6020 Analysis Using a Simultaneous ICP MS Without the Need of Reaction or Collision Cells

Willi Barger, Application ICP-MS/ICP-OES
Dion Tsourides, Director ICP NAFTA
SPECTRO Analytical Instruments, Mahwah, NJ, US
Outline

• Hardware
  – ICP-MS
    • Advantages of simultaneous ICP-MS
    • ICP as Ion source
    • Mass spectrometer
    • How does the detector work

• Simultaneous measurements
  – Precision of measurements
  – Interference Correction

• Summary
Why simultaneous detection?

• Get all information in one measurement
  – All isotopes of all elements
  – Low concentrations and high concentrations

• Eliminate noise by using ratio’s
  – Isotope ratio
  – Internal standard

• Change the method after the sample is measured
  – Every piece of information is there
  – Compensate the surprises in some samples
Advantages of Simultaneous Detection

- Calculating the ratio of two signals measured at the same point in time:
  - Elimination of all noise from the sample introduction system
    - Flicker noise from the plasma
    - Pulsation from peristaltic pump
    - Pulsation from Laser Ablation
  - Ratio of 2 signals
    - Isotope ratio
    - Isotope dilution
    - Element ratio (Geology, ex. REE pattern)
    - Quantitative analysis (internal Standard)
ICP as Ion source: Signal of 5 Isotopes
5 Isotopes Measured Sequentially
5 Isotopes Measured Simultaneously
Advantages of Simultaneous Detection

- Precision should be substantially improved
  - In theory by 1 – 2 orders of magnitude
Advantages of Simultaneous Detection

• Always record the complete mass spectrum:
  – Do the method development after the sample is measured
    • See unexpected interferences
    • Detect unexpected elements
    • Include interference corrections after the measurement is completed
  – Review spectra of samples that do not exist anymore
Suitable MS layouts: Mass Spectrographs

- Mattauch-Herzog (1934): double focusing magnetic sector field MS
Overview

Ion Optic

Mass spectrometer

Detector
Magnet and Detector with Detector cooling system
Detector with Cooling System
Semiconductor Direct Charge Detector “Ion 120”

- CMOS (Complementary Metal Oxide Semiconductor) technology
- 120 mm sensor
- 4800 channels
  - Two fixed gains
- Cooling to -17°C
- Designed for SPECTRO
Semiconductor Direct Charge Detector “Ion 120”

- Very robust detector
  - Survival after ion dose rates of $10^{13}$ ions/sec
    - The detector is not expected to be a consumable
  - No cross talk
    - Located between every high gain strip is a low gain strip
    - High and low gain part is connected to different sides of the detector
Semiconductor Direct Charge Detector “Ion 120”

• How does the detector work?
  – Every incoming ion is discharged and converted into an atom
  • Depending on the properties of this element, the atom:
    – Is pumped out as a gas or stays on the surface as a metal
  • The connected electronic is amplifying this current of electrons to the detector channels
    – This information is stored in different capacitors
    – The information is checked every basic integration cycle

• A potential change on the detector does not change the property of the detector to deliver one electron per incoming ion.
• → the detector is not expected to age
• → The detector is not expected to be a consumable
Detector Readout

- Two possibilities available in the software
  - **Counter Mode**
    - Forced readout every basic integration cycle
    - Every 20 ms readout,
    - Data transfer every 100 ms
  
  - **Threshold mode**
    - Check if a readout if required every 10 ms
    - Data transfer after replicate is complete
Non destructive read out, threshold mode

• Every basic integration cycle, the camera makes a non destructive readout of each channel and detector
• Only, when a certain threshold is exceeded, the channel goes through a reset
• If a channel is reset, a second readout happens immediately.
  – Correlated double sampling
  – Second readout acts as baseline for next readout
Threshold Mode with Correlated Double Sampling

5 signal levels on different channels

The total measurement time can be adjusted
Threshold Mode with Correlated Double Sampling

<table>
<thead>
<tr>
<th>Detector</th>
<th>Value</th>
<th>Calculation</th>
<th>Reset</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detector 1</td>
<td>600</td>
<td>10*60</td>
<td>10 reset</td>
</tr>
<tr>
<td>Detector 2</td>
<td>230</td>
<td>3*69 + 23</td>
<td>3 reset</td>
</tr>
<tr>
<td>Detector 3</td>
<td>90</td>
<td>1*54+36</td>
<td>1 reset</td>
</tr>
<tr>
<td>Detector 4</td>
<td>24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Detector 5</td>
<td>5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
10 Channels

- Average 20 channels/amu
- Multiple datapoints/peak
  - Set peak maximum
  - Set integration range
    - Whole peak for best precision
  - Set background correction
Peak definition for method

