XRF Workshop
Trace Analysis
Synchrotron radiation induced XRF

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Advantage
simultaneous qualitative & quantitative determination of major, minor and trace elements (down to ppm level)

Disadvantage
scattering radiation from sample & sample carrier ⇒ high background

Properties of Synchrotron Radiation:

- High Intensity
- High collimation vertical to the orbital plane (little angular divergence)
- Continuous energy distribution ⇒ monochromators can be used over a wide range of energies
- Photons are highly polarized in the orbital plane ⇒ significant background reduction in EDXRF
- Detection Limits in the ppb range for medium Z Elements

To improve detection limits:

Influence on detection limits:

\[ LLD = \frac{3 \cdot \sqrt{N_B} \cdot m_{\text{sample}}}{N_N} = \frac{3 \cdot t_B}{S(\text{cps/ng})} \]

- \( N_B \) reduced
- \( N_N \) enhanced
- Reduction of detection limits
Influence of radiation source upon S and IB:

- Intensity (larger S and IB)
- Spectral distribution (monochromatic excitation ⇒ smaller IB)
- Linear polarization (smaller IB)

Synchrotron radiation:

\[ LLD = \frac{3 \gamma \sqrt{J}}{\sqrt{t}} \]

Why Synchrotron Radiation?
- High Intensity
- High collimation vertical to the orbital plane (little angular divergence)
- Continuous energy distribution ⇒ monochromators can be used over a wide range of energies
- Photons are highly polarized in the orbital plane ⇒ significant background reduction in EDXRF

Detection Limits in the fg range for medium Z Elements

Synchrotron-produced X-ray beams have unique properties:

1. Continuous energy distribution ⇒ monoenergetic beams
2. Polarized in the plane of the electron beam orbit ⇒ important for background reduction in BRAKE experiments.
3. Highly collimated in the vertical direction ⇒ intense beams with little angular divergence.
4. Small source size ⇒ production of intense beams of small area is feasible.

Trace element analysis:
- Reduction of the background
- Enhancement of the signal intensity
- Monochromator energy tunability is possible.
- SR is the ideal X-ray source for signal enhancement.
Polarized radiation: dramatic improvements in signal to noise ratios, if the detector is located in the direction of the Polarization vector, because of the extreme anisotropic emission characteristics of the scattered radiation based on the classical dipole radiation. In this configuration, only the isotropic emission of the the fluorescence signal is detected.

Arranging the detector in the plane of the orbit of a Storage Ring makes use of this effect.

Energy tunability

With a monochromator monoenergetic radiation can be obtained from the intensive SR spectrum allowing to choose optimized excitation conditions for the analytical problem.

Example: Ti and Ba were separated, changing the excitation energy.

\[ E > E_{\text{Ti-K}} (4.96 \text{ keV}) \text{ and } E_{\text{Ba-La}} (4.46 \text{ keV}) \]

\( \Rightarrow \) Ti-K (4.51 keV) and Ba-La (4.46 keV) overlap completely

\[ E_{\text{Ti-K}} < E < E_{\text{Ba-La}} \text{, Ti-Ka peak can be separated} \]

When the excitation energy as set between the edges, the Ba-La peak was suppressed and the Ti-Ka peak can be separated, leading to an accurate determination of the Ti concentration.

Selective excitation - determination of trace elements in higher Z matrices

determination of trace elements in a matrix whose atomic number is higher than that of the analyzing element, such as Ni in Cu. In such materials the fluorescence radiation of the matrix element is so strong that the energy dispersive detector easily becomes saturated, resulting in low sensitivities.

By tuning the excitation energy just below the absorption edge the fluorescence radiation of the matrix element is suppressed.

