Rapid analysis of nutrients and toxic elements in food and beverages by TXRF

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Innovation with Integrity
Welcome

Speakers

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Itinerary

- Next Generation TXRF concept
- Application examples
  - Arsenic in rice
  - Lead in tea drinks
  - Nutrient elements in vitamin pills
  - Toxic metals in glucose
- Comparison with Atomic Spectroscopy
- Summary and outlook
Next Generation TXRF Concept
Functional principle of total reflection X-ray fluorescence (TXRF) spectroscopy

**Total reflection X-Ray Fluorescence spectroscopy**

- Samples must be prepared on a reflective media
- Suitable for liquids, solids, suspensions, films etc.
- Detection limits down to 0.1 ppb
Next Gen TXRF
Excitation and Detection Module
Next Gen TXRF
Excitation and Detection Module

2 Tubes
Mo, W, Cu, Cr, Ag

Detector
60 / 100 mm²

3 Monochromator

Sample Station
Next Gen TXRF
Samples and Sample Changer

Autosampler

- Horizontal sample orientation
- 90 quartz discs (30 mm)
- 2” wafer
- Microscopy slides
- Rectangular samples max. 54 mm
Next Gen TXRF
Samples and Sample Changer

Autosampler

- 6 internal instrument quality standards
Next Gen TXRF
Samples and Sample Changer

Automatic tray recognition

- Recognizes different tray types (disc / wafer / ...)
- "Ownership" for trays
- Automatic loading and starting of measurement jobs possible

LED light provides status information

- Tray identified, no job
- Tray and job identified
- Job running
- Job finished
Next Gen TXRF
Qualified for Routine Analysis

Satisfying requirements in service, research and industrial laboratories

- Provide better system stability over extended period of time
  - Monitor key parameters (Temp, humidity)
  - Implement temperature regulation

- Better data quality
  - automatic alignment and automated procedures (gain correction, tube & detector stability)
  - minimize sample contamination – optimized airflow

- Multi-user operation
  - Large sample holding capacity (90 samples) use of the night-shift
  - Sample loading/unloading during operation
  - User manager to allow multiple users to schedule their measurements
Arsenic in rice - Background
Source of As contamination
- Anthropogenic (mining activities, industrial air pollution)
- Natural/geological (especially in Bangladesh)

Overview limit values
- Proposal Codex Alimentarius (WHO, 2012):
  - 200 µg/kg inorganic As (polished rice)
  - 300 µg/kg inorganic As (raw rice)
- China: Limit value of 200 µg/kg inorganic As (As(III) + As (V))
- European Union: Limit values for As in rice proposed:
  - 200 µg/kg inorganic As (polished rice)
  - 100 µg/kg inorganic As (baby food)
Introduction/Background

Common analytical techniques for As in rice

- Atomic adsorption spectroscopy (AAS)
- Inductively-coupled plasma optical emission spectroscopy (ICP-OES)
- Inductively-coupled plasma mass spectroscopy (ICP-MS)

Advantages of these techniques

- Very low detection limits (down into the low ppb-range)
- Separate analysis of inorganic and organic As-compounds (ICP-MS)

Disadvantages of these techniques

- Laborious sample preparation (acid digestion)
- High demand on analytical staff
- High demand on laboratory infrastructure (Ar gas, cooling water, exhausts)
TXRF project „Arsenic in rice“

Cooperation partner

- Queens University Belfast, Institute for Global Food Safety

Work package 1

- Select rice sample examples from worldwide sources varying As concentrations
- Analyze, compare and evaluate TXRF measurements with existing data from ED-XRF and ICP-MS
- Include baby food and rice products compare different cooking methods

Work Package 2

- Development of an As speciation method rice extraction and selective binding of inorganic As
Arsenic in rice - Measurements
Arsenic in rice
Sample preparation

Samples

Reference standard:
- NIST1568a “Rice flour”

Real samples (obtained at a local supermarket)
- Parboiled rice
- Long grain rice
- Risotto rice
- Round grain rice
- Basmati rice
Arsenic in rice
Sample preparation

