling resistance. A low pressure Berner impactor was used for size segregated aerosol collection, which is capable collecting particles down to 15 nm in diameter on Si-wafer carriers.

Total X-ray reflection analysis (TXRF) is a time and cost efficient analysis capable to nondestructively analyze minute amounts of sample material. Specimen preparation in environmental TXRF usually includes preparation of a liquid sample on a carrier, which is then dried to give a small residue. Small deposits of aerosols can be analyzed likewise, if the Si-wafer with the aerosol is placed in an adapted sample holder.

TXRF measurements are usually carried out in air, so an Ar Kα peak at 2.957 keV that is interfering with the Ag L-lines around 2.984 keV will always occur and therefore be hampering the analysis of minute amounts.

In order to eliminate the argon peak it is obvious to work in a nitrogen atmosphere. To achieve that, we build a box for our TXRF instrument (Picofox, Bruker) that can be connected to a nitrogen gas container and opposing to that to a vacuum pump. The pump is required to apply a nitrogen flow for cooling. With the argon peak eliminated, determination of the Ag nanoparticles will be possible. For comparison single particles were also analyzed using electron micro probe analysis.
Determination of transmission efficiency of polycapillary X-ray lens by using twin detector configuration

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The energy dependent transmission efficiency of a polycapillary conical collimator (PCCC) was determined experimentally by using an X-ray tube based confocal X-Ray Fluorescence (XRF) set up with twin silicon drift X-ray detector configuration (SDD1 and SDD2). Both detectors were positioned in a plane perpendicular to the primary beam path. The entrance to the SDD1 was restricted with an ordinary pinhole collimator. The PCCC was mounted in front of the entrance window of the SDD2. The primary polycapillary lens attached to the exit of Mo-anode X-ray tube and the PCCC formed a confocal probing volume with effective diameter about 25 micrometers at 8.4 keV. Both detectors were operated simultaneously to collect X-ray fluorescence spectra during confocal scans carried out for a number of certified reference samples. The ratio of the characteristic peak intensities collected by both detectors was used to determine the transmission efficiency for several X-ray energies. The advantages of the proposed methodology are discussed in terms of the elimination of experimental uncertainties and X-ray/atomic fundamental parameters involved in the fluorescence emission, whereas the obtained results are compared with nominal values and existing literature data [1].

Study of main and signature sources of particulate matter pollutants in Limeira City (Brazil) using SR-TXRF

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Among the environmental pollutants, particulate matter presents itself as one of the most significant and important, because it can be issued by various sources, whether they be natural or anthropic. Limeira City presents itself as a significant centre for development and population growth. The objective of this study was to identify the main sources of particulate matter, taking into account its two fractions, coarse and fine, collected in Limeira City. After removal in acid, samples were analyzed by total reflection x-ray fluorescence analysis with synchrotron radiation at the Synchrotron Light Source Laboratory, Campinas, SP, Brazil. Samples were measured for 100 seconds, and a polychromatic (white) beam was utilized for excitation, in the energy range of 4-22 keV. X-rays were detected with a Si(Li) semiconductor detector with 165 eV resolution at 5.9 keV. The spectra obtained were analyzed using the Quantitative X-ray Analysis System for Windows (WinQxas).

By employing multivariate statistical analyses, namely, principal components analysis and cluster analysis [1], it was possible to determine the probable emission sources contributing to the formation of the particulate material. For the coarse fraction, the primary emission source, soil dust, contributed 57%, followed by 30% from vehicular emissions, and lastly, only 13% from industrial emissions. For the fine fraction, the primary emission source was soil dust, contributing 79%, followed by 13% from vehicular emissions, and lastly, only 8% from industrial emissions. The profiles of the signatures of vehicular emission sources, burning fuel oil and soil dust were compared with profiles submitted by other authors [2 - 4], and generally have a good agreement.

Comparison of sediment core analysis by mobile scanning XRF system and by PIXE

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Sediment cores provide fundamental information in environmental research studies like global climate change or pollution assessment. Several laboratory instruments based on X-ray fluorescence spectrometry have been developed these last years to analyze their elemental composition directly on the cores without any sampling.

We have improved our XRF mobile system \cite{1,2} to allow analysis of this kind of samples by adding a fully-automatic scanning system and a specific software for data acquisition. Helium flux was also improved to allow better analysis of light element. This system is then now able to analyze by 1mm step 1 meter long cores in one time with detection of elements from Na to U.

At the same time, we have developed a similar system on the PIXE system installed on the extracted beamline of the IPNAS cyclotron. The cores are analyzed by a 3 MeV proton beam and X-rays are detected by two detectors, the first one with a filter for trace element analysis, the second with a helium flux to detect low energy X-rays. A specific translation system and data acquisition have also been developed.

In order to evaluate the advantages and disadvantages of both systems, we have analyzed a core coming from lake Hazar (Turkey) that was previously analyzed with an XRF Avaatech system. The results will be compared and discussed.

\cite{2} F.-P. Hocquet, H. Calvo del Castillo, A. Cervera, C. Bourgeois, C. Oger, A. Marchal, M. Clar, S. Rakkaa, E. Micha, D. Strivay, Analytical and Bioanalytical Chemistry 399 (9), 2011, 3109
Determination of metals in groundwater, surface water and slurry of solid waste disposal sites in Campinas city, Brazil using SR-TXRF

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The problem of solid waste in most countries is on the rise as a result of rapid population growth, urbanization, industrial development and changes in consumption habits. Amongst the various forms of waste disposals, landfills are today the most viable for the Brazilian reality; both technically and economically. Constructive characteristics allow minimizing the effects of the two main sources of pollution from solid waste: landfill gas and slurry. However, minimizing is not synonymous with eliminating, consequently the landfill alone cannot resolve all the problems concerning solid waste disposal. The main goal of this work is to evaluate the content of trace elements in samples of groundwater, surface water and slurry arising from local solid waste disposals in the city of Campinas SP Brazil. Samples of surface and groundwater, slurry; were collected in the Delta, Santa Barbara and Pirelli landfills. At Delta and Santa Barbara values above the maximum permitted level established by CETESB [1] for Cr, Ni and Pb in samples of groundwater were observed, while at Pirelli, Pb concentrations were above the permitted. At Delta values above levels permitted by Brazilian legislation (CONAMA 357) [2] were still observed in surface water samples for Cr and Cu; whereas in slurry samples, values above the levels permitted were observed for: Cr, Ni, Cu, Zn and Pb. Slurry samples were prepared in accordance with two extraction methodologies, USEPA 3050B [4] and EPA 200.8 [5]. Concentrations of Cr, Ni, Cu and Pb obtained were higher than the limit established by CONAMA for most samples collected at different periods (dry and rainy) and also for the two extraction methodologies employed.

Growth tree rings of *Tipuana Tipu* as biomonitor of environmental pollution: quantification by Synchrotron Radiation Total Reflection X-ray Fluorescence

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Metals can be introduced in the environment naturally by the weathering of the mineral sand by no natural sources as fertilizers, pesticides, oil and coal combustions, vehicular emissions, mining, foundry, refinement and incineration of urban and industrial wastes. Nowadays many studies use the bioindicators, plants or animals capable to present qualitative and/or quantitative answers, when exposed to substances pollutant. Trees record and incorporate in their log, developed year after year, the impressions of the environment, becoming possible the study of the different environmental changes, including contamination, that have occurred over the life of these trees. The possibility to date the growth rings, combining with the information recorded in its structure to environmental and historical studies began to science called dendrochronology [1]. The selected species, *Tipuana tipu*, of the *Leguminosae* family, is native of Argentina and Bolivia and was introduced in Brazil as ornamental [2]. It is one of the most common trees in urban landscaping in Sao Paulo city.

The present project has as main objective the determination of the content of heavy metals in samples of growth tree rings of *Tipuana tipu*, previously dated, collected in strategically locations of São Paulo, using Synchrotron Radiation Total Reflection X-Ray Fluorescence (SR-TXRF). Samples were collected also in the Piracicaba (SP), local of little access and small flow traffic. The following elements were determined: K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Ba, Pb. Some trace elements present concentrations higher than considered as normal [3] in some periods. In São Paulo city, sample 2 collected in University of São Paulo Campus (Butantã), showed the highest toxicity, with concentration above the tolerable limit for the elements: Ti, Cr, Fe, Cu, Zn, Rb, Sr and Pb. For the samples collected in Piracicaba city, the sample 2 present highest concentrations for the majority of the elements when compared to the others four samples collected at the same place, exceeding the toxicity limits for: Cr, Fe, Ni, Cu, Zn, Sr and Pb. By the results obtained we can considerate that growth tree rings of *Tipuana tipu* specie can be used as bioindicators of environmental contamination.

