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ICP-MS Analysis of Trace Selenium in the Great Salt Lake

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Introduction

As part of the effort to preserve the water quality of one of the Western Hemisphere’s most important migratory bird habitats – the Great Salt Lake (GSL) in Utah – the GSL Water Quality Steering Committee [1] was established to recommend numeric water quality standards for some metals in the open waters of the lake [2]. The initial plan calls for recommendation of numeric water quality standards for selenium in the Great Salt Lake by the Utah Department of Environmental Quality (DEQ) to the USEPA by the end of 2007. Critical to determining baseline data for Se in the lake is the validation of a reliable analytical method.

Method Criteria

To meet the needs of the study, the successful analytical method must meet several requirements:

- High sensitivity must be achieved (due to required minimum detectable limit (MDL) of <0.5 ppb in the undiluted sample).
- Analysis must be performed with minimum sample dilution in order to retain sensitivity.
- The method must tolerate high total dissolved salt concentrations with minimum signal suppression and minimum signal drift.
- Method must avoid significant spectral interferences on at least one Se isotope.
- Method must be simple and reliable.

Because of the requirement for the lowest possible detection limit (<0.5 ppb), only sensitive techniques such as hydride generation atomic absorption (HGAA), graphite furnace atomic absorption (GFAA) or ICP-mass spectrometry (ICP-MS) were considered.

Round-Robin Study

As part of the method selection process, a recent round-robin study among seven laboratories was conducted by the Utah Division of Water Quality to compare ambient level Se measurements and low-level spike recoveries of Se in GSL waters using multiple techniques.

In addition to traditional GFAA and HGAA techniques, both conventional (non-cell) and passive and dynamic collision/reaction cell ICP-MS instruments were evaluated. Collision/reaction cell ICP-MS was considered due to its ability to remove polyatomic interferences in complex matrices such as GSL waters.

Sample Collection and Preservation

Two samples (1-m and 7-m deep) were collected from a single location near the middle of the south arm of the lake. In addition to native Great Salt Lake water, triplicate spikes were prepared. Sample identification numbers were applied randomly to all sample replicates and distributed "blind" to participating laboratories. A total of 36 samples were submitted to each participating laboratory for analysis. Each laboratory was free to choose the analytical technique, depending upon their proficiency and available instrumentation.

In all cases, standard analytical methods were employed. Analytical techniques included HGAA (EPA 270.3) GFAA (EPA 200.12), conventional (non-cell) ICP-MS (EPA 200.8 – Agilent 7500a) dynamic reaction cell (DRC) ICP-MS (EPA-200.8 modified – PerkinElmer Elan DRC II), and octopole reaction cell ICP-MS (EPA 200.8 modified – Agilent 7500ce).

Although all the techniques employed are commonly used for analysis of selenium in various environmental samples, Great Salt Lake water presented a significant challenge to most. Because of the very high level of dissolved solids, both spectral and nonspectral interferences were evident for all techniques evaluated. The levels of interferences ranged from slight to severe.

The final round-robin results for all participating laboratories using ICP-MS are presented in Table 1. Two techniques, hydride AA and octopole reaction cell ICP-MS provided sufficiently accurate and precise results. The remaining techniques, GFAA, DRC ICP-MS, and conventional (noncell) ICP-MS, showed significant positive bias and yielded unusable results. GFAA is known to suffer from interferences from chlorides and sulfates, which can be mitigated by the addition of nickel nitrate, but not eliminated. In the case of Great

<table>
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<th>Technique</th>
<th>% Recovery [Accuracy]</th>
<th>Std Dev / Mean [CV]</th>
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</thead>
<tbody>
<tr>
<td>DRC-ICP-MS measuring m/z 94</td>
<td>Average 558% 26.3%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 meter 478% 26.3%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7 meter 637% 25.9%</td>
<td></td>
</tr>
<tr>
<td>DRC-ICP-MS measuring m/z 96</td>
<td>Average 781% 32%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 meter 631% 43.8%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7 meter 931% 18.3%</td>
<td></td>
</tr>
<tr>
<td>Hydride AA (reference method)</td>
<td>Average 91% 7.9%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 meter 105% 1.5%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7 meter 77% 12.7%</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Summary of ICP-MS results from round-robin study
Salt Lake waters, the Cl and SO₄ concentrations are too high. Similarly, conventional ICP-MS suffers from too many polyatomic interferences to measure selenium in high Cl, high Br matrices. The DRC ICP-MS situation is a bit different. Like the octopole reaction cell instrument, the DRC ICP-MS system uses a collision/reaction cell to remove polyatomic interferences before they enter the mass spectrometer and are measured. Typically, reactive gases are used with the goal of separating the analyte from the interferant by shifting either the mass of the polyatomic interference or the analyte to a new mass via ion–molecule reaction. In this case, oxygen was used as the reaction gas. Oxygen readily combines with Se⁺ to form SeO⁺, effectively shifting the Se signal away from the Ar²⁺ interferences at m/z 78 and 80. The resulting analyte signal is measured at m/z 94 (⁷⁸Se¹⁶O⁺), and m/z 96 (⁸⁰Se¹⁶O⁺). However, the very large positive bias in the results, approximately 500–800%, suggests the presence of large, unknown interferences at the new masses. Furthermore, very specific reaction chemistry, such as that used in both DRC ICP-MS and hydride AA, limits the scope of the analysis to only a few related analytes.