1 ng Ni in 200 ng Cu
Total external reflection of X-rays

\[ \Phi_{\text{crit}} = \sqrt{2 \beta} \frac{20.7}{E} \sqrt{\rho} \]

\( \phi_{\text{crit}} \) [mrad], \( E \) [keV], \( \rho \) [g/cm\(^3\)]

\( \beta \approx 10^{-8} \) dispersion:
\( \delta \approx 10^{-6} \) absorption:

\( \delta = K f(E) \)
\( \sigma = K f_s(E) \)

\( K = \frac{r_0^2}{4\pi} N \rho \)

\( r_0 \) classical electron radius
\( N \) Avogadro's constant
\( A \) atomic weight
\( \rho \) density [g/cm\(^3\)]

Transmission / Reflection Coefficient

Advantages
- background reduction
- double excitation of sample
- small distance sample \( \rightarrow \) detector (~1mm) \( \rightarrow \) large solid angle
- angle dependence of fluorescence signal \( \rightarrow \) information about type of sample (bulk, particle, film, implantation)

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**Fundamentals of TXRF**

Angle dependence of fluorescence signal: information about type of sample:
- bulk
- particle (residue on surface)
- film, implantation (surface layer)

**Advantages of SR-TXRF**

- high flux
- wide spectral range - wide range of detectable elements
- linear polarisation in orbital plane - reduction of background
- low detection limits (fg range)
- small sample mass required

**SR-TXRF @ HASYLAB beamline L**

Experimental Setup @ HASYLAB beamline L

- Detector (SDD)
- CCD camera
- Cross Slits
- Monochromator
- Collimator
- Reflector
- Ta-wedge
- Vacuum chamber

**SR-TXRF with sample changer 8 stages**

8 fg detection limits in 1000s at 17keV
assuming an inspected area of 1cm², this value corresponds to 8E7 atoms/cm²

ML = intensity gain of 80-100
only small increase of scatter peak
Motivation:
To understand the effect of aerosols on global climate a detailed understanding of sources, transport, fate and the physical and chemical properties of atmospheric particles is necessary. The chemical speciation of the toxic elements is of relevance for the environmental impact.

Aerosol particle sampling device, 12-stage, round nozzle Berner low-pressure impactor for particle sizes of 0.06-12 µm (aerodynamic particle sizes).

Advantages of SR-TXRF:
- only small sample mass required
- sampling time can be diminished
- time resolved investigation of atmospheric events
- simple sample preparation (aerosols directly collected on reflectors)
- TXRF offers good sensitivity for XANES speciation of traces

Calibration curves obtained with mean values from three series for five times 1 µL cobalt standard solution spotted successively with a HP 500C printer on a quartz reflector.

29 min day time sampling in the city of Hamburg
8: 16 – 8 µm, 2: 8 – 2 µm, 0.13: 2-0.13 µm, Pb high in very small particles < 130 nm!
Comparison SRTXRF- TXRF in lab

- Detection limits in the pg/m³ range can be reached for a 20-min sampling time
- Further potential
  1. Time resolved trace element analyses in hazards/emergency situation using portable TXRF
  2. Potential to use in industrial/traffic processes where the time scale of the event is similar to the typical sampling durations
- Short time collection can allow one to study temporal variation of elemental concentrations in size-fractionated aerosol

Conclusions:

<table>
<thead>
<tr>
<th>Element</th>
<th>Regular</th>
<th>Ultimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>4513</td>
<td>13.98</td>
</tr>
<tr>
<td>Cl</td>
<td>282.8</td>
<td>12.72</td>
</tr>
<tr>
<td>Ca</td>
<td>70.2</td>
<td>25.49</td>
</tr>
<tr>
<td>Ti</td>
<td>48.7</td>
<td>17.68</td>
</tr>
<tr>
<td>Cr</td>
<td>23.4</td>
<td>8.51</td>
</tr>
<tr>
<td>Fe</td>
<td>12.4</td>
<td>4.51</td>
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<tr>
<td>Cu</td>
<td>4.5</td>
<td>1.63</td>
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<tr>
<td>Zn</td>
<td>3.5</td>
<td>1.26</td>
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<tr>
<td>Se</td>
<td>2.6</td>
<td>0.95</td>
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<tr>
<td>Br</td>
<td>2.4</td>
<td>0.88</td>
</tr>
<tr>
<td>Sr</td>
<td>3.4</td>
<td>1.23</td>
</tr>
<tr>
<td>Pb</td>
<td>5.3</td>
<td>1.92</td>
</tr>
</tbody>
</table>

Detection limits in the pg/m³ range can be reached for a 20-min sampling time.