Trace elements in Korean and Chinese red peppers were determined by an XRF spectrometer with three-dimensional polarization optics for identification of their production area. By optimizing the measurement conditions, linear calibration curves for 11 elements (Cl, K, Ca, Mn, Fe, Cu, Zn, Br, Rb, Sr, Cd) in red pepper were obtained, and the minimum detection limit for each element was sub-ppm levels. Principal component analysis using the concentrations of six elements (Cl, Ca, Fe, Zn, Rb, Sr) was performed to distinguish the production area, and the results showed that there is a different trend in the elemental composition for Chinese and Korean red pepper. It was clearly seen that these six elements were indicative of production areas for red peppers. By the linear discriminant analysis using 6 elements, it was possible to construct the discriminant for determination of Chinese or Korean red pepper. We successfully demonstrated in this study to determine the concentration of trace elements in red pepper with a rapid and easy way using the XRF spectrometer and to discriminate the production area of Korea and Chinese.

Black and white peppers of south-eastern Asia were also analyzed to identify their production area.

GEOCHEMICAL CHARACTERIZATION OF MARINE SEDIMENTS FROM THE MIDDLE WEST COAST OF PACIFIC OCEAN IN MEXICO

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Marine sediments from Mexico’s West coast in the Pacific Ocean, from Sinaloa to Jalisco, were analyzed by energy-dispersive X-ray fluorescence technique (EDXRF). Nine sediment samples were collected in May, 2010 at water depths between 55.5 and 1264 m with a box nucleate sampler type Reinneck. Sediments were dried and a granulometric analysis was performed. In the fraction size lesser than 100 µm, concentration and distribution of K, Ca, Ti, Mn, Fe, Cu, Zn, Ga, Ni and Pb were analyzed by the EDXRF technique and compared with the reference values given by the Environmental Protection Agency (EPA) and Ontario Ministry of the Environment (MOE). In order to know the status of the elements in marine sediments, the enrichment factor and other index were calculated. In the total fraction was also determined the pH, conductivity, total and organic carbon, as well as X-ray diffraction (XRD) and scanning electron microscopy.

Enrichment factors for K, Ca, Ti, Mn Fe, Cu, Zn, Ga and Ni, show they are conservative elements having concentrations in the range of unpolluted sites giving a base data line for the sampling zone. In spite of moderately enrichment factors in the <100 µm range, Pb concentration fraction was similar to those found in not influenced by anthropogenic activities sites nearby Mazatlan Harbor.

Results of XRD show predominant groups in all of the sampling sites as follows: silicates, aluminosilicates (secondary minerals) and quartz, SO\textsubscript{2} (resistant minerals) to leaching solutions over continental rocks. Aluminosilicate-composed sediments belong to the groups of feldspars, quartzes, kaolinites and amphiboles. Other present groups are oxides (hematite, iron oxide hydroxide), halures (halite), chlorite, carbonates (calcite) and sulphur (pyrite) and show the predominant groups of compounds present in these marine sediments. As a Quality Control, Certified Reference material was processed and analyzed at the same conditions.

Chemical characterization of Particulate Matter collected in Easten and South Europe.

The study was performed in twelve European Countries in the frame of the IAEA Regional TC project. The samples of PM10 fraction of Air Particulate Matter (APM) were collected in each country at two sites (urban and rural) during two seasons (winter and summer) in 2009, 2010 and 2011. The concentrations of PM10 were the highest in winter seasons 2010, 2011 and varied from 10 to 134 μg/m³ at urban sites and from 25 to 95 μg/m³ at rural sites. The values for summer were lower and varied from 4 to 40 μg/m³ at urban sites and from 12 to 30 μg/m³ at rural sites. In some locations the limit values were exceeded especially during winter time. Additionally the elemental concentrations were determined in APM by using nuclear or related analytical techniques. The values of the elemental concentrations did not exceed the limit values given by the European regulations. The following elements were considered: K, Cr, Mn, Fe, Cu, Zn, Se, Cd, Pb and Br. In parallel the meteorological parameters were measured and correlated with the elemental concentrations.
Chemical Analysis of Chlorine in Atmospheric Aerosol Samples by High Resolution X-ray Emission Spectroscopy

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Urban atmospheric aerosol pollution is one of the leading environmental problems in the world. In order to work out effective mitigation strategies the knowledge of particulate matter (PM) sources is essential. Chemical characterization of PM components is one way of source determination.

At the Institute of Nuclear Research in Debrecen, the characterization of atmospheric aerosol sources is done by following the hourly evolution of elemental components, single particle microscopy and statistical analysis. Despite the few thousand km distance from the oceans chlorine was found to be a major constituent of particulate matter in Hungarian cities; in some cases even 1-5% concentrations were measured. Single particle analysis using ion and electron microscopy was proved to be a good tool to determine the sources of coarse fraction chlorine [1]. However, in the case of the fine fraction (particles with aerodynamic diameter less than 2.5 μm) the above mentioned methods didn’t provide any useful additional information about the chemical composition of chlorine.

In this work the chemical characterization of fine fraction Cl was done using wavelength dispersive PIXE at the high resolution X-ray spectrometer of the Microanalytical Center at the Jozef Stefan Institute, Ljubljana [2]. The chemical state was determined by observing the shape, structure and shift of the Cl Kβ line. Pure compounds were used as reference. Finally, the capability of the method is demonstrated by measuring two aerosol samples which were collected during a winter campaign in Budapest, 2010.

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Monthly variations of ambient air particulate levels at Navrongo in the Sahel Savannah zone of Ghana.

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Abstract
Air pollution is ubiquitous and is generally seen as the most widespread and obvious kind of environmental damage. Ambient air particulates in Navrongo, a town in the Sahel Savannah Zone in Ghana prone to frequent particulate pollution episodes due to perennial harmattan dust and biomass burning mostly from bushfires has been investigated in this work. Gent air samplers with nuclepore of 47mm diameter were used to sample PM$_{10}$ ambient air particulates in two size fractions being the coarse (PM$_{10-2.5}$) and fine (PM$_{2.5}$). The mean PM$_{10}$, coarse and fine particulate levels obtained were found to be 111.00 µg/m$^3$, 79.00 µg/m$^3$, and 32.30 µg/m$^3$ respectively. High levels of particulate matter were obtained between the months of November and March being the period of harmattan and severe bush fires. The elemental and black carbon concentrations were determined using energy-dispersive X-ray fluorescence technique and smokestain reflectometer respectively. A total of 22 elements from Na to Pb were determined from each of the (PM$_{2.5}$) particulate on the sample filters. Source identification indicated high contributions of biomass burning to total ambient air fine (PM$_{2.5}$) particulates.
Black Carbon, Trace Elements and Particulate Matter levels in the ambient air of the Jomo Kenyatta International Airport, Nairobi

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This study is the first to report trace element concentrations of aerosol particles at an international airport in Africa. Studies like this are important since a degraded air quality in a world of increasing urbanization and industrialization constitutes a direct threat to human health [1].

With a growing global concern on the effect of airports on local air, this study was undertaken at the Jomo Kenyatta International Airport, Nairobi, between May 6th and May 17th 2011. Outdoor aerosol particles were collected using an Andersen™ dichotomous impactor, whereas personal samplers were used for indoor particle collection. The Andersen impactor collect particulate matter of size segregated coarse and fine fractions on Teflon filters. Coarse and fine particle fractions are defined as particles between 2.5 and 10 µm aerodynamic diameter and particles smaller than 2.5 µm, respectively. Indoors only fine particles, also known as PM2.5, were collected. Collection was carried out for 12 hours twice a day (day and night) outdoors and eight hours indoors. The shorter period indoors was chosen to mimic the normal working hours of the staff at the airport.

