

Spectroscopy

Solutions for Materials Analysis

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

The Great Salt Lake in Utah is one of the Western Hemisphere's most important migratory bird habitats. Recent concerns over increasing levels of anthropogenic pollutants including selenium have led to the formation of a multiagency task force to determine the levels of selenium and provide recommendations for its monitoring and control. The Utah Division of Water Quality recently conducted a round-robin study of selenium in ambient and spiked Great Salt Lake waters to determine the most practical analytical technique. Results showed that, of the techniques applied, only hydride generation atomic absorption and octopole reaction system ICP-MS were able to provide acceptable results. Octopole reaction system ICP-MS has the added advantage of being able to measure other elements at the same time.

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The Great Salt Lake in Utah is one of the Western Hemisphere's most important migratory bird habitats. As such, the water quality of the lake and its tributaries can have far-reaching consequences. However, while there are currently narrative standards for anthropogenic pollutants applied to the Great Salt Lake, actual numeric standards for metals have not yet been developed by the Utah Division of Water Quality. To this end, a recent cooperative effort (GSL Water Quality Steering Committee [1]) including The Nature Conservancy, the Great Salt Lake Alliance, Friends of Great Salt Lake, the State Division of Water Quality, the Jordan Valley Water Conservancy District, and Kennecott Utah Copper is working to recommend numeric water quality standards for some metals in the open waters of the lake (2).

Beginning with selenium, a nationally selected panel of scientific experts will analyze existing data and recommend additional research to determine how much selenium is entering the lake due to human activities, and how it is affecting the Great Salt Lake's bird population. The 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 EPA 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), less sensitive elemental analysis techniques such as inductively coupled plasma-optical emission spectroscopy

Table I: Chemical composition of Great Salt Lake, Dead Sea, and Ocean from Utah Geological Survey*

Source	Sodium	Potassium	Magnesium	Calcium	Chloride	Sulfate
Great Salt Lake	32.8	2.0	3.3	0.2	54.5	7.2
Ocean (typical)	30.8	1.1	3.7	1.2	55.5	7.7
Dead Sea	12.3	2.3	12.8	5.3	67.2	0.1

* Although the composition of Great Salt Lake water is similar to seawater, the total salt concentration (TDS) can vary significantly, up to 28% by weight. All measurements are dry weight percents.

(ICP-OES) or flame atomic absorption (FAA) were not considered. More sensitive techniques such as hydride generation atomic absorption (HGAA), graphite furnace atomic absorption (GFAA) or ICP-mass spectrometry (ICP-MS) were used. However, the extreme salinity of the Great Salt Lake has rendered these techniques problematic in the past. Great Salt Lake total dissolved solids range from ~9% to ~28%, depending upon season and location (Table I). Furthermore, Great Salt Lake water is alkaline, pH ~8.6 on average. At these extreme total dissolved solids values, the Se signal is enhanced greatly using both graphite furnace AA and conventional ICP-MS. Recent analytical results for Se have ranged from about 1 µg/L using hydride AA to about 120 µg/L using graphite furnace AA. Bromide, chloride, and sulfates are the primary sources of these interferences (3). Additionally, the argon dimers ($^{40}\text{Ar}^{40}\text{Ar}^+$, $^{40}\text{Ar}^{38}\text{Ar}^+$) can exaggerate the ICP-MS signal when ^{80}Se or ^{78}Se is used as the measured isotope (4). Another complicating factor is that the Great Salt Lake is intensely stratified with a sharp chemocline occurring at approximately mid-depth (5 m). The water column at and below this chemocline (the deep brine layer) is anaerobic and presents a highly reducing environment that can cause sample preservation, storage, and preparation difficulties.

Round-Robin Study

As a result of these challenges, 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 Great Salt Lake waters using multiple techniques. The goal of the study was to determine the most practical analytical method for use

in continuing studies. In addition to GFAA and HGAA, ICP-MS was selected for inclusion in the round robin primarily because of its reputation for high sensitivity and potential for rapid multi-element analysis without complicated sample preparation procedures. However, ICP-MS also has the reputation for low tolerance to samples containing high dissolved solids that could require unacceptably high dilution factors. It is also known that conventional ICP-MS analysis of selenium can suffer severe interferences in samples containing chlorine or bromine, both of which occur in high concentrations in the Great Salt Lake. For these reasons, conventional (non-cell) ICP-MS was not considered optimal for this application. However, collision/reaction cell ICP-MS, known to be effective at reducing polyatomic interferences in many sample types, was considered a possibility. Both conventional ICP-MS and passive and dynamic collision/reaction cell instruments were evaluated and the results compared with those obtained using GFAA and HGAA from multiple laboratories.

