Trace Element Speciation using IC-ICP-MS
Complete Inorganic Elemental Analysis Solutions

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Outline

• Overview of the Thermo Scientific™ QCell
• Simple and generic setup using Autotuning
• IC-ICP-MS

Applications
• Sensitivity Improvement using He-CCT
• Speciation of selenium using He-KED
• Removal of Xe isobaric interferences on $^{129,131}$I using O$_2$-CCT
• IC-ICP-MS for As and S speciation with O$_2$-CCT

• Summary
The QCell

- Proprietary design
  - 4 Flatapoles
  - Automatic low mass cut-off

- Zero-maintenance, Non-consumable
- 50% smaller volume for faster mode switching (<10s)
- Single mode interference removal with He for routine applications
- High ion transmission for improved sensitivity when using kinetic energy discrimination
- Can also use reactive mode with O₂, H₂ or NH₃ mixes
Automated QCell Optimization for CCT Mode

- Optimum CCT gas flow obtained using the default CCT Autotune
  - Generic autotune procedure
  - Independent of the nature of the gas used
  - He, O2, H2/He etc.

- Easy and effective way to configure the CCT settings

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas flow</td>
<td>7.2 ml min⁻¹</td>
</tr>
<tr>
<td>QCell bias</td>
<td>- 8 V</td>
</tr>
<tr>
<td>Quad bias</td>
<td>- 12 V</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas flow</td>
<td>0.4 ml min⁻¹</td>
</tr>
<tr>
<td>QCell bias</td>
<td>- 6 V</td>
</tr>
<tr>
<td>Quad bias</td>
<td>- 12 V</td>
</tr>
</tbody>
</table>
IC-ICP-MS for Speciation

- **Dionex ICS-5000 with RFIC**
  - Solvent path completely metal-free
  - Ion chromatography (IC) methods as well as liquid chromatography (LC) possible
    - Compatible with solvents
    - Working pressure up to 350 bar
  - RFIC: Eluent is electrolytically generated from UPW water
  - Supports also field-flow-fractionation devices (FFF)

* RFIC module not shown
Integrated Control in Thermo Scientific Qtegra software

- Thermo Scientific™ Chromelion™ software virtual interface
  - Control over the IC system from within Qtegra software
  - Seamless integration and emergency shutdown feature for unattended routine operation
  - Method editing, sample list creation and data evaluation within one software
A Complete, Integrated IC-ICP-MS System

- Very simple hardware connection:
  - Simple interchange between standard ICP-MS analysis and IC-ICP-MS
  - No need to turn off plasma

- A single software interface for both the IC and ICP-MS:
  - Chromeleon software interface built into workflow
  - Fully integrated analysis
  - No trigger cable required
  - One sample list
Sensitivity Improvement using He in the QCell

- Collisional focusing = Reduction of natural dispersion of the ion beam in the cell due to collisions with He atoms

- Effect is especially pronounced for ions with m/z ≥ 100!
- Gain in sensitivity of a factor 2-3!

“Collisional focusing doesn't get you any "new" ions, it just gives you back some of the ions which were lost by ion beam expansion in the unpressurized cell”

Cited from Ed McCurdy, (PlasmaChem archive, item 018123) (http://listserv.syr.edu/scripts/wa.exe?S1=plasmachem-l)

<table>
<thead>
<tr>
<th>Element</th>
<th>Sensitivity [cps ppb⁻¹] STD mode*</th>
<th>Sensitivity [cps ppb⁻¹] KED mode*</th>
<th>Sensitivity [cps ppb⁻¹] CCT mode*</th>
<th>Factor CCT/STD mode</th>
</tr>
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<tbody>
<tr>
<td>⁷Li</td>
<td>93,533</td>
<td>373</td>
<td>9,186</td>
<td>0.1</td>
</tr>
<tr>
<td>⁵⁹Co</td>
<td>118,329</td>
<td>41,265</td>
<td>132,526</td>
<td>1.1</td>
</tr>
<tr>
<td>¹¹⁵In</td>
<td>255,203</td>
<td>72,485</td>
<td>414,063</td>
<td>1.6</td>
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<tr>
<td>¹⁴⁰Ce</td>
<td>258,760</td>
<td>177,487</td>
<td>483,867</td>
<td>1.87</td>
</tr>
<tr>
<td>²³⁸U</td>
<td>392,218</td>
<td>488,379</td>
<td>1,277,818</td>
<td>3.25</td>
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</table>