Mass concentration levels of particulate matter (coarse and fine) and Black Carbon (BC) were determined gravimetrically and by use of a Black Carbon photometer, respectively. Trace elements were determined using the secondary target based Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometer at the Institute of Nuclear Science and Technology, University of Nairobi, Nairobi, Kenya. Quantification was done by the QXAS/AXIL software package.

The outdoor mass concentration range of PM10 and PM2.5 at Jomo-Kenyatta International Airport were 18 – 67 µg m⁻³ and 4 – 28 µg m⁻³, respectively. This is in most cases lower than the drafted Kenyan annual limits of 50 µg m⁻³ and 35 µg m⁻³, respectively. Similarly the concentrations were higher than the World Health Organization (WHO) 24-hour guideline value of 50 µg m⁻³ and 25 µg m⁻³, respectively, on a few occasions only. Median Pb mass concentration was 65 ng m⁻³ in the PM10 fraction. This is significantly lower than the WHO recommended limit of 500 ng m⁻³ in PM10. The concentrations of PM, BC and detected elements indicate that the air at the airport is not more polluted than at other public places in Nairobi, and many other busy places in Africa and elsewhere..


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Characterization of aerosol pollution in two Hungarian cities in winter 2009-2010

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One of the biggest environmental problems in European cities is the aerosol pollution. However, in order to find effective mitigation strategies one has to characterize the chemical and physical properties of particulate matter as well as to identify their sources.

In this work we studied the aerosol pollution in the two biggest cities in Hungary: Budapest (with over 2 million inhabitants) and Debrecen (with 200,000 inhabitants) in the winter of 2009 and 2010. Both cities has problem to keep the EU regulations concerning to the PM10 levels.

Parallel 24 hours aerosol samples were collected in urban background sites in Budapest and in Debrecen every day from the 9th of December 2009 to the 18th March 2010. The sampling sites were: the weather station of the Hungarian Weather Service at Gilice tér, Budapest and the garden of ATOMKI, Debrecen.

In each places Gent type two-stage samplers equipped with Nuclepore polycarbonate filters of 8 μm and 0.4 μm pore diameter were used. Coarse (particles with aerodynamic diameter larger than 2.5 μm) and fine (particles with aerodynamic diameter smaller than 2.5 μm) mass concentrations, elemental composition and black carbon content were determined using gravimetry, Particle Induced X-ray Emission (PIXE) and light absorption methods, respectively.

The concentration and composition of Budapest and Debrecen aerosol pollution has been compared. Our data showed that the average concentration was higher in Budapest than in Debrecen. The concentration of PM10 in Budapest was 30.46 μg/m³ in average, while in Debrecen it was 22.61 μg/m³. The average concentration of PM2.5 was 21.71 μg/m³ (Budapest) and 17.36 μg/m³ (Debrecen). The ratio of PM2.5/PM10 varied between 0.62 and 0.78. The lowest value was 0.62 obtained in Budapest in March 2010, while the highest was 0.78 in Debrecen in January and February 2010.

We studied the variation of concentration on weekdays and on weekends, too. The elemental composition of aerosol in the two cities was similar, with the difference that the concentrations of the anthropogenic components were higher in Budapest.

Aerosol sources were determined by PMF method, and the effects of meteorological conditions were also studied.

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Analysis of trace elements in atmospheric particulate samples by direct measurement with TXRF

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For studies of the health and environmental effects of aerosols particles, it is important to determine not only their concentration in air and size distribution, but also their chemical composition.

The most commonly used methods to measure trace elements content in atmospheric particulate matter are:

- the conventional spectroscopic analysis techniques (inductively coupled plasma-ICP and atomic absorption spectroscopy-AAS) which involve time-consuming chemical treatments and the risk of samples contamination;

- energy dispersive X-ray fluorescence techniques: filters are measured directly by X-ray fluorescence, but an appropriate calibration is needed and the detection limits for many elements are not so good;

- total-reflection X-ray fluorescence (TXRF): sample holders are used as impaction slides in a cascade impactor, filters are measured Òas they areÓ or after digestion and deposition of the digested solution on the quartz carriers.

The approach presented in this paper consists instead in the direct measurement of fine atmospheric particulate samples collected by carbon adhesive tabs mounted directly on quartz disk TXRF sample holders. The typical aerodynamic equivalent diameter of particles collected is mainly less then 10 µm.

This paper reports on the setting-up and validation of the TXRF measurement procedure. Angular scans varying the angle of incidence of the excitation beam while monitoring the fluorescence yield were performed, both on blank samples and on reference dust samples of known granulometry and composition. Also the role of sample azimuth orientation was evaluated. The method permits to avoid any sample treatment, thus reducing time for analysis and minimizing the risk of contamination in sample handling and chemical pretreatments. As a consequence, a great advantage is that a large number of environmental samples can be analyzed in a short time, that could be very useful in the environmental analysis of a wide area and/or for repeated monitoring.

The method was tested on atmospheric particulate matter samples collected at different urban and rural locations in a wide urban and industrial area in Veneto Region (Italy).
X-ray fluorescence analysis of precious metals nuggets


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In this work, portable XRF spectrometers PRIZMA-M(Au) (Yuzhpolimetall, Russia) and InnovX Omega (InnovXSystem, USA) were used in the development of the quantitative method of precious metals determination in gold, platinum, palladium and silver nuggets from Ural, Siberia and Far East of Russia.

Irregular shape, non-homogeneity and inclusions of other minerals are the important features of precious metals nuggets. As a rule, precious metal content is appreciably larger on the surface than in the bulk of the nugget. The inclusions may consists of quartz, iron oxides, native platinum and palladium (in gold nuggets), native gold (in platinum nuggets) etc. Besides, there may be cavities and porosity inside the nuggets. Silver nuggets have rather thick lay of patina on the surface. All these features should be taken into account in developing an analytical method.

About 100 nuggets of gold, 15 platinum and palladium nuggets and 10 nuggets of silver, containing Au 60 ÷ 90%, Pt 85 ÷ 90%, Pd 80 ÷ 90%, Ag 94 ÷ 98% respectively were used to develop the method. Several nuggets investigated were museum pieces (unique nuggets) and should be analyzed without any damage to them.

The following techniques were investigated:
1) XRF analysis without any sample preparation (the only technique suitable for museum nuggets);
2) cleaning of the nugget surface with hydrochloric acid solution before the XRF analysis;
3) pressing of small nuggets before the XRF analysis;
4) drilling of large nuggets and XRF analysis of the shavings.

We used both fundamental parameter approach and calibration with a set of standard samples of precious metals alloys. Measurement procedures were developed for every type of nuggets. The accuracy of the results were checked by ICP atomic emission analysis and density determination.

The investigations showed that pressing of nuggets before measurements alloyed to obtain rather accurate results without any other treatment. The relative measurement uncertainty for metal parts of the nuggets did not exceed 1%. The expanded uncertainty of the determination of gold in the bulk of the nuggets was about 10% the main source of the uncertainty being non-homogeneity of the sample. The accuracy is satisfactory because high precision is normally not required. However the technique is not suitable for museum pieces so their quantitative chemical composition can be approximately assessed by combination of XRF measurements and density determination.
Perspectives and opportunities in plant science research of synchrotron microscopy and spectroscopy techniques

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The research challenges and questions faced in plant science occur over multiple spatial and temporal scales and levels, involving complex reactions at physiological, physical and chemical interfaces between abiotic and biotic components of the soil and atmosphere. This paper focuses on recent breakthroughs in the study of plant morphological, structural and biochemical properties and delineates new frontiers in characterization processes.

Pushing the knowledge limits further undoubtedly involves the use of advanced, in-situ technologies in combination with interdisciplinary research, combining macroscopic measurements with micro-scale investigations. The necessity of molecular, environmental, and interfacial characterization within plant tissues and sub-tissues at sub-cellular level is becoming increasingly important, with an examination on localized and specific areas. Realistically, as biological based materials are highly heterogeneous and complex by nature, not a single technique can answer all the questions. With the advent of state-of-the-art synchrotron imaging/micro-spectroscopy based techniques, the simultaneous elucidation of physiological mechanisms and structural biochemistry at micro-scales can be undertaken in-situ and complementary investigations performed \[1\]. The challenge resides in sample preparation, sample environment for characterization and on the successive applications of the techniques. Indeed, resolving the distribution, status, competition and concentration of elements and molecules within the different morphological structures of a specific physiological tissue is essential for understanding the mechanisms involved in their regulation, allocation, absorption, transport, accumulation, functionality and bioavailability.