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 using a peristaltic pump. Sample water was passed through a 0.45-µm membrane filter and stored in 10-gal carboys. These samples were then acidified with nitric acid to pH < 1 and transported to Environmental Resource Associates (Aurora, Colorado) for preparation of replicates and spiking. In addition to native Great Salt Lake water, triplicate spikes were prepared according to Table II. Sample identification numbers were applied randomly to all sample replicates and distributed “blind” to participating laboratories.

Table IIa: Identification of replicates and spiking levels—1 m depth

Replicate Blind Sample #s	Spike Level into Great Salt Lake water (µg/L) 1 m depth
26, 52, 57	0
1, 58, 91	0.53
33, 44, 95	3.00
55, 62, 76	17.0
10, 74, 75	67.0

Table IIb: Identification of replicates and spiking levels—7 m depth

Replicate Blind Sample #s	Spike Level into Great Salt Lake Water (µg/L) 7 m depth
20, 37, 69	0
22, 31, 67	0.76
17, 32, 82	2.00
6, 42, 46	16.0
9, 23, 72	85.0

A total of 36 samples were submitted to each of seven participating laboratories for analysis. Because the samples were submitted blindly, the analyst did not know which samples were replicates and which were spikes. Each participating 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-collision cell) ICP-MS (EPA 200.8) (Agilent 7500a, Agilent Technologies, Palo Alto, California), dynamic reaction cell (DRC) ICP-MS (EPA-200.8 modified) (PerkinElmer Elan DRC II, PerkinElmer, Shelton, Connecticut), 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 seven participating laboratories are presented in Table III. 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 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 interferent 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.

Table III: Summary results of round-robin study

Participant	Technique	Sample Depth	% Recovery	Std Dev/Mean [CV]
Lab 1	ORS ICP-MS	Average	95%	19.4%
		1 m	95%	18.6%
		7 m	95%	20.1%
Lab 2	Hydride AA	Average	91%	7.9%
		1 m	105%	1.5%
		7 m	77%	12.7%
Lab 3	Hydride AA	Average	87%	5.9%
		1 m	95%	4.4%
		7 m	79%	7.5%
Lab 4	Hydride AA	Average	82%	5.9%
		1 m	94%	5.5%
		7 m	69%	6.2%
Lab 2	Conventional (non-cell) ICP-MS	Average	2950%	29.4%
		1 m	481%	24.2%
		7 m	5420%	33.8%
Lab 5	DRC-ICP-MS measuring <i>m/z</i> 94	Average	558%	26.3%
		1 m	478%	26.8%
		7 m	637%	25.9%
Lab 5	DRC-ICP-MS measuring <i>m/z</i> 96	Average	781%	32.0%
		1 m	631%	43.8%
		7 m	931%	18.3%
Lab 5	GFAA	Average	8210%	15.1%
		1 m	7110%	18.0%
		7 m	9320%	12.1%
Lab 6	DRC-ICP-MS	Average	250%	330%
		1 m	191%	281%
		7 m	320%	388%
Lab 7	Hydride AA	Average	82.1%	12.2%
		1 m	103%	14.9%
		7 m	54.3%	8.5

Table IV: Isotopic distribution of selenium and common interferences at each isotope by ICP-MS

Mass	74	76	77	78	80	82
% Relative abundance	0.89	9.36	7.63	23.78	49.61	8.7
Interference	Ge	⁴⁰ Ar ³⁶ Ar ³⁸ Ar ³⁸ Ar	⁴⁰ Ar ³⁷ Cl	⁴⁰ Ar ³⁸ Ar	⁴⁰ Ar ⁴⁰ Ar, ⁷⁹ BrH	⁸¹ BrH, ⁸² Kr

Octopole Reaction Cell ICP-MS Analysis of Great Salt Lake Waters

In addition to the known limitations to the analysis of Se by ICP-MS in highly saline waters that were outlined previously, other challenges to accurate selenium measurement by ICP-MS include:

- Selenium occurs in several isotopic forms — reducing the response of any one individual isotope (Table IV).