Conversely, octopole reaction cell ICP-MS uses simple, universal conditions to remove polyatomic interferences generically while maintaining the analyte (in this case, selenium) at its actual mass. Therefore, the use of octopole reaction cell ICP-MS presents the advantage over hydride AA of being able to simultaneously measure other trace elements in addition to selenium in saline samples. This will prove useful as the characterization of the Great Salt Lake progresses to other analytes.

Overall, octopole reaction cell ICP-MS was chosen for continued work because of its sensitivity, lack of bias, multielement capability, and ease of use.

**Determining Sensitivity**

The 7500ce ICP-MS system was operated in hydrogen mode in order to effectively remove argon-based polyatomic interferences on ⁷⁸Se. The typical response for ⁷⁸Se on the ORS ICP-MS system in H₂ reaction mode is ~ 1500 cps/µg/L. This allows linear calibrations from 0.1 to 1 ppb and a calculated detection limit of less than 10 ppt with a background equivalent concentration (BEC) of 6.45 ppt (Figure 1).

**Conclusions**

Because of the high levels of dissolved salts in Great Salt Lake water, most conventional techniques for the analysis of selenium in waters are inappropriate, resulting in significant positive bias. Of the techniques evaluated, including GFAA, conventional ICP-MS (no collision/reaction cell), DRC ICP-MS, hydride AA, and ORS-ICP-MS, only hydride AA and ORS-ICP-MS were able to provide consistent and presumably accurate measurement of selenium from ambient levels to samples spiked as high as 85 ppb.

ORS-ICP-MS provides the added benefits of simple sample preparation, high sample throughput, and capability for simultaneous multi-element analysis. As such, the Utah Division of Water Quality have recommended that USEPA begin the process of certifying ORS-ICP-MS as an available method for selenium analysis in hypersaline samples such as the Great Salt Lake.

**References**


![Figure 1. Se calibration at 0.1, 0.5, and 1 ug/L using mass 78. BEC= 0.0065 ppb, DL= 0.0085 ppb.](image-url)
User Profile –
Upgrading an Agilent 7500i to a 7500ce

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The Analytical Services Laboratory of the Wyoming Department of Agriculture is located in Laramie, Wyoming. The laboratory is composed of chemical and bacteriological sections and handles a broad range of sample types including water, dairy products, animal feeds and forage, fertilizers, petroleum products and natural gas, anti-freeze, pesticide and herbicide formulations and residues in water, plants and soils. Water samples alone cover a broad range of composition and include laboratory deionized, reverse osmosis and distilled water, bottled and drinking water, surface and ground waters, irrigation and stock waters, and wastewaters.

The basic cations and metals analyses were performed using a combination of sequential ICP-OES and atomic absorption techniques including flame, graphite furnace, cold vapor and hydride generation. These methods provide the flexibility to meet many of our clients needs, but they tend to be labor intensive and costly both in terms of time and resources because only one analyte may be run at a time. We lacked the ability to simultaneously scan a broad range of potential constituents. This limited our ability to meet part of the stated mission of the laboratory, to promote the health and economic well-being of the citizens of Wyoming.