* Performance of a typical iCAP Qc model
Speciation of Selenium with He-KED

- Many different Se compounds may be present in very low concentration
- Effect of collisional focussing is also enhancing performance in KED mode

<table>
<thead>
<tr>
<th>Column</th>
<th>Dionex IonPac AS-7 (2 x 250mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mobile phase</td>
<td>A: 50 mM NH₄Ac, pH 4.6; B: 50mM HNO₃</td>
</tr>
<tr>
<td>Gradient</td>
<td>0 - 3 min: 100% A 3 – 10 min 100% B</td>
</tr>
<tr>
<td>Injected vol.</td>
<td>20 µL</td>
</tr>
</tbody>
</table>

- Attainable IDL: 20 – 50 ng g⁻¹
Speciation of Selenium with He-KED

- Attainable IDL: 20 – 50 ng g⁻¹
Measurement of Iodine 129

- Radioactive nuclides of Iodine need to be monitored
  - $^{129}$I, $t_{\frac{1}{2}}$ 15.7 million years, $\beta$-decay
  - $^{131}$I, $t_{\frac{1}{2}}$ 8d, $\gamma$-decay

- Ar gas used for plasma generation may contain Xe impurities
  - $^{129}$Xe, $^{131}$Xe create background signal

- Isobaric interference $\rightarrow$ Not removeable with KED

- Use of 100% $O_2$ to generate XeO!
Performance of the Different Measurement Modes

• STD mode: Isobaric Interference clearly visible
• KED mode: Iodine Sensitivity drops
• CCT mode: No background from Xe, sensitivity comparable to STD mode
Effect of QCell Conditions

- Optimum $O_2$ CCT gas flow obtained using the default CCT Autotune!
IC-ICP-MS for Speciation of As and S

- Sample: Liquid sample containing As and S in strongly basic media

- Sample preparation: Dilution with UPW just before analysis

- Online Addition of internal standard (1ppb Rh in 2% HNO₃) via T-piece

- Expected species: anionic species of As and S, also oxoanions of Cr, Mo, W etc.

<table>
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<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column</td>
<td>Dionex IonPac AS-18 (2x250mm)</td>
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<tr>
<td>Mobile phase</td>
<td>KOH, automatically generated using RFIC</td>
</tr>
<tr>
<td>Gradient Conditions</td>
<td>0-5 min: 12-44mM KOH 8-10 min 44-52 mM KOH 12-15 min 52-100mM KOH</td>
</tr>
<tr>
<td>Injected vol.</td>
<td>20 µL</td>
</tr>
</tbody>
</table>
Analysis of Trace Level Sulfur

- Detection of $^{32}\text{S}$ is hampered due to:
  - High ionisation potential
  - Numerous spectral interferences ($^{16}\text{O}^{16}\text{O}^+$, $^{31}\text{P}^{1}\text{H}^+$, etc.)
  - Kinetic energy discrimination is not effective

- Conversion of S into SO in the QCell:

$$^{32}\text{S}^+ + ^{16}\text{O}_2 \rightarrow ^{32}\text{S}^{16}\text{O}^+ + ^{16}\text{O}$$