- Selenium has a high ionization potential, making it difficult to ionize in argon plasma, particularly in the presence of easily ionized elements like sodium.

- There are many common polyatomic interferences affecting all selenium isotopes (Table IV). These limitations are exacerbated in highly saline samples such as Great Salt

Table VI: Analytical sequence including calibrations, blanks, samples, and continuing calibration verification (CCV) standards. In all, 65 analyses were performed in the sequence, including four sets of CCVs and blanks

Sample Type	File Name	Description	Level/Dilution
CalBlk	009CALB	Matrix Blank	Level 1
CalStd	010CALS	Matrix 10 ppt	Level 2
CalStd	011CALS	Matrix 50 ppt	Level 3
CalStd	012CALS	Matrix 100 ppt	Level 4
Sample	013SMPL	Matrix Blank	1
Sample	014SMPL	Matrix Blank	1
Sample	015SMPL	Salt Lake 1	50
Sample	016SMPL	Salt Lake 6	50
Sample	017SMPL	Salt Lake 9	50
Sample	018SMPL	Salt Lake 10	50
Sample	019SMPL	Salt Lake 15	50
Sample	020SMPL	Salt Lake 17	50
Sample	021SMPL	Salt Lake 20	50
Sample	022SMPL	Salt Lake 22	50
Sample	023SMPL	Salt Lake 23	50
Sample	024SMPL	Salt Lake 26	50
Sample	025SMPL	Salt Lake 26 + 0.05 ppb spike	50
CCV	026SMPL	50 ppt CCV	1
CCB	027SMPL	Blank	1
Sample	028SMPL	Salt Lake 31	50
Sample	029SMPL	Salt Lake 32	50
Sample	030SMPL	Salt Lake 33	50
Sample	031SMPL	Salt Lake 37	50
Sample	032SMPL	Salt Lake 42	50
Sample	033SMPL	Salt Lake 44	50
Sample	034SMPL	Salt Lake 46	50
Sample	035SMPL	Salt Lake 47	50
Sample	036SMPL	Salt Lake 51	50
Sample	037SMPL	Salt Lake 52	50
Sample	038SMPL	Salt Lake 52 + 0.05 ppb spike	50
CCV	039SMPL	50 ppt CCV	1
CCB	040SMPL	Blank	1
Sample	041SMPL	Salt Lake 55	50
Etc...			

Table V: ICP-MS parameters used

ICP-MS Parameter	Value
Forward power	1550 W
Nebulizer flow	400 μ L/min
Carrier gas flow	1.2 L/min
Sample depth	8 mm
Hydrogen flow (ORS)	4 mL/min
Energy discrimination voltage (ORS)	2 V
Masses acquired	72, 74 (Ge- ISTD), 78 (selenium)
Integration time per mass	72, 74 – 0.5 s, 78 – 5 s
Replicate integrations	

Lake water because the major components are easily ionizable cations, Na and K, plus Cl and some Br. Easily ionized elements suppress the ionization of high ionization potential elements such as Se by preferentially ionizing in the plasma. Chlorine forms ArCl^+ in the plasma, directly overlapping ^{77}Se , the most commonly measured isotope. Bromine forms BrH^+ , which interferes with ^{80}Se and ^{82}Se , and finally Ar_2^+ produced in the plasma overlaps ^{76}Se , ^{78}Se , and ^{80}Se . Although it is possible to compensate for some of these interferences through the use of mathematical correction equations, it is not possible to correct for the interferences at isotopes 76, 78, 80, and 82. This leaves only 77 as a useful isotope, and the high and variable chloride concentration of Great Salt Lake samples makes this unreliable. As a result, collision/reaction cell ICP-MS was considered.

