Overcoming Challenges in Elemental Speciation Techniques

NEMC 2018

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Product Specialist
ICP-MS, ICP-MS/MS
Overview

- Plumbing Considerations
- Why LC Connections Matter
- Chromatography Examples
- ICP-MS Settings
Plumbing for Column Compartment Valve

1 – From Column
2 – To ICP-MS (Splitter)
3 – ISTD Loop
4 – ISTD from PeriPump
5 – ISTD Return to Bottle
6 – ISTD Loop

Position 1 – Loop Fill
1-2; 3-4; 5-6

Position 2 – ISTD Inject
1-6; 2-3; 4-5
Plumbing for Passive Seat Wash

Note 1 – 0.5mm ID tubing (PEEK Orange) to port 4 on ALS valve for passive needle seat wash

Note 2 – 0.12mm ID tubing (PEEK Red) to ICP-MS
ALS Valve
Plumbing
Diagram

1 – From Pump
2 – Needle Loop
3 – Plug
4 – From T-Splitter (0.5mm ID)
5 – Needle Seat
6 – To Column

Position 1 – Mainpass
1-2; 3-4; 5-6

Position 2 – Bypass
1-6; 2-3; 4-5

Note: When in Bypass and needle is lifted, mobile phase will backflush needle seat.
Final Plumbing Example
Why Plumbing Matters: Stainless vs. Poly Fittings

**Stainless Steel:**
- Agilent uses Swagelok type fittings with front and back ferrules
- Also available with a long nut

**PEEK (<400 bar system pressure):**
- Connections are changed frequently
- Connecting columns
- Pressure is less critical
- Fits on SS or PEEK tubing

**Polyketone:**
- Easy, hand tightened column connection
- Used up to 600 bar (PN: 5042-8957)
- Fits on SS Tubing
Why Plumbing Matters: Types of Fittings

**Swagelok**
- Two piece ferrule
- Used on Agilent LCs
- Short nut
- Also available with long nut

**Parker**
- One piece ferrule
- Short nut
- Very similar to Swagelok

**Waters**
- Longer nut
- Used on Alliance systems
Why Plumbing Matters: Types of Fittings

Swagelok

Waters

Valco

Parker

Rheodyne

Upchurch

0.09 in.

0.13 in.

0.08 in.

0.09 in.

0.17 in.

0.09 in.
Why Plumbing Matters: Make Proper Connections

- Leak
- Peak shape problem
- No dead volume
Why Plumbing Matters: Make Proper Connections
Why Plumbing Matters: Make Proper Connections
Why Plumbing Matters: Make Proper Connections
Why Plumbing Matters: Don’t Forget Dispersion

\[ R_s = 6.41 \quad 4.6 \times 150 \text{ mm}, \ 5 \mu m \]

\[ R_s = 6.65 \quad 4.6 \times 100 \text{ mm}, \ 3.5 \mu m \]

\[ R_s = 6.51 \quad 4.6 \times 50 \text{ mm}, \ 1.8 \mu m \]
Experimental – Arsenic

- Agilent 7800 – x lens, MicroMist, Ni Cones
- Agilent 1260 – BioInert, Quat Pump, Well-Plate ALS, TCC 6-port BioInert Valve

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column</td>
<td>Hamilton PRP X-100 SAX 250mm x 4.6mm, 10µm</td>
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<tr>
<td>Mobile Phase</td>
<td>6mM Ammonium Phosphate / 6 mM Ammonium Nitrate / 2% MeOH / pH 6.2</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>1.0 ml / min (isocratic)</td>
</tr>
<tr>
<td>Injection Volume</td>
<td>100 µl</td>
</tr>
<tr>
<td>Gas Mode</td>
<td>He</td>
</tr>
<tr>
<td>Integration Time</td>
<td>1.0 sec</td>
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<tr>
<td>Total Run Time</td>
<td>~20 min</td>
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</table>
Toxicity and pKa of Arsenic Species

As OHO
As O
OH

As(III) : pKa: 9.23
LD₅₀ 0.00127 g/kg

As(V) : pKa: 2.20, 6.97, 11.53
LD₅₀ 0.00479 g/kg

OH
CH₃—As═O
OH
MMA : pKa: 4.1, 8.7
LD₅₀ 1.12 g/kg

CH₃—As═O
OH
DMA : pKa: 6.2, [3.85]
LD₅₀ 0.329 g/kg

CH₃—As═O
CH₃
TMAO
LD₅₀ 5.54 g/kg

CH₃—As⁺—CH₃
TeMA

CH₃—As⁺—CH₂COO⁻
AB : pKa: 2.18, LD₅₀ 10.6 g/kg

CH₃—As⁺—CH₂CH₂OH
AC
Experimental – Arsenic 10pg each species
Experimental – Arsenic 5,000pg each species
Experimental – Arsenic #2

- Agilent 7800 – x lens, MicroMist, Ni Cones
- Agilent 1260 – BioInert, Quat Pump, BioInert Multi-Sampler, TCC 6-port BioInert Valve

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<td>~7 min</td>
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Experimental – Arsenic 10pg each species
Experimental – Arsenic 500pg each species

Overcoming Challenges in Elemental Speciation Techniques
Experimental – Arsenic Comparison

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Experimental – Arsenic Contamination

Watch out for contamination from the labware
- Amber glass may contain low levels of arsenic
- This includes sample vials
- Clear glass usually OK
- PFA/FEP bottles are best
Examples: Add PEEK Red Before Column
Examples: Add PEEK Blue Before Column
Examples: +0.5% HCl
Examples: +0.5% Nitric Acid
Experimental – Selenium

- Agilent 7800 – x lens, MicroMist, Ni Cones
- Agilent 1260 – BioInert, Quat Pump, Well-Plate ALS, TCC 6-port BioInert Valve

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<tr>
<th>Parameter</th>
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<tbody>
<tr>
<td>Column</td>
<td>Metrosep A Supp10 250mm x 4.0 mm</td>
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<tr>
<td>Mobile Phase</td>
<td>A – DIW / 2% Acetonitrile</td>
</tr>
<tr>
<td></td>
<td>B – 200 mM Ammonium Nitrate / 2% ACN / pH 9.5</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>1.0 ml / min (gradient)</td>
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<tr>
<td>Injection Volume</td>
<td>100 µl</td>
</tr>
<tr>
<td>Gas Mode</td>
<td>H₂</td>
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<tr>
<td>Integration Time</td>
<td>0.8 sec</td>
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<tr>
<td>Total Run Time</td>
<td>~30 min</td>
</tr>
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</table>
Experimental – Selenium 5pg each species
Experimental – Selenium 5,000pg each species
Experimental – Chromium

- Agilent 7800 – x lens, MicroMist, Ni Cones
- Agilent 1260 – BioInert, Quat Pump, Well-Plate
  ALS, TCC 6-port BioInert Valve

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<tr>
<td>Column</td>
<td>Agilent Bio WAX 50mm x 4.6mm, 5um</td>
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<tr>
<td>Mobile Phase</td>
<td>100 mM Ammonium Carbonate / 5 mM EDTA</td>
</tr>
<tr>
<td>Flow Rate</td>
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<td>Total Run Time</td>
<td>~3 min</td>
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</table>
Experimental – Chromium 3+ @ 5000pg
Chromium 6+ @ 50pg
ICP-MS Instrument Settings

- Nebulizer Gas Flow Rate
- Waste Pump Rate
- Conditioning
- Detector Integration Time
Acknowledgments

Mark Powell

Jenny Nelson
Questions?

Mark Kelinske

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