- Pregrinding in mortar
- Grinding in ball mill (Retsch MM400, 30 Hz/3 min, Zr vessel)
- Weighing of 100 mg
- Suspending in 5 ml Triton X-100 (1 Vol.-%)
- Internal standardization (10 mg/kg Y)
- 10 µl on quartz glass carriers (samples 3x, CRM 10x)
Arsenic in rice
Measurements

Measurement parameter
S4 T•STAR, S2 PICOFOX 800
- X-ray tube with Mo anode
- 50 kV/1000µA
- 60 mm² SDD
- Measurement time: 1000s
Arsenic in rice

Results

- Typical spectrum of NIST 1568a rice standard
- Detail view of the high energy range above 8 keV
Arsenic in rice

Results

- TXRF (blue) and ICP (grey) values are in good concordance
- New legal limits are 200 µg/kg (China, EU; yellow line)
- Detection limits are about 50 µg/kg (red line)
Arsenic in rice
Summary and Outlook

TXRF is suitable for the detection of As in rice

- Recent developments provide adequate detection limits for the analysis of As in rice
- A standard method to be used in labs with low-level infrastructure is in preparation

Ongoing technical improvements

- Optimize homogenization procedure
- Further increase of detector size
Lead in tea drinks
Lead in tea drinks

Background

Analytical task
• Analysis of lead in tea drink samples with regard to the legal limit of 50 µg/l

Test sample
• Lemon ice tea drink, commercially obtained at a supermarket
• Sample is labelled to contain sugar with a concentration of 7 g/100 ml
Lead in tea drinks
Samples and sample preparation

Sample preparation

- Blank sample
- Spiked sample 10 µg/l Pb
- Spiked sample 50 µg/l Pb
- Spiked sample 200 µg/l Pb

Addition of 500 µg/l Ga internal standard

Homogenization

Pipetting of 10 µl sample on carrier

Drying on hot plate at 40 °C

3x preparation on quartz glass carriers
  - Blank sample
  - Spike sample 10 µg/l Pb
  - Spike sample 200 µg/l Pb

7x preparation on quartz glass carriers
  - Spike sample 50 µg/l Pb

3x preparation on acrylic glass carriers
  - Spike sample 50 µg/l Pb
Lead in tea drinks
Measurements

Instrumentation
- S2 PICOFOX 800
- 50 W Mo-tube (50 kV/1000 µA)
- 60 mm² SDD

Measurement time
- 1200 s

Blank
Spike 10 µg/l
Spike 50 µg/l quartz discs
Spike 50 µg/l acrylic discs
Spike 200 µg/l
# Lead in tea drinks

## Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nominal concentration (µg/l)</th>
<th>TXRF values (µg/l)</th>
<th>Concentration</th>
<th>Standard deviation</th>
<th>Detection limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>~ 0</td>
<td></td>
<td>7,4</td>
<td>2,3</td>
<td>3,9</td>
</tr>
<tr>
<td>Spike 10 µg/l</td>
<td>10</td>
<td></td>
<td>6,2</td>
<td>2,3</td>
<td>3,6</td>
</tr>
<tr>
<td>Spike 50 µg/l quartz discs</td>
<td>50</td>
<td></td>
<td>48</td>
<td>2,1</td>
<td>2,4</td>
</tr>
<tr>
<td>Spike 50 µg/l acrylic discs</td>
<td>50</td>
<td></td>
<td>51</td>
<td>1,6</td>
<td>2,6</td>
</tr>
<tr>
<td>Spike 200 µg/l</td>
<td>200</td>
<td></td>
<td>193</td>
<td>3,9</td>
<td>2,4</td>
</tr>
</tbody>
</table>
Lead in tea drinks
Method detection limit

Detection limits
- MDL Pb: 6.4 µg/l
- LOQ Pb: 20.5 µg/l
- Recovery: 96.8% (50 µg/l Pb)
Lead in tea drinks

Summary

• The safe analysis of tea drinks regarding a limit value of 50 µg/l Pb is possible

• Sample preparation for TXRF is extremely simple, no digestion required

• TXRF does not require daily calibration

• Numerous other elements like Cu, As and Hg can be determined simultaneously
Nutrient elements in vitamin pills
Nutrient elements in vitamin pills