To fulfill that purpose, multi, interdisciplinary, and multifaceted synchrotron radiation (SR) based imaging techniques were successfully correlated and combined to provide highly sensitive spatially resolved chemical analysis. In particular, common wheat seeds \[2\] and hyperaccumulating \textit{Thlaspi Praecox} leaves and seeds were probed via SR-FTIR, to reveal the type, distribution and relative amount of functional and molecular groups, SR-X-ray spectro-microscopy, to obtain high resolution imaging of the morphology of the specimen by many contrast mechanisms (transmission, differential phase contrast, brightfield and fluorescence), and SR-X-ray computed microtomography, to elucidate non-invasively the 3D structural arrangements of organs and tissues. These combined studies are leading to significant new insights on plant morphology, structural biochemistry, reactivity and physiological relevance.

Applicability of ANGLE software for semiconductor detector efficiency calculations in 1–100 keV energy range

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ANGLE software for semiconductor detector gamma-efficiency calculations is recently upgraded for 1-100 keV energy range – becoming thus suitable for low energy photon detectors (LEPD) and extended range photon detectors (GMX), i.e. for quantitative X-ray spectrometry.

In various forms, ANGLE has been in use for 18 years now in numerous analytical laboratories worldwide [1-3]. Its purpose is to allow for the accurate determination of the activities of gamma-spectroscopic samples (now also X-spectroscopic) for which no “replicate” standard exists, in terms of geometry and matrix. It employs a semi-empirical “efficiency transfer” approach, which combines advantages of both absolute (Monte Carlo) and relative (traceable-source-based) methods to determine sample activity by gamma-spectrometry, while reducing the practical limitations of the latter methods and minimizing potential for systematic errors in the former.

ANGLE can be thus regarded as a key to gamma and X-ray spectrometry.

The physical model behind is the concept of the effective solid angle – a parameter calculated upon the input data on geometrical, physical and chemical (composition) characteristics of (1) the source (2) the detector and (3) counting arrangement (incl. intercepting layers between the latter two).

The program can be applied to practically all situations encountered in an analytical laboratory practice. Sources of various shapes and any matrix composition, measured on HPGe, LEPD, GMX, etc. can be treated. No standards are required, but a start-up “reference efficiency curve” (REC) must be obtained, generally as a one-time procedure. Although calibrated point sources are generally recommended for this purpose, any source/geometry can be chosen as the reference to provide the REC. More than one REC per detector might prove valuable in the interests of better accuracy: The closer the match between the REC and the actual absolute efficiency of the sample, the smaller the efficiency transfer and the more accurate the result (“near-relative” method).

ANGLE is characterized by (1) a wide range of applicability, (2) high accuracy, (3) ease-of-use, (4) short computation times, (5) flexibility in respect with input parameters and output data, including easy communication with another software and (6) suitability for teaching/training purposes. The ANGLE architecture also offers (7) potential for accommodating other efficiency calculation methods of semi-empirical or absolute (Monte Carlo) type. In addition, its current scope of applicability (8) can readily be extended to further/particular user's needs and/or fields of interest – it can be thus regarded as an “open-ended” computer code. A key aspect and difference from other approaches, which greatly enhances practicality is that (9) no “factory characterization” of the detector response is required. In fact any semiconductor detector may be used so long as some basic knowledge concerning its construction is available.

Application of methods and experiences of X-ray emission spectrometry on the evaluation of low-energy range of gamma-spectra

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Gamma-emission spectrometry is a widely used method of quantitative and nuclide-specific analysis of gamma emitting radionuclides. The advantages of this method are the multi-isotopic character, high sensitivity and simple sample preparation. The application of gamma-detectors mounted with carbon-epoxy windows allows the efficient detection of low-energy gamma rays down to 5 keV energy. The low energy (5 – 80 keV) range of gamma-spectra is mixed: not only gamma-rays but X-ray lines are present in the spectra. These X-rays come from at least two sources: several radioisotopes decay with electron capture emitting the characteristic X-rays of their daughter element. X-rays originate from photoelectric excitation of the main elements of the sample or the components of the measuring system or its shielding. Line overlaps are rather frequent in the low energy range of the spectra. Characteristic X-ray lines are usually multiplets, where the energy difference within the individual lines are significantly smaller than the energy resolution of the applied semiconductor detectors. Moreover the continuous background is definitely higher in the low energy range of the spectra. These characteristics are usual in X-ray emission spectra and X-ray spectrometry has well established methods to handle them. Background removal, peak deconvolution and fitting of multiplet lines are routine procedures of X-ray spectrum evaluation. The application of these methods and experiences on the evaluation of gamma-spectra can definitely improve the quality and reliability of the analysis. X-ray spectra evaluation computer codes are used extended with the necessary low energy gamma lines. Since germanium detectors are optimised for higher energies, in very critical cases Si(Li) X-ray detectors can be applied for the recording of the low energy range of gamma-spectra. These detectors have better energy resolution but – due to the smaller active volume dimensions – worse absolute efficiency in the low energy range. There are several radionuclides, whose all emission lines (X- or gamma lines) lie in the low energy range: $^{55}$Fe, $^{57}$Fe, $^{109}$Cd, $^{125}$I, $^{241}$Am. The accurate evaluation of the low energy gamma and X-ray lines are crucial in the analysis of these nuclides. Analysis of these nuclides are discussed on samples of environmental origin.
A relational database and web-interface to x-ray fluorescence related elemental data

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X-Ray Fluorescence Analysis (XRF) is a sensitive technique for qualitative and quantitative elemental determination. For spectral analysis and quantification it relies on the knowledge of atomic properties. These are related to the photoelectric cross sections, energy of the electron binding energies and hence the characteristic emission lines, the emission probabilities. The scattering cross sections together with the photoelectric cross section are used for the calculation of the attenuation of the exciting and emitted radiation. Atomic scattering factors are associated to the optical properties of materials and are used for the derivation of the index of refraction of a material. Total Reflection X-Ray Fluorescence Analysis and Grazing Incidence Fluorescence analysis are special configurations of XRF making use of flat smooth substrates and films as samples or sample supporting media. For the calculation of the exciting field intensities above and within the media knowledge of the atomic scattering factors is required.

A relational database has been created with a collection of data including the above mentioned properties. A dynamic website has been realised and linked to the database. A simple interface allows the search of data related to a given element and energy. The data is visualised in table form. Energy dependent data is also visualised graphically if energy intervals and steps are given.

A page with references points to the sources of all data included in the database.

The website can be consulted at https://data-minalab.fbk.eu/txrf/xraydata/
Experimental methods for materials investigation in the X-Ray Center of the TU Vienna

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The information about the atomic arrangements in crystalline solids and therefore the knowledge of the symmetry is an essential knowledge towards understanding the physical properties of the investigated material. Diffraction techniques together with the various applications are one of the most effective methods to investigate the microstructure of the crystalline parts on different length scales. The X-ray center of the Vienna University of Technology is founded on the grounds to act as a central research unit to offer various X-ray instruments like powder and single crystal diffractometers for the investigation of the atomic structure on single crystals, qualitative and quantitative phase analysis of polycrystalline materials, up to stress and texture investigation using modern equipment. Due to high intensity X-ray tubes micro diffraction experiments <200 μm are possible. Sample environment for 11K < T < 1470 K for the powder instruments for different atmospheres allows the investigation of in-situ phase transitions. Next to the diffraction technique the lab is equipped with a PANalytical Axios XRF spectrometer. The presentation will give a survey of the possible investigations based on some examples.
Characterization of layered materials by confocal micro-XRF and ATR-FT-IR imaging techniques

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Micro-X-ray fluorescence (micro-XRF) analysis is an essential tool for observing the elemental distributions of small regions. The polycapillary x-ray optics is very important in the development of the micro-XRF instrument in the laboratory. Moreover, a recent trend in micro-XRF is 3D elemental analysis by using confocal micro-XRF instruments combined with two polycapillary x-ray lenses. Our research group has constructed confocal micro-XRF instruments, and its spatial resolution (depth resolution) was 13.7 micro-meters at an energy of 11.4 keV (Au Lb) [1]. A fine focused x-ray tube (Mo target, 50 kV, 0.6 mA) and an SDD (Vortex-EX-60, sensitive area: 50 mm2, energy resolution: 130 eV) were used as well as two polycapillary x-ray focusing optics developed by XOS. The confocal micro-XRF nondestructively provides elemental depth information by scanning the sample in x-y-z directions, and has been used for analysis of forensic samples with a layer structure [2]. The elemental distribution in each layer was clearly shown, and yet, information on molecular species could not be obtained by this method. On the other hand, attenuated total reflectance FT-IR (ATR-FT-IR) is one of the methods for obtaining information on molecular species in micro regions. In addition, ATR-FT-IR imaging technique can be used to observe spatial heterogeneity of samples on a micro scale [3]. ATR-FT-IR imaging was performed using a PerkinElmer Spectrum 100 FT-IR spectrometer interfaced to a Spectrum Spotlight 400 FT-IR microscope. For ATR imaging, an ATR accessory employing a germanium hemispherical internal reflection element crystal with a diameter of 600 micro-meters was used.

