Today’s agenda

- EDXRF vs. TXRF principle
- TXRF Instrumentation
- Sample preparation
- Application Examples
- Comparing TXRF

... Friday, August 6, 9:00 am

Discovering the Selenium Metabolism and Its Impact for Health Prevention by TXRF

Traditional EDXRF

Samples for common XRF spectrometry (ED and WDXRF):

- Solids (cut, polished and put into suitable shape)
- Powders (as pressed pellets, fused beads or loose powders in liquid cups)
- Liquids (in liquid cups)

Necessary sample amount: from 1g to 10 g !!!
**Traditional EDXRF Quantification**

- **Absorption** of primary beam and fluorescence radiation
- **Secondary fluorescence enhancement**

\[ I_i = f(c_i, c_j) \quad \text{and} \quad c_i = f(I_i, c_j) \]

Concentration needs to be determined with matrix matched standards

DO YOU HAVE STANDARDS ???

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**Principles of Total Reflection X-ray Fluorescence Spectroscopy**

- Monochromatic radiation is totally reflected on a polished sample carrier
- Dramatic reduction of absorption and scattering

---

**Principles of Total Reflection X-ray Fluorescence Spectroscopy**

- Negligible absorption of primary beam and fluorescence radiation
- Negligible secondary fluorescence enhancement

\[ I_i = f(c_i) \quad \text{and} \quad c_i = f(I_i) \]

Samples are prepared as thin films or layers

→ matrix effects are negligible
Principles of TXRF Quantification

\[ C_i = \frac{C_{IS} \cdot N_i \cdot S_{IS}}{N_{IS} \cdot S_i} \]

- \( C_i \): Element concentration
- \( C_{IS} \): Internal standard concentration
- \( N_i \): Element net count rate
- \( N_{IS} \): Internal standard net count rate
- \( S_i \): Element sensitivity factor
- \( S_{IS} \): Internal standard sensitivity factor

Element sensitivity
- K-lines
- L-lines

TXRF in different sizes

Benchtop

- Chemical
- Chemical and depth profiling

Basic (commercially available) TXRF
- No vacuum chamber, no purge
- No moving monochromator or alignment
- SDD detector: high count rate, LN2 free!
- Samples on 30 mm substrate only
- Designed for chemical analysis only
- Mobile use possible (100V-230V)

Advanced benchtop TXRF
- Dual or single tube system
- Adjustable monochromator
- Substrate samples for TXRF
- Layered samples - depth profiling

Floor standing TXRF

Semiconductor

Contamination control/mapping of complete wafers
- Detection limits defined in atoms/cm², typical limit of \(10^7\) atoms/cm²
- Bridge tool for wafer handling, 150 - 300 mm compatible
- X-Y-\(\theta\) wafer stage - for enhanced accuracy across entire wafer
- Multitasking - simultaneous VPD* & TXRF operation for highest throughput
- Cleanroom class 100 or less

*) collection of the dissolved residue on wafer with a liquid HF droplet, droplet is dried for TXRF analysis in the wafer center
**Benchtop TXRF Instrument Design**

**X-ray tube**
- Metal ceramic
- air cooled
- 37 or 50 W
- Mo or W target
- Spot size: 1.2 x 0.1 mm² or 50 x 50 µm (microfocus)

**Excitation source Mo**
**Mo Kα excitation**

<table>
<thead>
<tr>
<th>Element</th>
<th>H</th>
<th>He</th>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
<th>Ne</th>
</tr>
</thead>
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<td></td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>Kr</td>
<td></td>
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</tbody>
</table>

**Monochromator**
- flat Mo / B₄C
- Multilayer (Incoatec)
- 17.5 keV
- 80% reflectivity

**Key to TXRF Sensitivity**
1. excitation spectrum
2. spectrum after prefiltration, filter component invisible here
3. emission spectrum of the tube
4. X-ray tube
5. monochromator
6. monochromatized excitation beam
7. detector
8. sample carrier
**Variable Incidence TXRF**  
**Rigaku Nanohunter**

- X-ray Tube
- Monochromator
- Cu
- Mo
- Shutter
- Sample
- Detector

All axes are full-automatically aligned and controlled.