- Peak maximum
  - ICAL procedure
- Integration range
- Background correction if necessary
Simultaneously measured mass spectra 10 sec
Simultaneously measured mass spectra 10 sec
Simultaneously measured mass spectra 10 sec

Counts [cps] <Active Sample: QC Blank 1% HNO3 [HG]>

QC 1/500 Merck VI ...
QC Blank 1% HNO3 ...
QC 1/500 CMS-1 [HG]
Simultaneously measured mass spectra 10 sec
Simultaneously measured mass spectra 10 sec
When you have the complete spectrum

• **Let the software do the job**
  – Subtract the blank spectrum
  – Let the software rebuild the measured net spectrum with the isotopic pattern of the elements and interferences
    • About 220 datapoints for 100 elements plus interferences
  – Get qualitative results for elements never calibrated and a standard is not available
  – See the unexpected
Fully simultaneous now means

- **On every measurement**
  - Every mass from 6 to 241
    - Li to Uranium
      - 241 as limit is set by the German BAFA
  - Low concentration to high concentration
    - Compared to most simultaneous ICP-OES
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## Precision: PGE Determination

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>0.58</td>
<td>0.60</td>
<td>0.66</td>
<td>0.64</td>
<td>0.61</td>
<td>0.68</td>
<td>0.65</td>
<td>0.64</td>
<td>0.64</td>
<td>0.85</td>
</tr>
<tr>
<td>RSD %</td>
<td>0.66</td>
<td>0.25</td>
<td>0.70</td>
<td>0.99</td>
<td>0.29</td>
<td>0.56</td>
<td>0.34</td>
<td>0.59</td>
<td>0.71</td>
<td>3.01</td>
</tr>
<tr>
<td>Sample 2</td>
<td>5.81</td>
<td>5.66</td>
<td>5.94</td>
<td>5.87</td>
<td>5.77</td>
<td>5.95</td>
<td>5.98</td>
<td>6.03</td>
<td>6.02</td>
<td>6.04</td>
</tr>
<tr>
<td>RSD %</td>
<td>0.21</td>
<td>0.32</td>
<td>0.22</td>
<td>0.17</td>
<td>0.14</td>
<td>0.16</td>
<td>0.16</td>
<td>0.26</td>
<td>0.21</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Results for synthetic samples with typical precious metal concentrations,
Sample 1: 0.6 µg/l, Sample 2: 6 µg/l

20 sec per replicate, In as internal Standard
Precision: Transient Signals
Precision: Transient Signal Ratio

22% Ni as internal Standard for sub ppm PGE
Precision: Transient Signal Ratio

Inhomogeneity in Ni vs PGE distribution in sample

Integration

Ratio Intensity

Time, sec

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# Multielement Isotope Ratio

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Li 6/7</th>
<th>B 10/11</th>
<th>Sr 86/88</th>
<th>Sr 87/88</th>
<th>Ag 107/109</th>
<th>Pb 204/208</th>
<th>Pb 206/208</th>
<th>Pb 207/208</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.08031</td>
<td>0.24503</td>
<td>0.11687</td>
<td>0.08578</td>
<td>1.08513</td>
<td>0.02491</td>
<td>0.45227</td>
<td>0.43387</td>
</tr>
<tr>
<td>2</td>
<td>0.08039</td>
<td>0.24516</td>
<td>0.11694</td>
<td>0.08591</td>
<td>1.08541</td>
<td>0.02499</td>
<td>0.45267</td>
<td>0.43350</td>
</tr>
<tr>
<td>3</td>
<td>0.08038</td>
<td>0.24515</td>
<td>0.11699</td>
<td>0.08592</td>
<td>1.08465</td>
<td>0.02494</td>
<td>0.45216</td>
<td>0.43396</td>
</tr>
<tr>
<td>Average</td>
<td>0.08036</td>
<td>0.24511</td>
<td>0.11693</td>
<td>0.08587</td>
<td>1.08506</td>
<td>0.02495</td>
<td>0.45237</td>
<td>0.43378</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.000044</td>
<td>0.000072</td>
<td>0.000060</td>
<td>0.000078</td>
<td>0.000384</td>
<td>0.000040</td>
<td>0.000268</td>
<td>0.000244</td>
</tr>
<tr>
<td>RSD%</td>
<td>0.054</td>
<td>0.030</td>
<td>0.052</td>
<td>0.091</td>
<td>0.035</td>
<td>0.162</td>
<td>0.059</td>
<td>0.056</td>
</tr>
</tbody>
</table>

100 µg/l multi-element solution (B at 1000 µg/l) with a sample uptake rate of 0.8 ml/min and 3 replicates, each of 30 seconds measurement time.