- 100% O$_2$
- 10% O$_2$ in He

- 10% O$_2$ in He @ 9mL min$^{-1}$ total flow rate

<table>
<thead>
<tr>
<th>Concentration [ng g$^{-1}$]</th>
<th>Intensity [cps]</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>2000</td>
</tr>
<tr>
<td>40</td>
<td>4000</td>
</tr>
<tr>
<td>60</td>
<td>6000</td>
</tr>
<tr>
<td>80</td>
<td>8000</td>
</tr>
<tr>
<td>100</td>
<td>10000</td>
</tr>
<tr>
<td>120</td>
<td>12000</td>
</tr>
<tr>
<td>140</td>
<td>14000</td>
</tr>
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</table>

Sensitivity: 265 cps (ng g$^{-1}$)$^{-1}$
LOD: 0.18 ng g$^{-1}$
BEC: 7.35 ng g$^{-1}$
Speciation of As and S Containing Anions

- Different As and S containing anions separated and individually detected
- Simultaneously, also metal based species as MoO$_4^{2-}$ can be detected

Instrumental Performance:

- LOD [SO$_4^{2-}$]: 4.8 ng g$^{-1}$
  BEC: 2.5 ng g$^{-1}$
- LOD [As (III)]: 0.02 ng g$^{-1}$
  BEC: 0.08 ng g$^{-1}$
The Need for Chromium Speciation Analysis

- Chromium concentrations in environmental samples are monitored due to widespread use in industrial applications
  - chromium plating, dye manufacturing and preservation of wood and leather materials.
- US EPA and the EU have specify maximum chromium concentrations in their drinking water directives.
- Cr is found in more than one chemical form, each with different chemical properties and behavior such as bioavailability and toxicity.
- Cr (III) is essential to human beings while Cr (VI) is highly toxic.
- Total Cr content in drinking water does not provide sufficient information to evaluate potential hazards to populations exposed to it.
The Need for Chromium Speciation Analysis

- Speciation analysis is required to determine the different Cr species.
- Speciation analysis is challenging as stability of Cr species is easily affected during collection and treatment.
  - low pH values may lead to the degradation of Cr (VI) to Cr (III) due to the increased redox potential,
  - high pH values may lead to the precipitation of Cr (III) as Cr(OH)₃
- An additional difficulty in the analysis of Cr by ICP-MS are the numerous spectral interferences (e.g. ³⁵Cl¹⁶O¹H⁺ or ⁴⁰Ar¹²C⁺) on the most abundant chromium isotope, ⁵²Cr
  - Collision Cell Technology is required for accurate determinations
Sample and Calibration Solution Preparation

- Standards were prepared using commercially available stock solutions (1000 μg/mL) of each chromium standard in a 0.1 mol/L ammonium nitrate solution adjusted to a pH of 4.

- Drinking water was collected in a PFA bottle previously rinsed with high purity nitric acid.

- The water was analyzed directly without dilution or pH adjustment in order to keep the species unchanged before analysis.
Instrument Configuration

• Separations were carried out using a Dionex ICS-5000 ion chromatography system.
  • Its metal-free solvent pathway is non-contaminating and thus perfectly suited for elemental speciation studies.

• A Thermo Scientific™ Dionex™ AG-7 anion exchange column (2 x 50mm) was used throughout this study.
  • This column is a guard column but its highly effective separation medium is able to completely separate both Cr species in less than three minutes.

• An iCAP Qc ICP-MS was used as a high performing elemental detector of the Cr species eluted from the ICS-5000 IC.
  • With the use of flatapole technology in the QCell collision cell, the system offers the selectivity to suppress spectral interferences while maintaining the high sensitivity for trace metal detection using IC-ICP-MS.
General Analytical Conditions

- iCAP Q ICP-MS equipped with a PFA-LC nebulizer
  - PFA-LC nebulizer with low dead volume & LC fittings for chromatographic analyses.

- Single collision cell mode, with kinetic energy discrimination (KED),
  - He collision gas for interference-free detection of $^{52}\text{Cr}^+$ and $^{53}\text{Cr}^+$.