The Decision for ICP-MS

By 2000 – 2001 the laboratory was facing an increasing need to more efficiently analyze samples. For our metals work we had long considered simultaneous ICP-OES, but ICP-MS was also an intriguing possibility. Our choice of technique and instrumentation rested on several considerations:

• Ability to meet current and future analytical needs and workloads
• Method requirements of USEPA, USFDA and other regulators
• Reliability
• Price
• Ease of regular maintenance
• Proximity of technical support and the cost of maintenance agreements
• Cost of expendable items (e.g. gas consumption, torches, spray chambers, nebulizers, cones, etc.)
• Length and steepness of the learning curve for both the hardware and software
• Ability to upgrade the existing instrument to new technology

It seemed that ICP-MS in general and the Agilent 7500i in particular met all these criteria. The 7500i was a non-octopole reaction system (ORS) instrument designed primarily for environmental work and included an ISIS auto-dilution system. The initial installation of our 7500i occurred in January, 2002. It was brought into full operation following onsite training in February, 2002. During the next couple of months we continued to analyze water samples by the older methods as well as by ICP-MS until we were confident of both the instrument and our ability to reliably handle the isobaric and polyatomic interferences that can limit the application of the method. For the next four years we used the instrument in this configuration. The reliability of the instrument and the productivity increases, while expected, still amazed. Used in combination with closed-vessel microwave digestion we were able to apply the method to an increasing list of sample types including:

• Animal and plant tissues
• Animal feed supplements
• Paint chips, milk and dry milk
• Soils, stream and lake sediments
• A variety of suspect foodstuffs

Surface and ground waters continue to compose the major portion of our routine sample load. Some of these waters can have very high concentrations of carbonates, bicarbonates, chlorides and sulfates all of which can create significant polyatomic interferences at masses of interest. Taken in combination with the variety of sample types, we saw a need to better deal with potential interferences and reduce the dependence on interference equations. Upgrading our 7500i to an ORS equipped instrument – making it the equivalent of a newer 7500ce – seemed a practical next step to meet our evolving needs.

Upgrading to the ORS

The upgrade was installed in January, 2006 and involved a major renovation of the instrument including hardware and software upgrades. The precision of the workmanship of the new and replacement parts was remarkable. Everything seemed to fit perfectly. The ISIS auto-dilution system was retained as a component of the system. Following two days of onsite training we were back in business running samples. Two weeks later we successfully ran an USEPA proficiency testing sample in both ORS and non-ORS modes with no need for reruns.

Final Changes

A drawback of this configuration...
was that the ISIS used a lot of sample, diluent and rinsing solution. We wanted to be able to analyze limited volume samples without dilution while retaining the flexibility that we had with the original and upgraded configurations. These aims were met and our instrument reached its current configuration by disconnecting the ISIS, upgrading the software and extending the calibration range of calcium, sodium, magnesium, silicon, strontium and barium using the He (collision) mode of the ORS. We currently cannot use this approach with USEPA regulated drinking waters, but this is seldom a problem with this type of sample.

These changes had some unexpected consequences. The sample consumption was reduced from approximately 7 mL with the ISIS to less than 1 mL without the ISIS. Not only did this help with running limited volume samples, but it also helped us significantly reduce our waste stream, consequently reducing the cost of waste disposal and making our operation safer. Because of the reduced rinsing times, the time to run a sample has been significantly reduced.

Daily Operation

The ORS instrument is tuned (or the tune is checked) each day of use with an aqueous solution of 7Li, 59Co, 89Y, 140Ce and 205Tl all at 10 ug/L concentration. The matrix of this tuning solution is typically 1% HNO3 and 1% HCl. In non-gas mode, sensitivity for 7Li, 89Y, and 205Tl is typically 20,000, 70,000 and 60,000 counts per second (cps) respectively. The ratio 156/140 representing CeO/Ce is tuned to approximately 1% or less. The ratio 70/140 representing Ce2+/Ce is maintained 1% or less. The ratio 70/140 representing CeO/Ce is tuned to approximately 156/140 representing CeO/Ce is tuned to approximately 20,000, 70,000 and 60,000 respectively. The ratio 156/140 representing CeO/Ce is tuned to approximately 1% or less. The ratio 70/140 representing Ce2+/Ce is maintained 1% or less. The ratio 70/140 representing CeO/Ce is tuned to approximately 20,000, 70,000 and 60,000 respectively.

In Hydrogen reaction mode, masses 56, 59, and 78 are monitored. H2 flow to the cell is set at 4 mL/min during tuning and analysis. Mass 78 (78Se, 38Ar40Ar, 40Ca38Ar, 43Ca35Cl) is the main focus of attention and is tuned to less than 10 cps (usually ~1cps). Mass 59 is again maximized at a value >5000 cps (usually ~10,000 cps). This tuning yields ~1000 cps for a 1ug/L Se standard (mass 78) during calibration and analysis.