In this work, layered forensic samples were measured by using two techniques in combination, i.e., confocal micro-XRF for elemental distribution analysis, and ATR-FT-IR imaging technique for molecular speciation of each layer. A comparison of the results obtained by two methods made the detailed characterization of layered structure possible.

References
The Use of Bio-Metal Concentrations Combined with Clinical Prognostic Factors to Assess Human Breast Tissues

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Worldwide, breast cancer is the most frequently diagnosed cancer in women and the leading cause of cancer death among women. It is estimated that more than 1.6 million new cases of breast cancer and 425,000 breast cancer deaths occurred in 2010. The concentrations of bio-metals are crucial for the homeostasis of human health and are proving to be a major discriminating variable in the classification of human tissues. Micro probe synchrotron radiation X-ray fluorescence (µSRXRF) techniques have been used to determine the localization and the relative concentrations of Zn, Cu, Fe and Ca in ductal breast cancer samples (which accounts for about 85% of all cases of breast cancer) and normal surrounding breast tissue. Clinical prognostic factors such as oestrogen receptor (ER) status, lymph node status, tumour size, grade, menopause status, and epidermal growth factor receptor (EGFR) status, can be used to predict patients who have a tumour of an aggressive nature and to identify the high risk patients who may benefit from the therapy. This is the first study that correlates the findings of the differences in the levels of certain elements between individual tumours, to the clinical prognostic factors available for each case. A total of 128 samples were scanned all of which were formalin fixed tissues arranged as micro arrays of 1.0 mm diameter and 10μm thickness. The experimental work was carried out at beamline I18, DIAMOND, UK, FLUO beamline at ANKA, Karlsruhe, Germany, and beamline L, Hasylab, DESY, Hamburg Germany.

Figure 1: An example of a scan showing the reference H and E stained image of a breast sample and the corresponding Zn, Fe, Cu and Ca distribution maps in the tumour (T) and the normal (N) regions. The dark areas of the reference image are the clusters of tumour cells regions.
XRF and XANES on Biological Samples.

What are the Affects of Tissue Fixing?

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Bio-metals are crucial for the homeostasis of human health and are proving to be a major discriminating variable in the classification of human breast tissues. Micro probe synchrotron radiation X-ray fluorescence (µSRXRF) techniques have been used to determine the localization and the relative concentrations of Zn, Cu, Fe and Ca in invasive ductal breast cancer samples and normal surrounding breast tissue. X-ray absorption near edge structure (XANES) spectroscopy technique have been used to identify the oxidation state of Cu, Fe and Zn in these samples in order to correlate the oxidation state of these metals to the carcinogenesis process. Mapping the distribution of trace metals and investigating the ionization state in biological materials have been performed on formalin fixed paraffin embedded breast tissue micro arrays (FFPE –TMAs) of breast carcinoma [1-4]. Recent studies by this group have included experiments to answer fundamental questions in this field, namely, does the fixing process affect the levels and distribution of metals in biological tissue? Does the fixing process change the ionization state of the metals in biological tissue? The aim of the work is to determine any effects the fixing process has on XRF and XANES data collection from biological tissues. This result could be of great benefit to the research community working in this area and in the first instance will direct the manner in which this groups studies are continued. The experimental work was carried out at beamline I18, DIAMOND, UK.

References


The Use of an In-Vivo X-Ray Fluorescence Spectroscopy System to Measure Strontium in Human Bone

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Using an in-vivo x-ray fluorescence system (IVXRF) that has been developed by our group, bone strontium measurements were performed in human subjects. The IVXRF system presents with the advantage of being non-invasive and presents with minimal risk and negligible radiation exposure, thus allowing for repeated bone strontium measurements over time. Measurements are performed at the finger and ankle bone sites, representing primarily cortical and trabecular bone, respectively. Using I-125 seeds as the photon excitation source, it is able to detect strontium K-alpha and K-beta x-rays at 14.2 keV and 15.8 keV, respectively. Normalization of the strontium peaks to the coherent peak at 35.5 keV corrects for factors such as positioning and bone volume. While the K-alpha x-rays relate to bone strontium levels, it is thought that the ratio of the two strontium peaks may impart information on Sr distribution in bone. Theoretically, the expected ratio is equal to 7 since the probability of emission for a strontium K-alpha photon is seven times larger than the probability of emission for a strontium K-beta photon. However, if it is assumed that strontium is uniformly distributed in hydrated cortical bone, then this ratio is lowered to 5.2, considering that the bone thickness is infinite at this energy. Interestingly, in the human subjects measured with this IVXRF system, ratios were observed to vary with time at both the finger and ankle bone during a period of Sr supplementation. Thus, more investigation is needed to help answer the variability observed in the K-alpha to K-beta ratios.
Study of the water influence on structural transformation of human breast lesions by combining WAXS and SAXS

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It is known that water content represents about 50% of mass of healthy breast tissues and aid to build their spatial arrangement[1]. During pathological progression, it occur changes into molecular structure of these tissues, however is not yet well established the role of water in this process[2]. Nowadays, wide (WAXS) and small angle x-ray scattering (SAXS) are used to get structural information of biological specimens like breast tissues[3]. Therefore, this work aims to study the influence of water on the structural arrangement of healthy and pathological human breast tissues using samples at native and lyophilized state.

WAXS scattering profiles were measured using a powder diffractometer Siemens D505 operating in back reflection mode. The x-ray tube was equipped with a Cu anode and the energy of 8.04 keV was selected. The photons scattered were recorded by a detection system composed by a monochromator of graphite and a scintillation detector of NaI at the momentum transfer range 2.00nm−1<q=4π.sin(θ/2)/λ<49.90nm−1. SAXS scattering profiles were measured at the Brazilian Light Source (LNLS). A focused monochromator of Si(111) was used in order to provide an x-ray beam of 8.35 keV. In this experiment, the intensity scattered were detected by a two-dimensional CCD between q=0.150nm−1 and q=8.500nm−1.

From WAXS scattering profiles at native state, it is identified peaks due to fatty acids molecules (q=13.9nm−1) for normal samples, and water molecules (q=19.8nm−1) for benign and malignant samples. However, for lyophilized samples, the peak associated to water molecular disappear and a peak at q=13.9nm−1 arises with high intensity than that for normal samples. This behavior indicates that the fatty acids molecules were disarranged in breast lesion, but after freeze-drying they rearrange themselves to form a well-organized structure. In supramolecular level, the SAXS scattering profiles revels that breast lesions presented high collagen-content (peaks between q=0.29nm−1 and q=1.17nm−1). Although, in this momentum transfer range the water just add a background to the scattering profiles, the collagen peaks are shifted to larger q, showing the affinity between these fibrils and water[4].

These initial results show the influence of water on spatial arrangement of breast tissues and its role during pathological progression. By other hand, more studies should be performed for a better understanding of this process.