- Dionex ICS-5000 anion exchange, isocratic elution with nitric acid
- Dionex AG-7 elutes both cations and anions
  - Cr (III) is present predominantly as $[\text{Cr(H}_2\text{O)}_6]^{3+}$
  - and Cr(VI) as $\text{H}_2\text{CrO}_4$, $\text{HCrO}_4^-$, $\text{CrO}_4^{2-}$ or $\text{Cr}_2\text{O}_7^{2-}$
  - depending on pH

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Forward power</td>
<td>1550 W</td>
</tr>
<tr>
<td>Nebulizer gas</td>
<td>0.80 L/min</td>
</tr>
<tr>
<td>Injector</td>
<td>2 mm I.D.</td>
</tr>
<tr>
<td>Cell gas flow / KED voltage</td>
<td>4.8 mL/min He / 2V</td>
</tr>
<tr>
<td>Dwell time</td>
<td>100 ms</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column</td>
<td>Dionex AG-7 (2 mm i. D., 50 mm length)</td>
</tr>
<tr>
<td>Elution</td>
<td>Isocratic</td>
</tr>
<tr>
<td>Mobile phase</td>
<td>0.4 mol/L HNO$_3$</td>
</tr>
<tr>
<td>Flow rate</td>
<td>400 µL/min</td>
</tr>
<tr>
<td>Injection volume</td>
<td>20 µL</td>
</tr>
<tr>
<td>Duration</td>
<td>150 s</td>
</tr>
</tbody>
</table>
Method Development

- 0.2 mol/L nitric acid as mobile phase.
- 0.3 mol/L nitric acid as mobile phase.
- 0.4 mol/L nitric acid as mobile phase.
Calibration

Cr (VI)
- $R^2 = 1.000$
- Sensitivity: 219 kcps ppb$^{-1}$
- LOD: 0.20 pg g$^{-1}$

Cr (III)
- $R^2 = 1.000$
- Sensitivity: 217 kcps ppb$^{-1}$
- LOD: 0.38 pg g$^{-1}$
**Duplicate Analysis and Spike Recovery**

Overlay of 20 repeated injections of Cr(VI) and Cr(III)

<table>
<thead>
<tr>
<th>Conc. spiked [ng/g]</th>
<th>Cr (VI)</th>
<th>Cr (III)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Found (ng/g)</td>
<td>Recovery (%)</td>
</tr>
<tr>
<td>2.34 of each</td>
<td>2.31 ± 0.01</td>
<td>99 ± 1</td>
</tr>
<tr>
<td>6.03 Cr (VI); 1.90 Cr (III)</td>
<td>6.01 ± 0.02</td>
<td>100 ± 1</td>
</tr>
<tr>
<td>1.87 Cr (VI); 6.20 Cr (III)</td>
<td>1.85 ± 0.01</td>
<td>99 ± 1</td>
</tr>
</tbody>
</table>
• Potable water was collected locally and analyzed using the proposed method.

• Only trace amounts of Cr (VI) could be detected in this sample.

• The amount of Cr (VI) observed was found to be 42.5 ± 1 pg/g.

• To confirm the peak is Cr and not affected co-eluting compounds causing spectral interferences (e.g. chlorine or carbon based polyatomic species), the isotope ratio 52Cr+/53Cr+ was calculated and corresponds well to the theoretical value of 8.81).
Summary and Outlook

- The QCell of the iCAP Q ICP-MS offers great versatility for a variety of challenging applications:
  - Powerful interference removal through He KED
  - Sensitivity Improvement by factor 3 for heavy elements
  - Removal of isobaric interferences after conversion into oxides
  - Effective reaction chemistry for mass shifting to less interfered regions
- The sophisticated autotune procedures automatically adjust the gas flows and lens voltages independently of the applied CCT gas
- Full control and seamless integration of chromatographic systems make IC-ICP-MS or LC-ICP-MS applications easier to implement than ever before
  - Implemented Control for almost any IC/LC device
  - Integrated support of separation devices like FFF
Thank you for your attention!