Further potential:
1. Time resolved trace element analyses in hazards/emergency situation using portable TXRF
2. Potential to use in industrial/traffic processes where the time scale of the event is similar to the typical sampling durations

Short time collection can allow one to study temporal variation of elemental concentrations in size-fractionated aerosol.
Absorption spectroscopy

The x-ray absorption spectrum shows a fine structure if it is sampled with a high resolution. Absorption involves electronic transitions, and the fine structure is affected by energy and density of electronic states and transition probabilities.

Influence of the environment: neighbouring atoms (EXAFS), bond type (XANES)

Variation of excitation energy

- Spectrum at each energy
- Spectrum evaluation (peak area; e.g., As-Kα ROI)

XANES: X-Ray Absorption Near Edge Structure, ends 50-100 eV above the edge
EXAFS: Extended X-Ray Absorption Fine Structure, starts 50-100 eV above the edge

Speciation of As in xylem of plants

Coop: Eötvös Univ. Budapest, Prof. Zaray, Dr. Mihucz

Speciation of arsenic in xylem of plants

Motivation:
Arsenic is contained in groundwater in Eastern Hungary (up to 2 µmol). Speciation of As in xylem is important to:
- understand how plants metabolise and transform As
- assess the health risk caused by As entering the food chain (different As species have different toxicity; e.g., As(III) and As(V))

Experimental:
- At two leaf stage: transferred in solution with arsenic compounds and reduced phosphate concentration
- After 30 days from germination (17 d arsenic):
  - stem cut 2 mm above root neck
  - sap collected with micropipettes
  - for 1 hour into PE vials immersed in ice salt bath

Experimental setup:

Advantages of XAS in TXRF geometry:
- TXRF offers good sensitivity for XANES speciation of traces (ppb range)
- only small sample volumes are required
- simple sample preparation (just pipetting some µl on reflectors)
- prevents unwanted oxidation of sample during preparation
Results:

- Speciation of As was possible down to the 30ppb level
- As(III) in nutrient solutions oxidises easily to As(V)
- Cucumber roots convert As(V) to As(III)

Motivation:

- Surface contamination levels are very low
  - SR-TXRF (LLD in the fg-range)
- Not only the contaminating element is of relevance, also chemical information of the contaminant
  - SR-TXRF XANES

Aim:

- Determination of location and oxidation states of iron-contaminations to trace possible sources.

IBM Wafer fluorescence maps:
Laboratory TXRF Analyzer Rigaku TXRF 300

SR-TXRF spectra of Fe-contamination found at P7

Advantages of SR-TXRF XANES:
- Multielement-analysis of Si-Wafer surface contaminations
- Wafer surface mapping (time consuming)
- Determination of contamination type (residual, surface layer, bulk)
- Analysis of the oxidation state of an element of interest
- All analyses can be done nondestructively within the same setup

GIXRF - theory (courtesy of Giancarlo Pepponi)

1923 Compton – discovery of total external reflection of x-rays
1954 Parratt – recursive method for layered systems approximated for “hard” x-rays
1972-1973 Henke – Lefèvre, M. Montel – non approximated solution (necessary in the soft x-ray region)
1991 de Boer – thorough description of theory with interlayer secondary excitation

GIXRF - ultra shallow implants

Incident x-ray beam
Sample
Detector

- Profile shape
- Quantification


(courtesy of Giancarlo Pepponi)
Simulations of relaxed structures of AsV defects using Density Functional Theory. Geometry optimization for AsnV defects (n = 1–4) with CASTEP plane wave density functional code, using fixed lattice parameters but flexible internal fraction coordinates (better optimization for defect environment).