Total sample consumption: <2 ml
## Isotope Ratio Uranium

### Instrumentation

<table>
<thead>
<tr>
<th>Instrument settings</th>
<th>SPECTRO MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma torch</td>
<td>Standard Quartz, fixed 1.8mm injector tube</td>
</tr>
<tr>
<td>Nebulizer</td>
<td>Standard Seaspray</td>
</tr>
<tr>
<td>Spray Chamber</td>
<td>Cyclonic baffled</td>
</tr>
<tr>
<td>Power</td>
<td>1500 W</td>
</tr>
<tr>
<td>Coolant gas</td>
<td>12 L/min</td>
</tr>
<tr>
<td>Auxiliary</td>
<td>2.5 L/min</td>
</tr>
<tr>
<td>Nebulizer</td>
<td>0.94 L/min</td>
</tr>
<tr>
<td>Sample aspiration rate</td>
<td>1.5mL/min</td>
</tr>
<tr>
<td>Readtime</td>
<td>200 sec (10*20 sec)</td>
</tr>
<tr>
<td>Replicates</td>
<td>12</td>
</tr>
<tr>
<td>Sample</td>
<td>Uranium solution MVI 20ppb</td>
</tr>
</tbody>
</table>

### 238 U 235 U

<table>
<thead>
<tr>
<th></th>
<th>BGC Intensity</th>
<th>BGC Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(&lt;x&gt;)</td>
<td>925798</td>
<td>2657.2</td>
</tr>
<tr>
<td>sd</td>
<td>9876</td>
<td>24.2</td>
</tr>
<tr>
<td>rsd</td>
<td>1.1</td>
<td>0.92</td>
</tr>
</tbody>
</table>

### Abundance U238 Abundance U235

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>238 U</td>
<td>235 U</td>
</tr>
<tr>
<td>99.7138</td>
<td>0.2862</td>
</tr>
<tr>
<td>0.0001</td>
<td>0.0001</td>
</tr>
<tr>
<td>0.0001</td>
<td>0.0524</td>
</tr>
</tbody>
</table>
Mathematical interference correction

• Lower formation of interferences formed by recombination in the interface
  – Different kinetic energy means different efficiency for transport to the detector

• Better precision of the mathematical correction due to simultaneous measurement
  – Depending on counting statistics
  – Calculations are based on concentrations
Doubly charged interference’s
use the isotopes with uneven masses

Correct for interferences here

$^{137}\text{Ba}^{++}$ Measure interference here

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Polyatomic interferences: Cl interference’s

- Addition of Cl to some defined As standards

Measure As on m/z 75 in High Gain
Measure Cl on m/z 35 in Low Gain
Polyatomic interferences: Cl interference

- Addition of Cl to some defined As standards or as a single Std

- Graph showing intensity vs. concentration ratio with points at 2.5 ppb As, 10 ppb As, 25 ppb As, 0.1% HCl, and 0.5% HCl.


- Detection Limit: 0.02113 [µg/l]
Do the rest at the same time

Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>51 V µg/l</th>
<th>52 Cr µg/l</th>
<th>75 As µg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Certificate</td>
<td>3.786</td>
<td>2.04</td>
<td>6.045</td>
</tr>
<tr>
<td>Nist1643e 0.1%HCL</td>
<td>3.885</td>
<td>2.007</td>
<td>6.096</td>
</tr>
<tr>
<td>Recovery</td>
<td>102.6</td>
<td>98.4</td>
<td>100.8</td>
</tr>
<tr>
<td>Nist1643e</td>
<td>3.845</td>
<td>2.002</td>
<td>6.122</td>
</tr>
<tr>
<td>Recovery</td>
<td>101.6</td>
<td>98.1</td>
<td>101.3</td>
</tr>
<tr>
<td>0.2% HCL 10ppb STD</td>
<td>9.92</td>
<td>9.99</td>
<td>9.74</td>
</tr>
<tr>
<td>10ppb STD</td>
<td>10.34</td>
<td>10.03</td>
<td>9.91</td>
</tr>
</tbody>
</table>

NIST 1643e was diluted 1:10
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    • Advantages of simultaneous ICP-MS
    • ICP as Ion source
    • Mass spectrometer
    • How does the detector work
• Simultaneous measurements
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• Summary
Summary

• SPECTRO MS
  – Measure the complete inorganically relevant mass range with every replicate in every sample
    • Get all information you want
    • Get all the additional information you need
    • Get all information you might need now or in the future
      – Think beyond what you are doing now
    • Method development after the sample is measured
    • Post measurement reprocessing for additional quantification
      – Quantitative mode or in Semi Quantitative mode
    • Never reanalyze a sample

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Summary

• SPECTRO MS
  • Interferences: Keep it simple
    – Low transmission of interferences to detector
    – A simple mathematical correction can often do the job
      » Can be added to the sample after the measurement
    – A more precise correction compared to sequential measurements is possible due fully simultaneous measurements
• Thank you very much for your attention

• Questions