Improve Analysis Precision for ICP-OES and ICP-MS for Environmental and Geological Applications

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Stanford University

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Outline

• Metals geochemical cycling in our environment
• Analysis of metals for the environmental and geological applications
• Brief review of ICP-OES and ICP-MS
• Comparison and selection criteria between ICP-OES and ICP-MS
• Choices of trace metal analysis tools
• Application resources
Metals in the Environment

Natural sources

Geochemical cycling

Industrial sources

Uptake in Food Chain

Wastes
Environmental Sample Analysis

• Waters – drinking-, surface-, ground-, waste-
• Soils – soils, sediments, foliage, biota
• Sludges – solid and digested waste
• Air – chimney exhaust filters, air filters of contaminated sites, dusts

• Applications:
  • Trace metal analysis in drinking water and wastewater
  • Trace metals analysis in solid waste and groundwater
Geological Analyses

• Typical samples: rocks, sediments, slags, ceramics, cements
• Types of work: survey work, quality control, raw material screening
• Applications:
  • Rare earth element analysis
  • Digested rock sample analysis
  • Isotope ratio analysis
• Different needs:
  • Robust to deal with high and low analyte concentrations and demanding sample preparation
  • Matrix tolerance (TDS) and stability to avoid signal drift
  • Detection limits (traces)
  • Precision and high throughput for isotope analysis
General Sample Preparation

- Some samples just require preservation in dilute acid
- Others need full acid digestion with HNO$_3$ and/or HCl and Aqua Regia e.g. soils and solid wastes
- Digestion can be on a hot plate or using a microwave
- Complete digestion is achieved dependant on method used (for total or water soluble metals)
- Some applications need to extract elements from samples (soil and sediments)
- Samples may require filtering after digestion
How Does ICP-OES Work?

- Sample atomization in argon plasma
- Liquid sample introduction
- Excited elements emit specific wavelengths of light
- Detection of light as amplified signals
What is ICP-MS?

Inductively Coupled Plasma - Mass Spectrometry

1. Sample Introduction
2. Elements in sample ionized in Inductively Coupled Plasma
3. Sampling Interface
4. Interference removal - CRC
5. Quadrupole Mass Spectrometer
6. Detector

1. Sample Introduction
2. Elements in sample ionized in Inductively Coupled Plasma
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# Comparison ICP-OES – ICP-MS

<table>
<thead>
<tr>
<th></th>
<th>ICP-OES</th>
<th>ICP-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Detection Limit</strong></td>
<td>(&lt;1ppb)</td>
<td>(&lt;1ppt)</td>
</tr>
<tr>
<td><strong>Linear Dynamic Range</strong></td>
<td>10⁶</td>
<td>10⁹</td>
</tr>
<tr>
<td><strong>Isotope Ratio Analysis</strong></td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td><strong>Matrix tolerance</strong></td>
<td>high</td>
<td>lower</td>
</tr>
<tr>
<td><strong>Coupling for Speciation</strong></td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td><strong>Speciation</strong></td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td><strong>Sample recovery</strong></td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>
Choose Between ICP-OES and ICP-MS

Important factors to consider:

• Applications and regulations
  • What is your application?
  • Does the application need to be regulated?
  • What is the detection limit?

• Sample types and concentration range
  • What matrix for the samples do you use?
  • What concentration range are the samples in?

Other factors to consider:

• Cost ownership
  • How much budget do you plan for?
  • How clean is the working environment for analysis?

• Operator skills/expertise
  • Will you have a dedicated personnel to run it?
Steps to Ensure Good Precision in ICP-OES and ICP-MS

- Ensure peristaltic pump tubing changed regularly and inspected daily
  - Check it’s not crushed (as a result of the pump clamps being left on) or worn before use
- Choose best nebulizer type for your samples
  - Glass concentric good for general use
  - High solids nebulisers (e.g. Parallel path type) for heavier matrix samples
  - Low flow if you’re limited in sample volume
- Optimize the nebuliser gas flow for the most stable signal, while meeting other required criteria
- For ICP-OES ensure mirror positions optimized before run, using auto-optimization routines on the instrument as required
- For ICP-MS, ensure interface cone orifices are free from deposited material and ion lens and detector voltages optimized as required before operation
Environmental Community Pages

Website: thermoscientific.com/environmental-community

Comprehensive analytical information provided on the community and landing pages:

- Featured brochure/flyers
- Application/technical notes
- White papers
- Poster notes
- Articles
- Case studies
- Webinars

Community and landing pages with hyperlinks:

- Environmental
- Air quality
- Water analysis
- Drinking water analysis
- Wastewater
- Chromium (VI)
- Hydraulic fracturing
- Water analysis resource library
- Water regulations
- Environmental knowledge library
Recent Related Webinars

- Speciation using IC-ICP-MS
  - Complete Inorganic Elemental Speciation Solutions for Environmental Applications
    - www.spectroscopyonline.com/Environmental
- Overcoming interferences in ICP-OES and ICP-MS
  - Demystifying Interference Removal
    - http://info1.thermoscientific.com/content/CMD_KL_Webinars?kl=ENV_#&rid=10518
- Cost and ownership
  - Speed and Cost of Ownership
    - http://info1.thermoscientific.com/content/CMD_KL_Webinars?kl=ENV_#&rid=10432
- The basics of ICP-MS
  - Fundamentals of ICP-MS
- Sample preparation:
  - Demystifying sample preparation for trace metal analysis (April 28, 2015)
    - www.spectroscopyonline.com/spec/Demystifying
Improve Analysis Precision for ICP-OES and ICP-MS for Environmental and Geological Samples

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School of Earth, Energy, and Environmental Sciences
Stanford University
Stanford University Environmental Measurements Facility (EMF)

- Established in 2006 by Dean Pam Matson
- Provides quantitative analyses and technical expertise to members of the Stanford community needing to conduct gas, solid, and water measurements
- Accessibility, affordability, and convenience
- Customized analyses for the research needs
Stanford School of Earth, Energy and Environmental Sciences

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For Solid Samples
- Freeze Dryer (FD)
- CN Analyzer (EA)
- XRF
- FTIR

For solid/aqueous samples
- CEM Digester (Mars)
- ICP-OES
- ICP-MS
- Mercury Analyzer (MA)-Off-Site

For aqueous and gas samples
- Discrete Analyzer (DA)
- Ion Chromatograph (IC)
- Carbon Analyzer (TOC)
- Gas Chromatograph (GC)

What instrument should I use for my analysis? Which ICP?

New Calculator for preparing your solutions.

EMF Updates: 1/14/2015 4:10:10 PM
Nitrate/Nitrite Chemistry has been changed to Imidazole ...more
Analyses We Provide:

- Gas samples for green house gas analyses- \( \text{N}_2\text{O}, \ \text{CH}_4, \ \text{CO}_2, \ \text{CO}, \ \text{O}_2, \ \text{and} \ \text{N}_2 \).
- Solid samples-direct analysis for metal elements inn soils and sediments: composition or digestion for later ICP and ICP-MS analyses.
- Aqueous samples for elemental and molecular analyses.
- Most analyses require high precision and accuracy due to the low levels of analytes.
Samples We Work With

- **Sample Sources**: Environmental and geological samples plus other research samples.
- For solid and gas samples, analyses are pretty straightforward.
- For aqueous samples, we have very challenging situations.
- Sample types and matrix are very diversified.
  - Simple samples: field collected solutions
    - Ground water
    - Surface water
  - Complex samples: lab created solutions
    - Reaction samples- various matrix and composition.
    - Extraction (acid, salt, mixed, organic, carbonate)
    - Digestion (Nitric acid, HCl, HF, Aqua Regia)
Some Typical Projects Creating Samples

- Arsenic cycling in Cambodia and China.
- Microbial remediation of heavy metals
- Mineral weathering
- Surface soil and water contamination from coal power plants
- Spectranomics
- Radiology research for development of new technology
- New drug developments
- New material developments
- ...
ICP-OES and ICP-MS

• Were used for environmental and geological sample analysis for many years due to its great sensitivity, accuracy and precision, and versatility

• Helps us better understand the environmental pollutions of heavy metals

• Both instruments have been improved to increase their popularity:
  • ICP-OES: both radial and axial view for increases of linear dynamic range
  • ICP-MS: collision/reaction cell technology for reduction of spectral interference

• However, there are many factors impacting the measurement precision that are still not easy to overcome or neglected for everyday use
Covered Factors to Improve Precision

• Among them, some special sample preparation and rinsing have not been paid much attention. By improving sample preparation and customizing rinse solutions, some interesting results were obtained:

1. Improved the analysis precision
2. Made impossible samples to possible to minimize extra sample preparation
3. Eliminated or reduced dilution of samples in order to minimize the error introduction and detection
General Solutions for Improving Analysis Precision-1