Samples

- Three different vitamin pills from local drugstores
- Analysis of nutrient elements and comparison with nominal concentrations
- 8 Elements
  Mg, P, Ca, Cr, Zn, Se, Mo, I

Sample preparation

- About 100 mg suspended or dissolved in 5 ml 1% Triton X-100
- Addition of 10 µl Y standard (1g/l)
- Homogenization
- 10 µl pipetted on quartz carrier, dried in vacuum
Nutrient elements in vitamin pills

Measurement parameter

S4 T•STAR

- Dual X-ray tube configuration Mo (17.5 keV) and W-Brems (35 keV) excitation
- 50 kV/1000μA
- 60 mm² SDD
- Measurement time: 1000s
Nutrient elements in vitamin pills

Results

- Accurate quantification of nutrients in % / high ppm range possible
- Actual concentrations are significantly different from nominal values
- Risk of overdose to be considered
Nutrient elements in vitamin pills

- Mo excitation allows highly sensitive detection on Cr and Se
- W-Brems excitation suitable for quantification of Mo and I
Nutrient elements in vitamin pills

Detection limits

- One digit ppb limits for most metals
- Improved performance for light elements
- Sub-ppm detection of I puts TXRF ahead of ICP-OES
Toxic metals in glucose
Toxic metals in glucose S4 TStar configuration

Catalyst analysis applying different excitation energies

- Issue of line overlaps when applying Mo X-ray tube
- Spectrometer S4 T•STAR equipped with Mo and W X-ray tube
- 3 excitation energies
  - Mo-K, 17.5 keV
  - W Bremsstrahlung, 35 keV
  - W-L, 8.4 keV
Toxic metals in glucose
S4 TStar

Samples

- Glucose at different concentrations (0.1%, 0.5%, 1%, 5%)
- Spike with 2 ppm metal concentration (Cr, As, Pd, Cd, Sb)
Toxic metals in glucose
S4 TStar W-Brems excitation

Spectrum W-Brems excitation

• Well separated peaks of Pd, Cd, Sb
Toxic metals in glucose
S4 TStar W-Brems excitation

Results

- Count rates of W-Brems excitation below Mo excitation (40% for Pd)
- LOQ typically in the sub-ppm range
- Dilution of high matrix samples strictly recommended
- More uniform sample layer
- Improved reproducibility
Toxic metals in glucose
S4 TStar Mo excitation

Outstanding performance

- Low ppb quantification limits for As and Cr
- Similar performance for V, Co, Se, Pt etc. (not shown)
Light elements

- W-L excitation for quantification of light elements (Na to V)
- Improvement by a factor of 3 or more
- LOQ for Cr down to 3 ppb
- Quantification of Na, Mg, Al to be tested soon
Comparison with Atomic Spectroscopy
AAS, ICP-MS, ICP-OES
## Competition
### ICP

<table>
<thead>
<tr>
<th>Feature</th>
<th>ICP</th>
<th>S4 T-STAR</th>
<th>Benefit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detection limits</td>
<td>sub-ppt (MS) sub-ppb (OES)</td>
<td>sub-ppb</td>
<td>MS with outstanding performance</td>
</tr>
<tr>
<td>Element range</td>
<td>(Li to F) Na to U</td>
<td>Na to U</td>
<td>still significantly higher LOD for some elements</td>
</tr>
<tr>
<td>Sample types</td>
<td>liquid only</td>
<td>Liquids, solids, suspensions, wafers, films, slides</td>
<td>outstanding flexibility of TXRF</td>
</tr>
<tr>
<td>Process time</td>
<td>daily calibration, &gt;1 h for sample prep, fast measurements</td>
<td>No calibration, fast sample prep, long measurements</td>
<td>Fast in case of unknown samples; slow in routine analysis</td>
</tr>
<tr>
<td>Operating costs/a</td>
<td>$12k – $20k</td>
<td>&lt; $5k</td>
<td></td>
</tr>
<tr>
<td>Other features</td>
<td>ICP-OES: no ICP-MS: LC coupling, laser ablation</td>
<td>depth profiling, material analysis, pot. non-destructive</td>
<td>TXRF adds features, perfect fit to any ICP</td>
</tr>
</tbody>
</table>
## Cost comparison
### TXRF versus ICP-MS