Once stabilized – about 15 minutes to get the spray chamber cooled to 2°C – tuning in the non-gas mode can take less than 5 minutes. Add another 5 minutes or less to do a pulse/analog tune and we are ready to run samples. Time spent tuning using the ORS in both He- and H2-modes was reduced from about 30 minutes to less than 15 minutes. These time savings are primarily due to changes in the tuning pages which allow the user to select tuning parameters that are used in all three modes of operation.

Interference Correction Equations

The ORS has not eliminated the need for correction equations, but greatly reduced their use. Collision mode (He-mode) primarily removes polyatomic interferences by kinetic energy discrimination (KED) but not isobaric interferences or interferences from doubly charged ions. We have successfully used H2 reaction mode to eliminate the isobaric interferences of Ar on Ca at mass 40 and of the N dimer on Si at mass 28. Polyatomic interferences at the 56 mass (56Fe, 89Y, and 205Tl) and the 78 mass are also eliminated using this mode.

There is still a need for interference corrections at masses where isobaric overlap can occur (e.g. 115Sn on 115In), interference from doubly charged ions (e.g. 43Ca and 44Ca from 86Sr and 88Sr respectively) and when isotopes have nearly equal abundance (e.g. summation of 206Pb, 207Pb, and 208Pb). With these considerations we have reduced our use of interference equations from 15 in our basic non-ORS method currently used for USEPA regulated drinking water analyses to 5 in the equivalent ORS method.

The Bottom Line

Our aim continues to be achieving lower method detection limits (MDL) while applying a robust method that can handle the many types of samples we analyze. Table 1 contains a list of analytes and MDLs obtained for acidified water matrices with the ORS in the most recent configuration of our 7500 (without the ISIS). The calibration ranges used for this method include:

- Ca, Na: - 0.1 to 200 mg/L
- Mg: - 0.1 to 50 mg/L
- K: - 0.1 to 20 mg/L
- Si: - 0.010 to 10 mg/L
- Fe: - 0.020 to 5 mg/L
- Sr, Ba: - 1 to 2000 ug/L
- Trace metals: - 1 to 2000 ug/L
- Hg: - 0.050 to 1 ug/L

<table>
<thead>
<tr>
<th>Element</th>
<th>Conc (ug/L)</th>
<th>Element</th>
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<td>Ca</td>
<td>4</td>
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<tr>
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<tr>
<td>Fe</td>
<td>0.6</td>
<td>Zn</td>
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</table>

Table 1. ICP-MS (ORS) Method Detection Limits (MDL).

Conclusions

Adding ICP-MS to our analytical tool box and upgrading to ORS capability has allowed us to make our laboratory operations more efficient, safer and more environmentally sound while improving the quality of our data and speeding the time of analysis.
7500ce ICP-MS: Isotope Dilution Applications using Custom Databases

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The ChemStation software on the Agilent 7500 ICP-MS contains a very useful tool, the ‘custom database’, which we have utilized to help with some complex isotope dilution mass spectrometry (IDMS) uncertainty calculations.

IDMS is used for high accuracy quantitative analysis in a variety of matrices, where an accurate uncertainty statement is required. This may be for a number of reasons, such as:

• Reference material characterization
• Participation in international inter-laboratory comparisons
• Provision of reference values for proficiency testing (PT) schemes
• Reference material characterization

The approach frequently adopted at LGC is an exact matching double IDMS procedure. The mass fraction of the analyte is calculated according to the following equation;

\[ C_s = C_X \cdot \frac{m_Y - m_{Yc}}{m_X - m_{Yc}} \]

Where,

- \( C_s \) = mass fraction of analyte in sample X
- \( C_X \) = mass fraction of analyte in primary standard Z
- \( m_Y \) = mass of spike Y added to sample X to prepare the sample blend B (B=X+Y)
- \( m_{Yc} \) = mass of sample X added to the spike Y to prepare the blend B
- \( m_Zc \) = mass of primary standard spike Y to prepare the blend B

To make the calibration blend Bc (Bc=Y+Z) \( m_{Yc} \) = mass of spike Y added to the primary standard solution Z to make the calibration blend Bc

\[ R_B = \frac{m_B}{m_Zc} \]

\[ R_{Bc} = \frac{m_B}{m_B} \]

\[ R_Y = \frac{m_Y}{m_B} \]

\[ R_{Yc} = \frac{m_Y}{m_B} \]

\[ R_{Zc} = \frac{m_Zc}{m_B} \]

\[ R_{Z} = \frac{m_Zc}{m_B} \]

In order to calculate these uncertainty contributions it is necessary to obtain the %RSD of the measured isotope ratio for each solution analyzed.