Use of human primary tooth enamel as a biomarker for lead, manganese and iron uptake during prenatal and neonatal development

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Lead (Pb) and manganese (Mn) may affect neurodevelopment of children by direct toxicity. There is also evidence that Pb and Mn may affect neurodevelopment indirectly by disrupting healthy metabolism of iron (Fe). There is considerable interest in improving the understanding of metabolic interactions affecting uptake of essential and toxic elements during the early stages of child development. To do this, it is necessary to have a reliable biomarker of exposure to these elements during the pre- and neonatal periods. In this work, we examine pre- and neonatal exposures to trace metals using the enamel of 151 primary teeth gathered from children in Quebec, Canada, as a biomarker for Pb, Mn and Fe exposure. In primary tooth enamel, divalent cations may substitute for isovalent calcium (Ca) sites in the hydroxyapatite crystal, the main component of which enamel is formed. The highly conservative nature of the hydroxyapatite crystal allows for its use as a biomarker for Pb, Mn and Fe exposure over the period of enamel formation (14 weeks in utero to 11 months after birth). Once teeth are shed naturally, they can be prepared for analysis in an energy dispersive x-ray fluorescence spectrometer.

Enamel-lead (PbE), manganese (MnE), and iron (FeE) concentrations were analyzed using energy dispersive x-ray fluorescence (EDXRF) spectrometry. Tooth samples were irradiated for one hour live time using a 40 kV palladium x-ray tube and characteristic x-rays were detected with an X-Flash silicon drifted detector. Pb-L\(\alpha\) and L\(\beta\), Mn-K\(\alpha\) and Fe-K\(\alpha\) signals were fit using a custom curve-fitting routine and normalized to the Ca-K\(\alpha\) signal. The curve-fitting routine was developed to provide a unique solution to the deconvolution of overlapping Gaussian peaks at Cr-K\(\beta\) and Mn- K\(\alpha\) lines. Absolute PbE, MnE and FeE were extracted using Pb-, Mn- and FeE-doped NIST Bone Ash Standard pellets as calibrators. The minimum detectable limits of Pb, Mn and Fe for the EDXRF system will be presented. The potential use of the present curve-fitting routine for other problems of deconvolution in x-ray spectrometry will be discussed.
Tissue contamination with implant components after metal-on-metal hip resurfacing arthroplasty.

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Each year, over 2 million endoprostheses are implanted worldwide and since polyethylene wear particles are considered to play a central role in causing aseptic loosening due to osteolysis [1] the use of endoprosthesis with metal/metal bearing increased especially in surface replacement within the last years. This kind of prosthesis is usually made of a CoCrMo alloy which releases higher amounts of metallic abrasion in the surrounding tissue than the metal/PE combination [2]. Our main objective is to extend the knowledge regarding the cobalt content in the bone matrix, measured at samples with different lifetimes, investigated in a previous work [3].

Our goal is to examine whether the incorporation of heavy metals influences the histological situation and the mineralization of the bone tissue. X-Ray Fluorescence measurements at the BAMline [4] @ BESSY II, using Compound Refractive Lenses (CRL) to focus the X-Ray beam, allow a screening of the bone tissue with a resolution of 1 µm x 1 µm. The high spatial resolution allows to investigate e.g. osteocytes or bone mineralization fronts, providing information about the Cobalt-transport mechanisms in the bone tissue. Furthermore, the determination of heavy metal concentrations in bone tissue is a method to show a relation between bone resorption and the deposition of heavy metals. The results of the investigation provide data for risk assessment of periprosthetic metal contamination and give a basis for optimizing metal/metal pairings. The first high-resolution elemental mappings of bone tissue taken from explanted resurfacing hip implants will be shown and discussed.

References

Energy Dispersive X-ray Fluorescence Analysis Study

of Human Semen

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More than 200 human semen samples obtained from men undergoing routine infertility evaluation were analyzed by using Energy Dispersive X-ray Fluorescence technique. Samples of 250 μL were frozen at -196 C, lyophilized and analyzed as a thin target for 11 elements: S, K, Ca, Fe, Cu, Zn, As, Br, Sr, Y and Pb. The excitation was carried out by using X-ray tube with Mo target operated at 35 kV/35 mA. Gallium was used as internal standard. Semen analysis in subfertile population of IVF patients was performed according to WHO guidelines. Patient were divided in two groups of diagnosis: normozoospermia and abnormal (OA, OAT, asthenozoospermia and oligozoospermia). The aim of the study was to compare concentrations of the measured trace elements in fertile and infertile men and to evaluate correlations between trace elements and sperm quality parameters.

Key words: human semen, trace elements, EDXRF, male infertility

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Application of total reflection X-ray fluorescence analysis for the determination of some elements in milk and dairy products

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Milk and dairy products are well-balanced sources of minerals and trace elements. Widely applied analytical methods for elemental analysis of milk and dairy products, e.g. flame and graphite furnace atomic absorption spectrometry, inductively coupled plasma optical emission and mass spectrometry, include either preliminary dry or wet ashing or microwave-assisted digestion of organic matrix [1]. Such techniques of sample preparation are time-consuming and additionally milk samples are relatively difficult to mineralize, due to high content of milk fat and complex organic compounds.

The present study reports the feasibility of the direct analysis of minerals (P, S, Cl, K, Ca) and trace elements (Fe, Ni, Cu, Zn, Br, Rb, Sr, Pb) in different types of milk, kefir, cream, yoghurt and infant formulas by means of total reflection X-ray fluorescence spectrometry (TXRF). All measurements were carried out using the benchtop TXRF spectrometer S2 PICOFOX (Bruker Nano GmbH) [2].

The influence of self-absorption effects in the quantification procedure was investigated with respect to the internal standard used and the sample mass analyzed [3].

The sample preparation procedure involved dilution milk samples with bidistilled water, addition of internal standard (Ga) and drying of sample aliquot onto a quartz glass sample carrier [2, 3]. Mathematical planning of experiment was used for studying the sources of errors in the sample preparation for TXRF. The dependences of the sample preparation error on the degree of dilution with water and the aliquot of milk pipetted onto sample carrier were studied for samples with different fat content. It was shown that for the determination of elements with atomic number \(Z \leq 20\) dilution has to be 1:2 as minimum. The recommended value of sample aliquot is 5 \(\mu\)L.

Precision was found to be approximately 4-5 % for P, S, Cl, K, Ca, Zn, Br, Rb and Sr; 16-18% for Fe, Cu and Pb. Reference material IAEA-153 (trace elements in milk powder) was used to test the accuracy of proposed technique. The data obtained by direct TXRF analysis of dairy products has been compared to that obtained by wavelength dispersive X-ray fluorescence analysis of dried pressed samples [4].

Evaluation in trace elements changes in urine, hemolymph and Malpighian tubules of *Rhodnius prolixus* using SR-TXRF

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*Rhodnius prolixus* is one of the most important vectors of the Chagas’ disease that is ranked as one of the most important in Latin America in terms of social and economic impact, affecting about 18 million people, with about 100 million people living in what are considered to be high risk zones, and approximately 300,000 new cases occurring every year with around 21,000 deaths annually [1].

Water and ion metabolism in insects is regulated in large part by both Malpighian tubules and hindgut [2]. The Malpighian tubules filter hemolymph and secrete a liquid that is often compared with the primary urine in vertebrates. Insect neuropeptides, stimulate fluid secretion by the Malpighian tubules or fluid reabsorption by the tubules or hindgut, respectively [3]. The transport regulation of Malpighian tubules is certainly one of the key points for insect homeostasis and, certainly, it is also important for Trypanosoma cruzi transmission [4].

In this work, we investigated changes in the trace elements chlorine (Cl), potassium (K) and calcium (Ca) in *Rhodnius prolixus* as insect model using urine, hemolymph and Malpighian tubules samples collected in different days after feeding the insects with blood. The Synchrotron Radiation Total Reflection X-ray Fluorescence (SR-TXRF) measurements were carried at the X-ray Fluorescence (XRF) beamline facility in Brazilian Synchrotron Light Laboratory LNLS/Brazil and SR-TXRF.

The observation reveals that the concentration of chlorine increased in Malpighian tubule and in urine samples. The potassium decreased drastically in the Malpighian tubules and after increased on fifth day after feeding, in the urine samples potassium increased on second day. The calcium was maintained on tubules and urine samples. In the hemolymph samples all three elements maintained their concentrations.