<table>
<thead>
<tr>
<th>Installation</th>
<th>S4 T-STAR</th>
<th>ICP-MS</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrument price</td>
<td>123,500 €</td>
<td>130,000 €</td>
<td></td>
</tr>
<tr>
<td>Installation</td>
<td>4,500 €</td>
<td>5,000 €</td>
<td></td>
</tr>
<tr>
<td>Training</td>
<td>4,900 €</td>
<td>9,000 €</td>
<td>2 days onsite + courses for 2 users</td>
</tr>
<tr>
<td>Gas supplies</td>
<td>0 €</td>
<td>8,000 €</td>
<td>Argon, He, H₂</td>
</tr>
<tr>
<td>Electrical supplies</td>
<td>0 €</td>
<td>600 €</td>
<td></td>
</tr>
<tr>
<td>Exhaust</td>
<td>0 €</td>
<td>3,500 €</td>
<td>if exhaust system already exists in building</td>
</tr>
<tr>
<td>Peripheral devices</td>
<td></td>
<td>28,000 €</td>
<td>microwave</td>
</tr>
<tr>
<td><strong>Sum</strong></td>
<td><strong>132,900 €</strong></td>
<td><strong>184,100 €</strong></td>
<td></td>
</tr>
</tbody>
</table>
## Cost comparison
### TXRF versus ICP-MS

<table>
<thead>
<tr>
<th>Operation / year</th>
<th>S4 T-STAR</th>
<th>ICP-MS</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Service contract (std)*</td>
<td>9.483 €</td>
<td>10.000 €</td>
<td></td>
</tr>
<tr>
<td>Gas</td>
<td>0 €</td>
<td>7.000 €</td>
<td></td>
</tr>
<tr>
<td>Standards</td>
<td>100 €</td>
<td>4.000 €</td>
<td></td>
</tr>
<tr>
<td>Electrical power</td>
<td>200 €</td>
<td>2.000 €</td>
<td></td>
</tr>
<tr>
<td>Spare parts</td>
<td>1.965 €</td>
<td>3.300 €</td>
<td>TXRF: X-ray tube, carriers ICP: detector, torch, cones, injector</td>
</tr>
<tr>
<td><strong>Sum</strong></td>
<td><strong>11.748 €</strong></td>
<td><strong>26.300 €</strong></td>
<td></td>
</tr>
</tbody>
</table>

*) Bruker standard care contract incl. 1 preventive maintenance per year
## Cost comparison

**TXRF versus ICP-MS**

<table>
<thead>
<tr>
<th>Total (5 years)</th>
<th>S4 T-STAR</th>
<th>ICP-MS</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Installation</td>
<td>132.900 €</td>
<td>184.100 €</td>
<td></td>
</tr>
<tr>
<td>Operation costs</td>
<td>58.740 €</td>
<td>131.500 €</td>
<td></td>
</tr>
<tr>
<td>Man hours</td>
<td>120.000 €</td>
<td>185.000 €</td>
<td>100 k€/a, 220 working days, 50 samples/d</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>311.640 €</strong></td>
<td><strong>500.600 €</strong></td>
<td></td>
</tr>
<tr>
<td>Costs / sample</td>
<td>5.67 €</td>
<td>9.10 €</td>
<td></td>
</tr>
</tbody>
</table>

Sources:  
- Automotive study 2015  
- EPA study 2007  
- ICP-OES cost calculator  
- Discussion forums  
- Bruker data
Summary and outlook

- TXRF is a powerful tool for the accurate quantification of nutrient and toxic elements in food and beverages
- LOD values are typically in the low ppb range for certain metals
- In addition the detection of light elements like Mg or P and critical compounds like I and other halogenides is possible
Q & A

Any Questions?

Please **type in** the questions you may have for our speakers in the **Questions Box** and click **Submit**.
Thank you for your attention!

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