Collision/Reaction Cell ICP-MS

Collision/reaction cell ICP-MS is a technique that uses ion-molecule chemistry to eliminate polyatomic interferences from the mass spectrum of an ICP-MS. The mechanisms are varied and are described elsewhere (5), but the technique has enabled ICP-MS to become virtually free of polyatomic interferences. One type of collision/reaction cell uses an octopole ion guide within a small collision cell, called an octopole reaction system (ORS, Agilent Technologies) to achieve the desired reduction in polyatomic interferences. In this work, the instrument was operated with the ORS in reaction mode using pure H_2 cell gas,

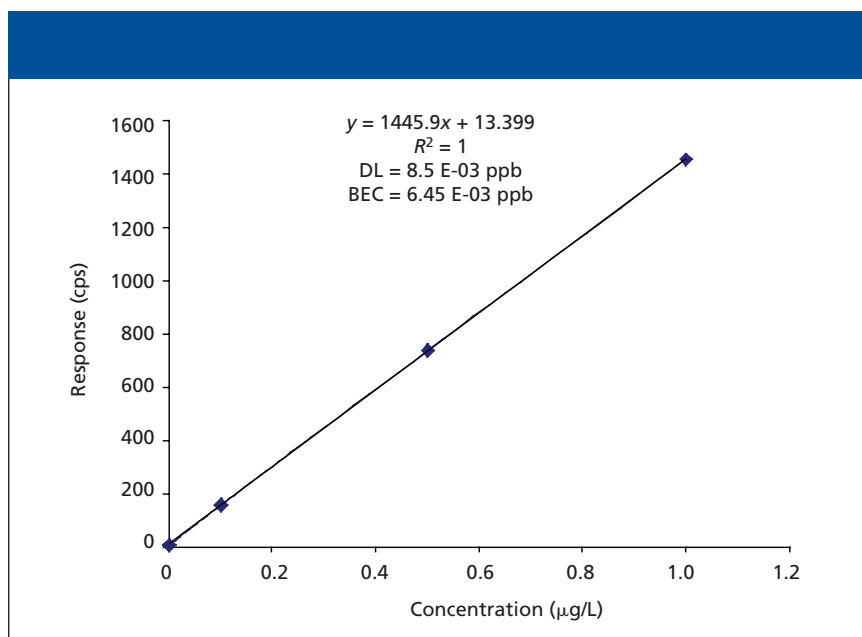


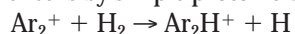
Figure 1: Se calibration at 0.1, 0.5, and 1 μ g/L using mass 78. BEC = 6.5 ng/L, DL = 8.5 ng/L.

Table VII: Detailed results of ORS ICP-MS (Lab 1) analysis of 1- and 7-m samples*

Spike Amt ($\mu\text{g/L}$)	Mean ($n=3$)	%RSD	% Recovery
Depth = 1 m			
0	0.5	22	
0.5	0.9	2.2	74.8
3.0	2.6	0.6	69.1
17	16.7	3.1	94.9
67	69.9	5.7	103
Depth = 7 m			
0	1.0	15	
0.8	1.2	12	28.1
2.0	1.6	24	17.5
16	8.9	9.8	45.9
85	61.5	41	61.9

* Samples were run in random order, and the identities were not known to the analysts at the time of analysis.

which effectively eliminates plasma-based spectral interferences (including Ar_2^+) from the mass spectrum. The result is that the two most abundant isotopes of selenium, 78 and 80, are made available for interference-free analysis. As shown in the following equation, the mechanism of removal of the Ar_2^+ interference is by simple proton transfer:



Se reacts very slowly with H_2 , but the Ar_2^+ interference is rapidly moved one mass higher (Ar_2H^+) and away from Se. In addition, because hydrogen is the lightest cell gas, loss of analyte signal due to scattering in the reaction cell is minimized. Because the Ar_2^+ interference is independent of the sample matrix (it is a product of the argon in the plasma only), interference removal is independent of the sample composition or concentration. This is important because the salt concentration of Great Salt Lake waters can vary considerably. However, if Br is present, it can form BrH^+ in the plasma and in the reaction cell as a result of reaction with H_2 . $^{79}\text{BrH}^+$ would interfere with ^{80}Se . Therefore, in this work, ^{78}Se , the second most abundant Se isotope, was chosen for analysis.