**Variable Incidence TXRF**  
**Evaluation of Distribution on Surface**

- Film Type
- Intermediate Type
- Particle Type

**Benchtop TXRF**  
**Instrument Design**

**Detector**
- Silicon Drift Detector
- 10/30 mm$^2$ XFlash®
- Energy resolution 130-150 eV

**Advantage**
- No need for liquid nitrogen
- Fast, almost no dead time

**Excursion**  
**ED Detector Technology**

<table>
<thead>
<tr>
<th>Detector</th>
<th>SDD XFlash</th>
<th>Si(Li)</th>
<th>PIN-Diode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
<td>+++</td>
<td>+</td>
<td>+++</td>
</tr>
<tr>
<td>Media</td>
<td>No</td>
<td>N$_2$</td>
<td>No</td>
</tr>
</tbody>
</table>
| Energy resolution | < 123 ...
149 eV | < 129 eV | 175 eV ...
260 eV |
| Detector area | 10 / 30 /
(100) mm$^2$ | 30 / 80 mm$^2$ | 7 / 25 mm$^2$ |
| Thickness | 450 µm | 3500 µm | 500 µm |
| High energy efficiency | + | +++ | + |
| Count rate | $> 10^5$ | $10^3$ ...
$10^4$ | $10^3$ |
Excursion
Count Rate vs. Resolution

Sample Carrier

Sample Carrier

Our first spectra!

1. Start of spectra
2. Si fluorescence peak of quartz glass
3. Ar fluorescence peak from air
4. Fluorescence peaks of the elements Ca, Fe, Zn, and Pb
5. Kα1,2-fluorescence peak of the 1-ng-Ni sample
6. Characteristic Mo line from X-ray tube
7. Compton- and Rayleigh scattering peaks
Sample Preparation

**Chemical TXRF Sample preparation**

**Basics**
Samples for TXRF analysis must be prepared as thin films or micro particles.

- Thin film for qualitative analysis: max. 100 µm
- Micro particle for qualitative analysis: max. 500 µm

**Sample preparation**

**Liquid and digested samples**

- You'll need just a few steps for the preparation of liquid samples:
  - fill sample in micro tube
  - add internal standard
  - homogenize
  - pipette on carrier

  Note: high matrix samples may require a dilution step

**Final steps**

- dry by heat / vacuum
- load the instrument
- start data acquisition
Sample preparation
Suspensions

Suspensions can be analyzed just after dilution

- dilute sample with distilled water
  - add internal standard
  - homogenize
- pipette on carrier

Sample preparation
Solid and powder samples I

Solids are ground to fine particle size and resuspended for direct analysis without digestion

- fill powder in mortar
  - grind carefully (<50 µm)
  - weigh about 20-50 mg
- transfer to tube

Sample preparation
Solid and powder samples II

Solids are ground to fine particle size and resuspended for direct analysis without digestion

- fill powder in mortar
  - grind carefully (<50 µm)
  - weigh about 20-50 mg
- transfer to tube

Sample preparation
Microparticles

Microparticles are measured semi-quantitatively and non-destructively

- dab vacuum grease on carrier
  - pick-up some particles with a (glass) rod
  - drop particles on grease
**Application Examples**

**Environmental research and monitoring**
- **Description of the application**
  - Sewage & fresh water analysis
  - Aerosol analysis
  - Filter analysis
  - Contaminated soils

**Benefit by TXRF**
- mobile analysis (ship, truck)
- ppb detection limits
- fast and simple sample preparation
- direct sampling on sample carrier
- detection limits < 1 ng/m³
- direct measurements (qualitatively)
- simple extraction for quantification
- mobile analysis (truck)
- screening for contaminated hot spots

**TXRF Applications**

**Low levels of detection**

Detection limits of
- mono-element standards
- NIST water standards

\[ \text{LLD (\mu g/l)} = 3 \cdot \frac{c (\mu g/l)}{I_{\text{net}} (cts)} \cdot \sqrt{2 \cdot I_{b} (cts)} \]

- \( c \): Concentration (\mu g/l)
- \( I_{\text{net}} \): Net intensity (cts)
- \( I_{b} \): Background intensity (cts)

**Medical and Pharmaceutical**

**Description of the application**
- Blood, Serum and urine
- Impurities in nutrients/pharma
- Authenticity
- “Heavy Metals” Analysis

**Benefit by TXRF**
- ppb detection limits
- fast and simple sample preparation
- comparable results than AAS simultaneous analysis
- element fingerprint ease of sample prep
- USP requirements (10mg/kg) readily achievable

**USP = US Pharmacopia**
Detection limits are in the low to middle ppb range.

**Detection Limits in Biological Matrices**

- **urine**
- **whole blood**
- **blood serum**

**TXRF Applications**

**Blood, Serum and Urine analysis**

- Detection limits are in the low to middle ppb range.