Variation of elemental composition in ribs of Wistar rats submitted to simulation of breast cancer radiotherapy using µXRF

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Therapeutic doses of radiation have been shown to have deleterious consequences on bone health. Among the treatment strategies used for breast cancer treatment, the most used are radiotherapy and chemotherapy. Radiotherapy may be given as well as or instead of surgery to destroy the cancer cells using high-dose x-rays. Protocols vary considerably, but generally whole body irradiation totals from 10 to 15 Gy, whereas local therapy totals from 40 to 70 Gy. In clinical practice, the quantitative evaluation of bone tissue relies on measurements of bone mineral density values, which are closely associated with the risk of osteoporotic fracture. Improved survivorship rates of cancer patients receiving radiotherapy increase the importance of understanding the mechanisms and long-term effects of radiation-induced bone alteration of its basic elemental composition. In this work we compared P, Ca, Fe, Zn and Sr contents in dorsal ribs of female Wistar rats (Rattus norvegicus) which were irradiated simulating radiotherapy procedures to breast cancer with a single dose of 20 Gy. The determination of the elements content was performed using synchrotron radiation microbeam at the X-ray Fluorescence beamline at Brazilian Synchrotron Light Laboratory (LNLS). Results showed that elements content varied within the ribs of rats submitted to radiotherapy in comparison to the control group.
Rh speciation in cancer cell lines by K-edge SR TXRF XANES

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Dinuclear metal-metal bonded complexes have attracted great attention because of their chemical reactivity, high catalytic activity in many reactions. These complexes, mainly rhodium, ruthenium and rhenium are also known for their cytostatic properties since the 1970s and are among the most promising non-platinum anticancer complexes. It was shown that dirhodium tetraacetate exhibits appreciable cytostatic activity against a variety of cell lines, including L1210 tumor, sarcoma 180, Ehrlich ascites, P388 lymphocytic leukemia, etc. Among the recognized non-platinum antitumor agents are dinuclear carboxylates species of Rh, Re, and Ru.

Some years ago it was elucidated that Rh(II)-Rh(II) carboxylate can interact with DNA giving a biologically active metal-metal-bonded system, which is the primary target in the design of replacements for platinum anticancer agents. To elucidate the possible binding modes of DNA to the dirhodium core Rh-Rh, interactions with nucleobases, nucleotides, dinucleotides were studied. Our recent investigations proved (data not published), that some types of the Rh complexes prepared in the laboratory of the Department of Organic Chemistry at ELTE can get into the cells, and these findings are in good correlation with the biological data. The experimental data obtained at HASYLAB beamline L will help to understand the mechanism of the biological effect of Rh complexes.

X-Ray Absorption Near Edge Structure (XANES) analysis in combination with Synchrotron Radiation induced Total reflection X-Ray Fluorescence (SR-TXRF) acquisition was used to determine the oxidation state of Rh in human cancer cells. The applied geometry enables the acquisition of two types of spectra using a single method of sample preparation and the same reflector: the TXRF spectrum yielding elemental analytical information as well as the XANES spectrum containing information on the oxidation state and molecular environment of Rhodium. The big advantage of the investigation using SR-TXRF-XANES is the reduction of the sample preparation to a minimum: the cells available in a suspension can be directly pipetted on the Si reflectors, dried, inserted in the vacuum chamber and measured. XANES spectra of several dirhodium complexes were recorded and compared with those obtained on different cell lines.

The SR-TXRF setup – a vacuum chamber with an 8 stage sample changer - installed at Beamline L with the 50mm² Silicon Drift detector available there was used for the experiments. The absorption spectra were recorded by tuning the energy of the incident beam across the K absorption edge of Rh using the Si(111) double monochromator. The evaluation of the XANES spectra was performed as a fingerprint method by comparison of the measurements of the unknown samples to those of the standards.
Determination of low Z elements in human serum of patients with idiopathic thrombocytopenic purpura by total reflection X-ray fluorescence

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Idiopathic Thrombocytopenic Purpura (ITP) is a blood disorder characterized by an abnormal decrease in the number of platelets in the blood. ITP results from development of an antibody directed against a structural platelet antigen (an autoantibody). The cause of ITP is not known and their diagnosis requires that other disorders be excluded through selective tests. In this work, forty patients suffering from ITP and sixty healthy volunteers (Control Group) were analyzed. All the serum samples had been collected from people who live in the urban area of Rio de Janeiro City/Brazil. Blood was collected into vacutainers without additives. The measurements were performed at the X-Ray Fluorescence Beamline at Brazilian National Synchrotron Light Laboratory (LNLS), in Campinas, São Paulo using a polychromatic beam with maximum energy of 20 keV for the excitation and an Ultra-LEGe detector with resolution of 148 eV at 5.9 keV. Standard solutions with Vanadium as internal standard were prepared for calibration system. It was possible to determine the elemental concentrations of the following seven elements: O, Na, P, S, Cl, K and Ca. The Student’s t-test was used to analyze significant differences ($\alpha = 0.05$) between group of patients with ITP and the control group. The elements that presented significant differences were: Phosphorous, Sulphur, Chlorine, Potassium and Calcium. These results will help the biomedical field with regard to early diagnosis and improved medical treatment. Thus, our findings indicate that these elements can be related to the important biochemical processes in ITP.
Distribution of Fe, Cu and Zn in the spheroids prostate cells by X-Ray fluorescence with synchrotron radiation

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Spheroids cell (three-dimensional multicellular aggregates) is the useful culture technique for tissue engineering or regenerative medicine research, pharmacological and toxicological studies, and fundamental studies in cell biology. In this work, we investigated Fe, Cu and Zn distribution (mapping) in spheroids derived from tissue prostate with cancer (PCa) and Benign Prostatic Hyperplasia (BPH). The measurements were performed in standard geometry of 45° incidence, exciting with a white beam and using an optical capillary with 20 µm diameter collimation in the XRF beam line at the Synchrotron Light National Laboratory (Campinas, Brazil). The distribution of the elements Fe, Cu and Zn were determined. The results showed that most elements analyzed presented non-uniform distribution.
Iron speciation in human cancer cell lines by K-edge SRTXRF-XANES

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X-Ray Absorption Near Edge Structure (XANES) analysis in combination with Synchrotron Radiation induced Total reflection X-Ray Fluorescence (SR-TXRF) acquisition was used to determine the oxidation state of Fe in iron-overloaded human cancer cells. The Fe K-Edge XANES measurements in fluorescence mode and grazing incidence geometry were carried out using the TXRF vacuum chamber setup at the beamline L at the Hamburger Synchrotronstrahlungslabor (HASYLAB) at DESY. The feasibility of the SR-TXRF XANES analysis was shown in detail in our previous study [1].

The excitation energy was tuned from 7015 eV to 7500 eV in varying steps (10 eV to 0.5 eV) across the iron K-edge at 7112 eV. To get reasonable peak to background ratios the acquisition time for each spectrum was set between 5 and 15 seconds depending on the Fe fluorescence intensity of each sample. At least two repetitive scans were performed for each specimen to increase the signal to noise ratio. For energy calibration the absorption of an iron foil was recorded in transmission mode simultaneously during all XANES measurements.

Different human colorectal cancer cell lines (HCA-7, HT-29) were prepared at 2nd Institute of Pathology (Budapest, Hungary). The samples have been prepared without treatments or with treatments with different iron forms. The cellular uptake of iron was investigated recently with different analytical techniques [2]. During the sample preparation the cells were treated with Fe^{2+} or Fe^{3+} salts (i.e. FeSO_{4}, FeCl_{3}, Fe^{3+}citric) and transferrin. Main aim was to gain information about the iron compound inside the cells after these treatments. Because the data quality could be improved significantly based on the results of the feasibility study, we were able to analyze a total of 43 samples prepared using different iron treatments. Principle component analysis (PCA) and hierarchical clustering was performed in order to pool samples showing similar XANES. We observed that independently of the chemical treatment the two cell types can be differentiated unbiased and without using a priori knowledge by their XANES using PCA & clustering.

References


Characterization of GSR patterns produced by handguns with polygonal rifling barrels by X Ray Fluorescence for shooting distance estimation

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One of the most important aspects of the criminal investigation of a shooting incident is the target-to-muzzle distance determination. This determination can establish the relative positions of the shooter and the victim or even help to establish the shooters intent.