• Sample prep
  • Digestion (solid and liquid)
  • Filtration (0.2 μm filter) to ensure solution is particulates free
  • Dilution-Dilution usually can solve much of the problem but it could introduce error.
• Acidification
  • Carbonate samples: Pre-acidification will release the CO$_2$ generated
  • PIPES: acidification will precipitate PIPES and then, run the samples
• Acid selection:
  • Use nitric acid over HCl
  • Use nitric and/or HCl for digestion if HF can be avoided
• Dry-down and redissolve-HF digested samples
General Solutions for Improving Analysis Precision-2

• Rinse solution
  • Dilute acid (3% nitric acid)
    • For most of samples such as water, digestion, extraction
  • Water
    • For any samples that could precipitate in acid condition
  • Matching matrix solution/compatible rinse solution
    • For samples that precipitate in acidic condition but need more cleaning power, NH₄OH can be used for halogens if metals are not present and interested in or matching/ compatible solution
Problems We Ran into

• Matrix build-up: sampler and skimmer cones are easy clogged with matrix build-up and reduces signal intensity over time of the sample analysis

• Plasma shut down: after running a few samples, the plasma shut down and the sample running stops

• Precipitation/clogging: reaction of sample buffers or solutions with rinsing solution to generate precipitates and clog the nebulizer and tubing
Case Study - Matrix Build-up or Signal Loss

• Causes:
  • High HCl caused down-drift dramatically over time.
  • High TDS

• Solutions:
  • High acid conc.: Dilution with DI water to <5 or 3% acid concentration in final solution
  • High TDS:
    • Dilution with dilute acid (nitric acid over HCl) if compatible.
    • Dilute with compatible solution but not causing problems with ICP analysis
Impact of High HCl Matrix on ICP-OES Analysis

- High concentration of acids etc.
  - Many types of geological and environmental samples require digestion by acid. High HCl can cause down-drift dramatically over time.

- 25% of concentrate HCl.
- Almost no elements detectible.
- Take about 30 min. rinsing to bring the signal back.
Solution for High Matrix Samples

QC monitoring after diluting acid concentration to 5% with DI water
Case Study: Plasma Shut-down

• Causes: carbonate extracted samples
  • Na$_2$CO$_3$/NaHCO$_3$ is used to extract P in soil samples
  • CO$_2$ was produced during rinsing with 3% nitric acid and sample flushing
  • Produced CO$_2$ either shutdown plasma if the concentration is high or cause bad precision when it is low
Solutions for Plasma Shut-down

- Solutions:
  - Pre-acidify the samples to release the CO$_2$ from solution.
  - Take over night to complete the CO$_2$ release.

QC monitoring after pre-acidified carbonate solution
Case Study: Precipitation Clogging

**Causes:**
- Buffer or solution reacts with the rinse solution, then forms precipitate to clog the nebulizer and tubing

**Examples:**
- Sodium dithionate extraction
- Humic acid samples
- DNA solution
- Oxalate extraction
- PIPES

**Solutions:**
- Switching rinse solution to water, or other dilute acid, or with extra cleaning solution
1. Samples of Sodium Dithionite Extraction

- Sodium Dithionite is used with citrate and bicarbonate to extract crystalline Fe in environmental research.

- Problems:
  - High sodium and sulfur contents
  - Elemental sulfur was formed during rinsing and sample flushing
  - Precipitation of sulfur compounds
  - Clogging nebulizer or line
  - Not possible to run samples

- How to deal with it:
  - Dilution with DI water
  - Switching rinse solution from 3% nitric acid to DI water, it minimized the reaction/decomposition of NaS$_2$O$_4$
2. Humic Acid Samples on ICP-MS

- Humic acid can precipitate in acidic condition
- If dilute acid is used as rinse solution, ppt will be formed either in sample tubes or line
- Nebulizer and tubing get clogged
- Nebulization gets impacted

**Drift Using 3% Nitric Acid as Rinse**

**Water rinse**

QC monitoring after switching rinse to DI water
3. DNA Solution on ICP-MS

- DNA was used in drug development research
- DNA can precipitate in acidic condition
- If dilute acid is used as rinse solution, ppt will be formed either in sample tubes or line
- Nebulizer and tubing get clogged.
- Nebulization gets impacted
QC Variation of DNA Samples after Switching to DI Water Rinse on ICP-MS

![Graph showing variation of DNA samples over time with standard deviations for Li, Na, P, Br, and Rb.](image)
QC after Switching Rinse with Extra Cleaning of 5% of NH$_4$OH