Further studies are being carried out with the WIEN2K code

Least-squares fit of EXAFS Fourier Transform implementing the DFT calculated structures, assuming the co-presence of Substitutional As, AsnV and SiAs precipitates.

FCC Diamond structure

As isolated in Si

substitutional As As4V


"Correlation of local structure and electrical activation in arsenic ultrashallow junctions in silicon"


(courtesy of Giancarlo Pepponi)

Plasma Ion Imersion Implantation
Pulsed Laser Annealing
Dependence on laser power and number of pulses

Origin of fluorescence signal in depth for different incident angles:

(courtesy of Giancarlo Pepponi)
Combination of XRR+GIXRF

Structural + Elemental analysis

modelling uses the same formalism

GIXRF is a further development

- sensitive to electron density and its changes:
  - material density
  - film thickness
  - optical constants
  - roughness

reveals elemental surface concentrations:
  - material composition
  - in depth elemental information

GIXRF for thin films

generated by Dieter Ingerle

GIXRF can only determine surface mass concentration!
Ambiguity thickness vs. density (combination with GI-XRD???)

GIXRF measurement data fitted to calculated values. This comparison shows the ambiguity of GIXRF concerning density and thickness. For the left side a layer-density of 6.7 g/m³ was used, while on the right 6.1 g/m³ was used.

GIXRF + XRR for thin films

courtesy of Dieter Ingerle

The use of data from both detectors combines the benefits of both techniques and thus reduces the ambiguities of the fitting-procedure, increasing the confidence in the found solution.

EDXRF

Standard XRF

Total Reflection XRF

Absorption Spectroscopy in fluorescence mode (XAS)

Disadvantages
- complex setup and data evaluation
- time consuming measurements

Advantages
- spatially resolved analysis (10 – 60µm)
- 2D & 3D resolution
2D and 3D Imaging of Human Tissue using confocal SR-microXRF

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Confocal Synchrotron µ-XRF Setup

- SDD-Vortex detector
- Microscope + CCD Camera
- Monochromator
- Cross Slits
- Beam stop
- Poly capillary
- 45°
- Beam monitor 2
- Sample stage
- XYZ
- Beam monitor 1
- Multilayer
- ML → intensity gain of 80-100
- only small increase of scatter peak
- Detection Limits: pg/mg (ppb) range
- Resolution down to 50 nm!!

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Results

SR µ-XRF Mapping of Human Bone

- Focal size: ~10-20 µm
- Depth resolution: ~15-20 µm

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Results

- Sr, Zn, Ca, Pb scatter

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Element Distribution in Double Tidemark - Maps

Distribution of Zinc and Lead at the border of non-calcified and calcified articular cartilage

- outer Tidemark (TMa)
- inner Tidemark (TMi)
- non mineralized cartilage (NMCAR)
- mineralized cartilage (MCAR)
- subchondral bone (BONE)

Elemental maps - Cortical bone:

- qBE
- Ca-Ka
- Zn-Ka
- Sr-Ka
- Pb-La

**SF3-A1:**
- Mapsize: 600µm x 500µm
- Pixelsize: 15µm x 10µm
- Counting Time: 10 sec. / Pixel
- Normalization: cps & 100mA R-C

Zn and Pb in cement lines - sign. higher

Correlation of qBEI and µ-XRF Data:

3. Selecting ROIs:
- bone packets (red borders)
- cement lines (yellow areas, width 10µm)

4. Transferring ROIs to µ-XRF maps:
- correlation X-Ray intensities
- bone morphology
Effects of Strontium Ranelate Treatment:

\[ qBEI \]

Serum levels determine Sr uptake during bone formation

Biopsy sample - single case:
- 12 month SrR treatment
- 6 month stopped

Biopsy Sample: 4567KB

Serum levels determine Sr uptake during bone formation

Biopsy Sample: 4567KB

Effects of Strontium Ranelate Treatment:

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