Forensic laboratories use chemografic tests as the standard procedure for this kind of analysis. This methodology implies a great deal of sample processing which includes several chemical reactions.

This work demonstrates the suitability of Energy Dispersive X-Ray Fluorescence (XRF) as alternative for the chemografic methodology when handguns with polygonal rifling barrels are used. XRF has the big advantage of being fast, non-destructive and without chemical preparation.

Using plain white cotton tissue, as a tentative model, and Glock’s 17, 19 and 26 handguns, several samples were prepared by shooting pieces of tissue at several distances. Four squares (3x3 cm\textsuperscript{2} each) of the target were cut and analysed directly at the X-ray beam.

The spectrometer used in this work to quantify Cu, Zn, Sb, Ba and Pb consists of an X-ray tube (PW 1140; 100 kV, 80 mA) equipped with a changeable secondary target, in molybdenum. The X-ray tube, the secondary target and the sample are in a triaxial geometry. The X-ray beam is collimated throughout two silver apertures, and the beam size is 1.5 cm. The characteristic radiation emitted by the elements present in the sample is detected by a Si(Li) detector, with a 30 mm\textsuperscript{2} active area and 8 μm beryllium window. The energy resolution is 135 eV at 5.9 keV. Quantitative calculations are made by the fundamental parameters method.

The pattern distribution for concentrations of Cu, Zn, Sb, Ba and Pb, was obtained as a function of the shoot distance.

It was demonstrated that there is a similar behaviour for all elements. Lead is the element presenting higher concentration, reaching 1000 µg/g in some cases, followed by Sb, Ba, Zn and Cu. All concentrations decrease from the internal part, to the outside and the distribution shows a tendency that could be defined by a mathematical function.
Depth elemental imaging of near surface of the forensic samples by confocal 3D-XRF

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XRF is non-destructive analytical method of the solid sample. XRF has been widely used to geological and industrial minerals, environmental, archeological, cultural heritage, forensic science etc. [1]. A micro-X-ray beam can be created in the laboratory by various focusing X-ray optics. Previously, non-destructive 3D-XRF analysis had not been easy because of the high penetration of fluorescent X-rays emitted into the sample. A recently developed confocal micro-XRF technique combined with polycapillary X-ray lenses enables depth-selective analysis [2]. By scanning the sample in x-y-z directions, 3D elemental images and depth elemental profiles are obtained. We discussed the possibility of discrimination of leather samples related to forensic science.

The polycapillary full lens was attached to X-ray tube (Mo anode, 50 kV, 0.6 mA) and the polycapillary half lens was attached to the SDD (Vortexs-EX-60, sensitive area : 50 mm$^2$, energy resolution : 130 eV). Both polycapillary X-ray lenses were set in the optimum confocal geometry, as shown in Fig 1. Using confocal 3D-XRF instrument, we obtained depth profiles and depth elemental images. The samples were natural leather and synthetic leather. We discussed another approach of discrimination. Cluster analysis is applied for assigning a set of samples into groups (called cluster) so that the samples with similar characteristics are categorized in the same cluster. The detailed results will be shown on the poster.

Reference
Quantitative analysis of the trace elements zinc, strontium and lead in human bone by energy dispersive x-ray fluorescence analysis

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In the human body trace elements are present in minute quantities and while some of them, for instance zinc (Zn) or strontium (Sr), play an important role in human health, there is a growing number of toxic trace elements, among them lead (Pb), involved in development of numerous diseases.

In bone metabolism the concentrations of the vital trace elements Zn and Sr and the toxic element lead Pb are of great interest.

In this study the concentrations of Zn, Sr, and Pb in four human osteoporotic fractured femoral neck samples, previously analyzed by synchrotron induced micro x-ray fluorescence analysis (SR-µXRF), were determined by quantitative x-ray fluorescence analysis. For the quantification an approach using external standards with matrix very similar to human bone was chosen. Two materials suitable for standards were tested: calcium sulfate dihydrate (CaSO₄ • 2H₂O), commonly known as Gypsum, and milled pig bone.

The measurements were performed with the EDXRF-Spectrometer Epsilon 5 (PANalytical, Almelo, The Netherlands) featuring a three-dimensional polarizing optical geometry. For ideal excitation conditions Germanium (Ge), Zirconium (Zr) and Molybdenum (Mo) were used as secondary targets. The spectrometer has a variable tube voltage of 25-100 kV with a maximal power of 600 W and is equipped with a HPGe detector.

The organic parts (bone marrow, fat, periosteum) of the bone samples was removed and after dehydration and drying the samples were grinded in a disc mill. The pig bone meal was separated in terms of particle size to a <80 µm and 80-200 µm fraction. Both particle sizes were analyzed and no significant difference with respect to the major and trace elements present in the sample matrix was found.

For each matrix (pig bone meal <80 µm particle size, pig bone meal 80-200 µm particle size and CaSO₄ • 2H₂O) a sets of 11 standards with equal amounts of Zn, Sr and Pb was prepared. The standards were pelletized and cover a range of 0-125 µg/g added concentration.

An error analysis of the calibration curves using confidence and prediction bands was performed. The calibrations were validated with the IAEA H-5 Animal Bone Standard. The results obtained were in excellent agreement with the certified values. The Detection Limits (LOD) for Zn and Pb in pig bones and calcium sulfate dehydrate are 1.5 µg/g and for Sr 0.5 µg/g. The Quantification Limits (LOQ) for Zn and Pb were 5 µg/g and for Sr 2 µg/g.

Sample preparation of the human bones was carried out similarly to the pig bones. Human bone meal was separated to <200 µm and 200-1000 µm particle size. The quantification of the human femoral necks shows a very high relative uncertainty for lead due to the concentrations being near the quantification limit of about 5 µg/g. The concentration of Zinc varies in the range of 90 µg/g to 150 µg/g whereas the concentration of Strontium varies in the range of 30 µg/g to 70 µg/g.
Distribution of trace elements in the mineralized matrix of human osteosarcoma tissue

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Osteosarcoma is the most common primary bone malignancy, typically occurring during the adolescent growth spurt, but there is a second, smaller peak in the elderly \cite{1}. It is characterized by the production of tumour osteoid and immature bone matrix by malignant cells \cite{2}. With today's combination of chemotherapy and surgery long-term survival rates of more than 70\% have been reported. However, very little is still known about the etiology of the tumour. In order to further improve treatment and to develop new treatment strategies it is pivotal to get more insight into the fundamental biology of the disease.

In recent years, dramatic changes in minor and trace elements were found in various different cancer types - e.g. breast cancer, prostatic carcinoma \cite{3-7}. These metals bind to proteins - so called metalloproteins - that perform different biological and physiological functions \cite{4}. However, very little is known about trace element levels and accumulations in osteosarcoma. Six bone samples of human osteosarcomas are obtained following surgical resection at the Dept. of Orthopaedics, Medical University of Vienna, Vienna, Austria. Three samples were histologically identified as high-grade (G3) osteoblastic osteosarcomas and three as chondroblastic sarcomas. The samples contained tumour tissue as well as adjacent normal healthy bone tissue as an internal control. The study was approved by the ethics committee at the Medical University. The undecalcified samples were examined by quantitative backscattered electron imaging using a pixel resolution of 1 µm. Grey-level images were generated to differentiate between healthy bone tissue and the mineralized and non-mineralized tumour tissue. Areas of interest were analyzed with Synchrotron Radiation induced confocal micro x-ray fluorescence analysis (SR µ-XRF) to determine the distribution of Ca, Sr, Zn, Fe in tumour tissue and healthy bone. Measurements were performed at the FLUO beamline at ANKA sing a beam size of 15x12 µm\textsuperscript{2} and a depth resolution of 20 µm at Au-L\textsubscript{α}, with primary excitation energy of 17 keV. Our measurements revealed significant differences between healthy bone and calcified cancerous tissue. A positive correlation of Fe and Zn and an accumulation of these elements in calcified cancerous tissue could be observed. Furthermore, the Ca content of mineralized malignant tissues was in general higher than in healthy bone. These findings of differential accumulation of trace elements in normal and malignant bone samples may lead to new insights into basic tumour biology of osteosarcomas.

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