**Food and beverages**

- **Dietary supplements**
  - The poison is everywhere
- **Phytoforensics**
  - Don’t forget the halogenides
- **Rum**
  - How do we detox a drunken sailor...
- **Water and juice**
  - Always crystal clear?
- **Wheat flour**
  - Se-rich wheat, rich farmer

**TXRF Applications**

**Dietary supplements**

- Suspension of 20-50 mg sample in 1 ml Triton X-100 solution
- Addition of Ga (internal standard)
- Homogenize in a ball mill with a special adapter (Retsch MM400, 30 Hz, 3 min)

**Arsenic in Fish Oil**

- Fish oil for human consumption
- The spectrum shows an As contamination of about 3.7 mg/kg
- Conclusion: fish oil prepared for pet food (vet grade)
Thallium in Seaweed
- Seaweed obtained locally (OTC)
- Contaminations of Ti (26 mg/kg), Br (4 mg/kg), As (0.130 mg/kg), Tl (0.07 mg/kg)

Results
- Even smallest sample amounts allow the determination of element ratios in nanoparticles
- S2 PICOFOX “Standardless” analysis applied

Industrial applications
 analytical question
- Element ratios in CdSe nanoparticles coated with ZnS

analytical issues
- Extremely small sample amount (R&D)
- Non-destructive method preferred

TXRF measurement
- Transfer of nanoparticles to quartz carrier by cotton bud
- Standardless quantification

TXRF Applications
Dietary Supplements

TXRF Applications
Nanoparticle characterization

Summary - 3σ Detection Limits
Low background = low detection limits

<table>
<thead>
<tr>
<th>&quot;ppt&quot;</th>
<th>&quot;ppb&quot;</th>
<th>&quot;ppm&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh water</td>
<td>sewage, mining sol.</td>
<td>soil</td>
</tr>
<tr>
<td>Glass, wash coats</td>
<td>wine</td>
<td>Food</td>
</tr>
<tr>
<td>Blood, serum, urine</td>
<td>Pharma</td>
<td>Peptides</td>
</tr>
</tbody>
</table>

Measurement time: 1000s
Comparison
TXRF versus AAS & ICP-OES

Sample application

<table>
<thead>
<tr>
<th></th>
<th>TXRF</th>
<th>ICP-OES</th>
<th>AAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct analysis of solids</td>
<td>Qualitative, quantitative with lower sensitivity</td>
<td>not possible</td>
<td>GF-AAS only</td>
</tr>
<tr>
<td>Sample amount</td>
<td>ng to µg range</td>
<td>mg range</td>
<td>mg range</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>GF-AAS µg range</td>
</tr>
</tbody>
</table>

During operation

<table>
<thead>
<tr>
<th></th>
<th>TXRF</th>
<th>ICP-OES</th>
<th>AAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multielement analysis</td>
<td>Yes</td>
<td>Yes</td>
<td>Sequential only</td>
</tr>
<tr>
<td>Standardless</td>
<td>Yes (with restrictions)</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Meas. time</td>
<td>300 – 1000 s</td>
<td>&lt;10 s per element</td>
<td>&lt;10 s per element</td>
</tr>
<tr>
<td>Calibration</td>
<td>Internal standardization</td>
<td>External, element-specific, to be updated</td>
<td>External, element-specific, to be updated</td>
</tr>
</tbody>
</table>

Cost of operation

<table>
<thead>
<tr>
<th></th>
<th>TXRF</th>
<th>ICP-OES</th>
<th>AAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Consumables</td>
<td>(X-ray tube)</td>
<td>(Nebulizer parts)</td>
<td>Cathode lamps</td>
</tr>
<tr>
<td>Power consumption</td>
<td>Low (150 W)</td>
<td>High (HF generator 2.5 – 3.6 kW)</td>
<td>Low</td>
</tr>
<tr>
<td>Water consumption</td>
<td>none</td>
<td>&gt; 0.5 l/min</td>
<td>~1.5 l/min (GF only)</td>
</tr>
<tr>
<td>Gas consumption</td>
<td>none</td>
<td>Carrier/burning gas (Ar, N₂), 15-20 l/min</td>
<td>FAAS: burning gas (C₂H₂), 1.5-8 l/min GF: Carrier gas (Ar,N₂)</td>
</tr>
</tbody>
</table>
Comparison

TXRF versus AAS & ICP-OES

Other practical issues

<table>
<thead>
<tr>
<th></th>
<th>TXRF</th>
<th>ICP-OES</th>
<th>AAS</th>
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<tbody>
<tr>
<td>Method recognition</td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Maintenance needs</td>
<td>Low</td>
<td>High</td>
<td>Medium</td>
</tr>
<tr>
<td>Instrument size and weight</td>
<td>Compact benchtop 37 kg</td>
<td>Large benchtop 190 – 290 kg</td>
<td>Benchtop 30 – 200 kg</td>
</tr>
<tr>
<td>Mobile use</td>
<td>Yes</td>
<td>Impossible</td>
<td>Hardly possible</td>
</tr>
<tr>
<td>Online (LC)</td>
<td>no</td>
<td>yes</td>
<td></td>
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</table>

TXRF can be an alternative to AAS and/or a complement for existing ICP-OES systems

Major benefits of chemical TXRF

- flexibility with regard to sample types
- easy multi-element analysis without external calibration
- low maintenance and operating costs
- small size of the system (mobile and remote location use)

Comparison

TXRF versus AAS & ICP-OES

Literature and references


Thank you

Any Questions?