ORS ICP-MS Optimization

The ICP-MS system mentioned earlier was operated in hydrogen mode in order to effectively remove argon-based poly-

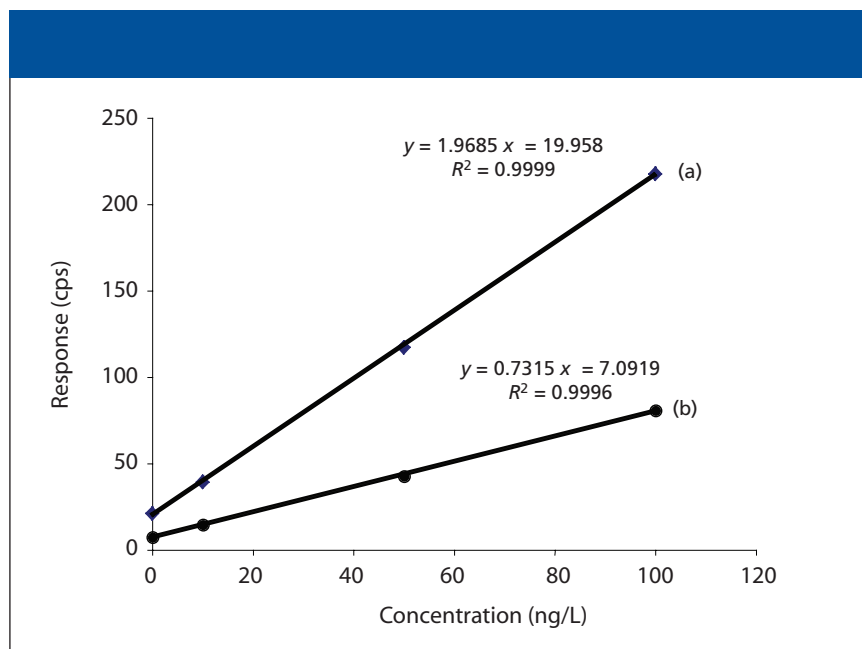


Figure 2: Effects of methanol addition on selenium response: (a) 1% methanol added and (b) no methanol added.

atomic interferences on ^{78}Se . ICP-MS parameters are presented in Table V. Optimization of cell parameters to reduce Se background at mass 78 involves setting generic conditions including 2 V of energy discrimination and 4 mL/min of hydrogen flow. These conditions work equally well for any argon-based polyatomic and generally are used without further optimization.

Determining Sensitivity

The typical response for ^{78}Se on the ORS ICP-MS system in H_2 reaction mode is $\sim 1500 \text{ cps}/\mu\text{g L}^{-1}$. 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).

Dilution and Sample Preparation for ORS ICP-MS Analysis

Preserved Great Salt Lake samples were diluted 50-fold (200 μL into 10 mL) with a diluent containing 0.1% nitric acid and 1% methanol. This reduced the total dissolved solids from $\sim 25\%$ to $\sim 0.5\%$. At this dilution factor, a 10-ppt detection limit is required to achieve the desired detection limit of 0.5 $\mu\text{g/L}$ in the undiluted samples. Standards were matrix matched to samples (0.5% sodium chloride) to compensate for ionization suppression effects, and

5 $\mu\text{g/L}$ germanium was added as an internal standard. Methanol (1%) was added to all standards, samples, and blanks because it is known to enhance the sensitivity for selenium (7). Figure 2 shows the effects of methanol addition to matrix-matched standards. The lower calibration (Figure 2b) was performed without methanol addition; the upper calibration (Figure 2a) with addition of 1% methanol. The response using methanol is approximately three times higher, resulting in improved counting statistics at very low concentrations.

The samples were then loaded into the autosampler as part of the sequence shown in Table VI, which also included initial calibration standards and blanks and periodic continuing calibration verification (CCV) standards.

Results and Discussion

Results for both the 1-m and 7-m samples as analyzed using the ORS ICP-MS system are presented in Table VII. In general, the data for the 1-m samples are much better in terms of both recovery and precision than that at 7 m. This is attributed to the difference in redox potential between the two sampling depths (that is, the 7-m depth is persistently anoxic). Several factors might be involved. For example, spiking solutions were added as elemental selenium dis-

solved in 1% nitric acid. It is possible that this Se underwent reduction and precipitation. It is also possible that organic volatile forms of Se could be formed (such as dimethyl selenide) and lost from solution. Further investigation into sample collection, preservation, and preparation is expected to resolve this problem.