When an isotope ratio report is generated, the individual replicate isotope ratios, the average ratio, the standard deviation and %RSD are obtained. An example of the database which we have setup for our Se IDMS work is shown. The database takes some time to set-up, but once established is a great time-saving tool.

An example of the database which we have setup for our Se IDMS work is shown. The database takes some time to set-up, but once established is a great time-saving tool.

References
New Fileview Plus
Data Extraction
Software for the
Agilent 7500 Series
Charles Lingel
Infoconix Inc., USA, charles@infoconix.com

Introduction
Developed from the widely popular Fileview data extraction software, new Fileview Plus contains all the features found in the original version plus many new functions users have requested. New features of Fileview Plus include:

- **Customizable Grid View**
  A great feature is the flexibility to select from counts average, replicate counts, concentration, RSD, units, detector mode, and internal standard reference – and to display these fields simultaneously on the same grid. Up to four different column configurations can be stored and recalled with a mouse click.

- **Auto View Function**
  With the Auto View function, all new data can be automatically imported and displayed in the grid in real time as a sequence progresses. When the Fileview Plus grid is open, new data columns appear as each sample acquisition finishes. The user can review all data generated in a tabulated form, in real time, in a single location.

- **MDL, IDL and BEC Calculator**
  Method detection limit (MDL), instrument detection limit (IDL), and background equivalent concentration (BEC) can now be automatically calculated, exported and saved for every sample batch. This is a great tool that can be used to easily track instrument performance over time.

- **CCV and CCB Calculator**
  Continuing calibration verification (CCV) and continuing calibration blank (CCB) data can be exported in a tabulated form. “Out of range” values can be displayed in a separate column (ranges are user configurable). Data can also be exported to a spreadsheet application.

- **IS Plot Engine**
  The Internal Standard (IS) plotting engine creates two output formats to easily troubleshoot instrument performance:
  - A graphical plot showing normalized data.
  - A grid showing all the tabulated count information.
  This calculation requires a reference value (normally the calibration blank) against which all other samples are plotted.
  The graphical plot can be printed directly from Fileview Plus or copied to the clipboard and pasted into another application.

- **Print Capabilities**
  The Fileview Plus grids print data directly with options that include portrait and landscape orientation, margin adjustment, scaling, and automatic formatting (vertically, horizontally, or both) in multiple pages. The element and header information is printed on each page.

Other new features include semiquant data extraction and data file search capabilities. Fileview Plus works with all 7500 Series ChemStation on Windows 2000 or Windows XP revisions and is distributed and supported worldwide by FullQuant Corp. in the US.

Ordering Information
For more information, to purchase Fileview Plus or for a 15 day free trial, visit the Fileview Plus website at www.fileviewplus.com

Features like printing capabilities, automated grid update, replicate information, internal standards plotting engine and IDL calculator are only a few of the great new tools Fileview Plus offers.
8 Months Until 4500 Series End of Support

A reminder that Agilent will continue to fully support all 4500 Series instruments until their End of Support (EOS) date of October 31, 2007. This includes the renewal of support contracts, which can be purchased pro rata – to run to EOS date. After EOS date, service parts will be available from Agilent until supplies are exhausted, and labor-only contracts can be purchased for a further 1 year after EOS date. These labor-only contracts are available under Agilent’s Asset Maximization program (Asset Max). Ask your Agilent support sales representative for details.

Labs that rely on their Agilent 4500 for all ICP-MS analysis, where the 4500 is the only ICP-MS in the lab, are advised to plan now to replace their instrument. Contact your Agilent support sales representative for more information.

New Agilent ICP-MS Users

A very warm welcome to all companies and institutions that have recently added an Agilent ICP-MS to their analytical facilities. Remember to join the Agilent web-based ICP-MS User Forum – the place where you can exchange information relating to your 7500.

To access the Forum, you will simply need to log-in to the Agilent web site, or register if you haven't already, and enter your instrument's serial number on your first visit only. Look for the link to the ICP-MS User Forum from: www.agilent.com/chem/icpms

Trade Shows and Conferences


CANAS Konstanz, 18-21 March 2007, Germany, www.canas.de


Agilent ICP-MS Publications

To view and download these latest publications, go to www.agilent.com/chem/icpms and look under "Library Information"

- High-Throughput Semiquantitative Screening of Ambient Air Samples by ORS-ICP-MS and Integrated Sample Introduction System (ISIS), 5989-6123EN

Front page photo: Agilent ICP-MS staff: Masa Endo, Product Support, Tokyo Analytical Division and Glenn Carey (standing), Product Support Engineer, Europe