Application of Reaction Cell ICP/Ms for Improved Detection Limits for As and Se in Salt Impacted Water Samples

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Reaction Cell ICP MS

- Overview of ICP technology
  - ICP: The plasma
  - ICP: Optical Emission
    - Interferences
  - ICP: Mass spectrometry
    - Interferences
  - Collision Cell Technology
- Overview of Reaction Cell Technology
  - Layout of cell
  - Control of reactions
  - Interferences removed
  - Salt impacted water analysis
- Next steps
The plasma

- Created by passing argon through a series of tubes that are wrapped by an RF coil.
- Energy supplied by the RF generator creates and contains the argon plasma.
- Plasma temperatures are around 6000-7000K.
- Liquid droplets that contain the sample matrix and elements of interest are introduced into the plasma where they are instantly dried to a solid then converted to a gas.
Optical Emission

- Energy from the plasma will excite electrons in the atoms causing a shift to a higher energy level.
- Electrons drop down to fill the lower orbital and a photon is released. Wavelength of light released is characteristic of the element.
- Interferences based on overlapping wavelengths; different orbital changes for elements.
- Detection simply by measuring intensity of light at various wavelengths.
ICP/OES - Limitations

- Subject to spectral interference
- Difficult to analyze more electronegative elements
- Detection limits not as good as ICPMS
  - Detection limits not suitable to As, Se, Sb
ICP/MS

- Same plasma created for MS as for optical.

- Elements in the plasma absorb more energy and release an electron. This forms a positively charged ion.

- For MS, identification and quantification is based on measuring the mass and quantity of the positive ions created.

- During this process other interactions are taking place that can form interferences.
• Interface needed between the plasma and the ion focusing region of the MS
  • Plasma at high temps and atmospheric temperature
  • MS end at low vacuum and lower temperatures.
• Nexion system goes through a 3 cone system to reduce pressure.
  • Three cone system eliminates need for ion focusing lenses.
The beam of material coming out contains:
- Non-ionized material
- Photons
- Ions of interest
Neutral material can collect on components reducing performance and cause drift.
Photons might cause incorrect ion counts if they reach the detector.
Nexion unit uses a quadrupole mass filter at a right angle to the beam.
Positively charged ions deflected whereas the photons and neutrals aren’t affected and are removed from the beam.
Quadrupole Ion Deflector
After exiting the quadrupole deflector the ions enter the quadrupole mass filter.
Quad works by adjusting voltages and Rf to allow certain mass/charge ratios to pass.
Rapid scanning of different masses.
Ions of a specific m/z are then counted in the electron multiplier.
Interferences

- Interferences are when something from the sample, the plasma or some combination carries a mass to charge ratio similar to what you are looking for.
- Argon is the gas used to generate the plasma and can combine with itself or other elements to form interferences.
- Oxygen from the sample matrix can combine with argon to form a polyatomic species $\text{ArO}^+$ with a mass of 56 amu.
- One of the most prevalent isotopes for Iron is mass 56.
- $\text{ArO}^+$ will cause high background if we use mass 56 for iron,
  - Other isotopes can be used for iron but at lower intensity and therefore poorer detection limits.
ICP : Interferences

<table>
<thead>
<tr>
<th>Potential Interfering Species</th>
<th>Analytes Impacted</th>
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<tbody>
<tr>
<td>$^{12}$C$^{15}$N, $^{12}$C$^{14}$NH</td>
<td>$^{27}$Al</td>
</tr>
<tr>
<td>$^{38}$ArH</td>
<td>$^{39}$K</td>
</tr>
<tr>
<td>$^{40}$Ar</td>
<td>$^{40}$Ca</td>
</tr>
<tr>
<td>$^{35}$Cl$^{16}$O</td>
<td>$^{51}$V</td>
</tr>
<tr>
<td>$^{35}$Cl$^{16}$OH</td>
<td>$^{52}$Cr</td>
</tr>
<tr>
<td>$^{36}$Ar$^{16}$O</td>
<td>$^{52}$Cr</td>
</tr>
<tr>
<td>$^{40}$Ar$^{12}$C</td>
<td>$^{52}$Cr</td>
</tr>
<tr>
<td>$^{38}$Ar$^{16}$OH</td>
<td>$^{55}$Mn</td>
</tr>
<tr>
<td>$^{40}$Ar$^{16}$O</td>
<td>$^{56}$Fe</td>
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<tr>
<td>$^{40}$Ar$^{16}$OH</td>
<td>$^{57}$Fe</td>
</tr>
<tr>
<td>$^{40}$Ar$^{35}$Cl</td>
<td>$^{75}$As</td>
</tr>
<tr>
<td>$^{40}$Ar$^{37}$Cl</td>
<td>$^{77}$Se</td>
</tr>
<tr>
<td>$^{40}$Ar$^{40}$Ar</td>
<td>$^{80}$Se</td>
</tr>
</tbody>
</table>
Collision Cell Technology

• Works on the idea that the polyatomic (i.e. molecular) interferences are larger in size than the single elements.
• When both pass through a field of inert gas, the larger polyatomic will collide with more gas atoms than the smaller element.
• At the end of this process, the larger interfering compound has lower energy than the smaller element.
• An energy barrier is placed at the exit of the cell that is adjusted accordingly and will only allow the higher energy elements to pass through.
Collision Cell Technology

• Easy to set-up.

• Background is reduced

• Some reduction in target elements as well though.
• Reaction cell is based on true chemical reactions; not just kinetic energy reduction through collisions.
• More reactive gases are used; not just inert gases.
• The goal is to convert the interfering ion into a species that no longer interferes.
• Can also create new species with the target element that avoids the interfering ions.
• Reaction cell technology if properly set-up can reduce the interference without reducing the target element.
  • Preserves detection limit.
• Need to avoid creation of new interfering species.
• The DRC uses an active quadrupole to control reaction and prevent unwanted reactions.
Layout of cell
Std Mode - no added Chloride
Std Mode - 1 ppm Chloride
Std Mode: - 100 ppm Chloride
Std Mode - 1000 ppm Chloride
Std Mode- 10000 ppm Chloride
DRC Mode - no added Chloride
DRC Mode - 1000 ppm Chloride
DRC Mode 10000 ppm Chloride
DRC vs Std mode: 1000 ppm Chloride

![Graph showing the comparison between DRC and Std mode for 1000 ppm Chloride concentration. The graph compares chloride, arsenic (corrected), selenium (corrected), and TRUE values at 2 ppb and 5 ppb.](image-url)
DRC vs Std mode 10000 ppm Chloride
Conclusions and Next Steps

• At chloride ion concentrations greater than 1000 ppm the DRC mode will yield more accurate data than standard operation mode ICP MS.
• Other flow-rates and other reactive gases could further improve the quantification of As in DRC mode.
• A full MV to be done after optimization of gases and flow settings.