As an indicator of both the degree of ionization suppression in the samples compared to the standards and blanks and of the long-term stability of the analysis, internal standard response was monitored over the course of the sequence (Figure 3). If instrument performance had changed as a result of salt buildup in the interface cones or ion optics, it would be apparent from the internal standard recoveries. No net change in instrument response was evident. A single analysis showed significant reduction in internal standard response but did not cause an outlier in analyte response. The cause of this anomaly is unknown. In addition to raw sensitivity (response), calibration accuracy also was monitored periodically by checking 50-ppt CCV samples and blanks after every 10 sample runs. The results are shown in Table VIII.

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,

Table VIII: Periodic calibration stability check samples (CCV and CCB)**

File	Sample	⁷⁸ Se Measured (ppt)	% Recovery
026smpl.D	50 ppt CCV	50.0	100
027smpl.D	Blank	0.0	
039smpl.D	50 ppt CCV	51.0	102
040smpl.D	Blank	-.20	
052smpl.D	50 ppt CCV	67.0*	134
053smpl.D	Blank	3.0	
063smpl.D	50 ppt CCV	53.0	106
064smpl.D	Blank	0.0	

* This CCV was run immediately after a high sample.
 ** Recovery of 50 ppt calibration check standards and blanks analyzed after every 10 samples. The file names are indicative of the run position in the sequence. CCVs were run as run 26, 39, 52, and 63. With the exception of run 52, where the recovery was 134% because of carryover from a previous sample high in Se, all recoveries were near 100%.

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. Because there are no suitable certified reference materials available (appropriate concentrations in a similar matrix), accuracy was determined from spike recoveries. ORS ICP-MS provides the added benefits of simple sample preparation, high sample throughput, and capability for simultaneous multielement analysis. As such, we (Utah Division of Water Quality) have recommended that EPA begin the process of certifying ORS ICP-MS as an available method for selenium analysis in hypersaline samples such as the Great Salt Lake.

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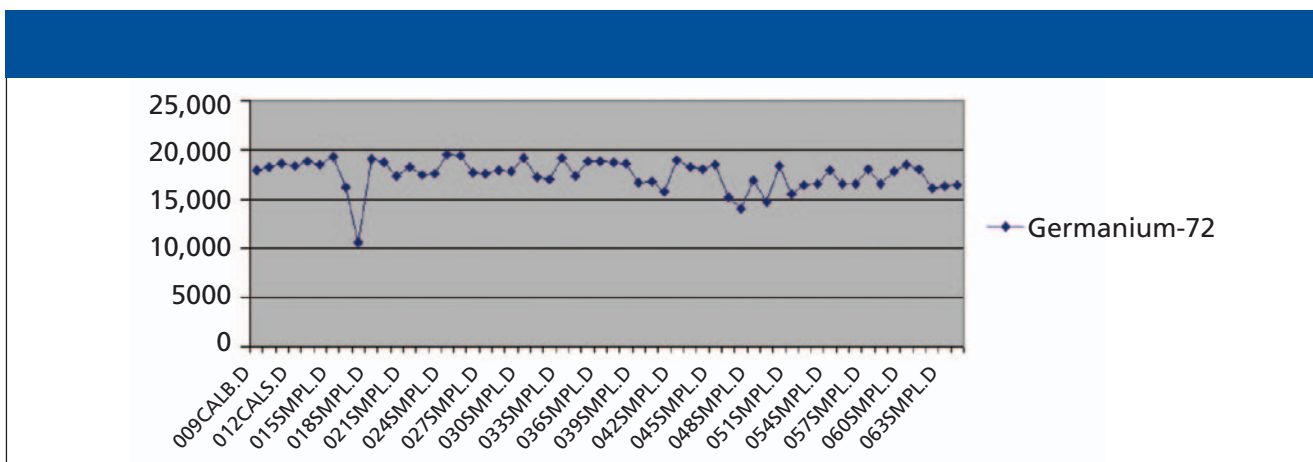


Figure 3: Internal standard (germanium) response over the course of the analytical sequence including both 1- and 7-m samples.