<table>
<thead>
<tr>
<th>Conc. ppb</th>
<th>Na</th>
<th>P</th>
<th>As</th>
<th>Br</th>
<th>Cs</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>122.1</td>
<td>120.5</td>
<td>117.1</td>
<td>115.9</td>
<td>113.2</td>
</tr>
<tr>
<td>50</td>
<td>121.9</td>
<td>119.9</td>
<td>116.7</td>
<td>115.6</td>
<td>112.9</td>
</tr>
<tr>
<td>100</td>
<td>121.6</td>
<td>119.7</td>
<td>116.6</td>
<td>115.5</td>
<td>112.7</td>
</tr>
<tr>
<td>150</td>
<td>121.3</td>
<td>119.5</td>
<td>116.4</td>
<td>115.3</td>
<td>112.5</td>
</tr>
<tr>
<td>200</td>
<td>121.0</td>
<td>119.2</td>
<td>116.3</td>
<td>115.2</td>
<td>112.3</td>
</tr>
<tr>
<td>250</td>
<td>120.8</td>
<td>118.9</td>
<td>116.1</td>
<td>115.1</td>
<td>112.1</td>
</tr>
<tr>
<td>300</td>
<td>120.5</td>
<td>118.6</td>
<td>115.9</td>
<td>114.9</td>
<td>112.0</td>
</tr>
<tr>
<td>350</td>
<td>120.2</td>
<td>118.4</td>
<td>115.7</td>
<td>114.7</td>
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<tr>
<td>400</td>
<td>119.9</td>
<td>118.1</td>
<td>115.4</td>
<td>114.4</td>
<td>111.9</td>
</tr>
</tbody>
</table>

Stdev: 0.61, 0.68, 1.21, 1.32, 0.76
4. Oxalate Extraction on ICP-OES

- 3% nitric acid as rinse
- Oxalate extraction solution caused back pressure of nebulizer increase
- Results started fluctuating or drifting
## Improvement of Standard Deviation After Switching Rinse Solution on ICP-OES

<table>
<thead>
<tr>
<th>Rinse Solution</th>
<th>Al3961</th>
<th>Al3961</th>
<th>Ca3179</th>
<th>Fe2599</th>
<th>Fe2599</th>
<th>K_7664</th>
<th>Mg2852</th>
<th>Mn2576</th>
<th>Mo2020</th>
<th>P_2136</th>
<th>Si2516</th>
</tr>
</thead>
<tbody>
<tr>
<td>3% Acid</td>
<td>0.28</td>
<td>0.27</td>
<td>0.03</td>
<td>0.28</td>
<td>0.23</td>
<td>0.06</td>
<td>0.03</td>
<td>0.02</td>
<td>0.01</td>
<td>0.02</td>
<td>0.08</td>
</tr>
<tr>
<td>1% Oxalic Acid</td>
<td>0.07</td>
<td>0.05</td>
<td>0.01</td>
<td>0.05</td>
<td>0.05</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
<td>0.02</td>
</tr>
</tbody>
</table>
5. PIPES Samples on ICP-OES

- PIPES is used as biological buffer
- PIPES can precipitate in acidic condition
- If dilute acid is used as rinse solution, precipitate will be formed either in sample tubes or line
- Nebulizer and tubing get clogged
- Nebulization gets impacted

What we did:
- We pre-acidified samples with dilute acid and stored samples in fridge overnight to help with the precipitation of PIPES
- Make sure precipitate settle to bottom
QC Monitoring before and after Precipitating PIPES

**PIPES Samples with 3% nitric acid on ICP-OES**

![Graph showing concentration over time for Ca, Fe, and U](image)

- **Conc. ppm**
- **Time, min.**
- **Ca**
- **Fe**
- **U**

- **0 5 10 15 20 25 30 35**
- **0 50 100 150 200**

Our Findings

• Dilution
  • Dilute with dilute acid, nitric or HCl, preferred acid is nitric acid
  • Dilute with water or compatible solution if any matrix could precipitate in acidic condition.

• Pre-acidification
  • PIPES samples - pre-acidify the samples with dilute acid to precipitate PIPES
  • Carbonate extraction samples - should be pre-acidified and let CO₂ escape

• Customizing rinse solutions based on the matrix and compatibility
  • Oxalate matrix should use dilute oxalic acid
  • Samples with humic acid matrix should use water and dilution
  • Samples with protein/DNA should use water
  • ...

• Clean nebulizer and spray chamber with both acid and base solutions
Take-home Message

• Sample prep: Dilution is a very effective way to improve the precision during sample prep, but error introduction can impact the precision. So, make decision based on your precision requirement of research project
• Pre-treat samples if needed to eliminate problems
• Customize rinse solution to prevent precipitation
Thank You for Attending the Webinar

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