Low Level Detection of Priority Inorganic Pollutants in Water

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Priority List of Pollutants

- Consists of 16 metals and/or transitional elements.
- Enter the human food chain via:
  1. dissolution of metal rich ores in water
  2. Plant and animal uptake
  3. Contamination from Industrial Processes
Arsenic

• 20\textsuperscript{th} most abundant element in the earth’s crust.
• Acutely toxic and carcinogenic
• Inorganic forms found in water are more toxic than organic forms found in tissue
• Is mobile at neutral pH and in reductive or oxidizing conditions.
International guidelines for Arsenic

- Ranges from 7ug/L (ppb) in Australia to 50 ppb in the U.S.
- Current Canada guideline = 25ppb
- Alberta proposing a reduction to 5ppb
- Public Health Goal for Arsenic = 0.004ppb

Problem

Standard lab detection limits = 0.2 to 1.0 ppb
<table>
<thead>
<tr>
<th>Laboratory methods of analysis of Inorganic Pollutants</th>
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<tbody>
<tr>
<td><strong>Atomic Absorption</strong></td>
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<td>One element analyzed at a time</td>
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<td>Long run times and higher costs</td>
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<td><strong>ICP-OES</strong></td>
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<tr>
<td>Rapid analysis of several elements</td>
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<tr>
<td>Not sensitive enough to meet regulatory criteria for certain elements</td>
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<tr>
<td><strong>ICP-MS</strong></td>
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<tr>
<td>Rapid analysis of all elements</td>
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<td>Low detection limit</td>
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<td>Large dynamic range</td>
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Polyatomic Interferences

- Are created within the plasma
- Results in the formation of a product that has the same mass:charge ratio as the analyte of interest e.g. $^{40}\text{Ar}^{35}\text{Cl}^+$
  - Arsenic, selenium, chromium, vanadium

- Can be corrected for by:
  1. Mathematical corrections
  2. Chemical Resolution
Chemical Resolution

Ion lens system  Dynamic Reaction cell  Analyzing quadrupole

$^{75}\text{As}^+$  $^{40}\text{Ar}^{\text{35Cl}}^+$
Chemical Resolution

Optimization of DRC Gas Flow using Methane

- CPS
- DRC Gas Flow in mL/min

Se 80
ArAr+
Objective

• To compare the operation of an ICP-MS in Standard mode (mathematical corrections) and in Dynamic Reaction Cell mode (chemical resolution)
  • Instrument detection limits
    – Effect of different matrices on precision
  • Accuracy and precision at low pollutant concentrations
  • Effect of different matrices on accuracy
Comparison of Instrument Detection Limits for Arsenic

- IDLs determined in Standard mode and DRC mode at three salt concentrations:
  1. 0 ppm chloride
  2. 1000 ppm chloride (elevated groundwater)
  3. 19000 ppm chloride (seawater)
Matrix Effect on IDLs for Arsenic

Instrument detection Limit (μg/L)

Water 1000 ppm Cl Seawater

0.028 0.035 0.349 0.077 0.533 7.898

DRC Mode
Standard Mode

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Matrix effect on Instrument Detection Limits (IDL)

Instrument Detection Limits µg/L

Vanadium  Chromium  Selenium

Standard Mode
- 0ppm K
- 1000ppm K

DRC Mode
- 0ppm K
- 1000ppm K
Accuracy and precision of Low Level Element Detection

• Analysed for Vanadium, arsenic chromium, selenium

• Each analyte was determined with 10 replicates at 2 concentrations:
  1. 0.2ug/L
  2. 2.0ug/L

• Compared the relative standard deviation and the mean of each analyte in DRC and Standard mode
Low Level Detection of Elements

0.2ug/L

2.0ug/L

% Relative Standard Deviation

V51  0.17  1.7
As75  0.22  2.2
Cr52  0.21  2.1
Se78/82  0.22  2.0
Se80/77  0.24  1.9

DRC

Standard

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Detection of Arsenic in Different Matrices

- Four levels of arsenic (0, 2, 10, 25ug/L) were spiked into 3 salt solutions:
  1. 0ppm Chloride
  2. 1000ppm Chloride
  3. Seawater (19000ppm Chloride)
Detection of Arsenic in potassium solutions

- Four levels of arsenic (0, 2, 10, 25ug/L) were spiked into:
  1. 0 ppm potassium chloride
  2. 1900ppm potassium chloride (1000 ppm of potassium)

- Compared DRC to Standard mode
Spiked Arsenic Concentration

% Recovery

DRC - no K
DRC - 1000K
Standard No K
Standard - 1000K
Summary

- ICP-DRC-MS shows improved performance over standard ICP-MS:
  1. DRC improves the precision of the results for low pollutant concentrations and in the presence of interfering substrates (most environmental samples) using chemical resolution
  2. Accuracy of the DRC is consistent with or better than standard mode operation
  3. DRC uses chemical resolution to prevent errors that may arise due to mathematical corrections in standard mode
Acknowledgements

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