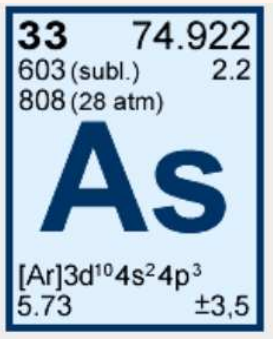
Applied Speciation and Consulting, LLC

Trace Arsenic and Selenium Analysis

The movement of "zero tolerance" arsenic and selenium associated with drinking water, wastewater, soil, and groundwater regulatory limits necessitates the demand for absolute results. Most analytical techniques applied for arsenic and selenium analysis retain inherent interferences which can often bias results, especially at lower concentrations. Therefore, Applied Speciation and Consulting employ state-of-the-art methods and instrumentation to surpass current and prospective demands for trace arsenic and selenium quantification.



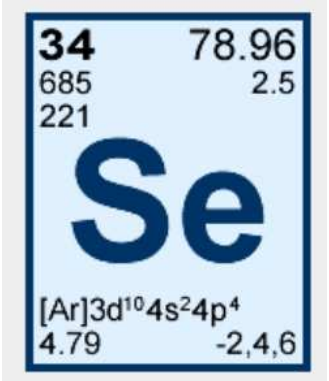
In the recent years, inductively coupled plasma mass spectrometry (ICP-MS) became one of the most common detectors for the determination of trace metals in environmental samples. While ICP-MS can be used to determine most analytes of environmental concern at ppt levels, conventional ICP-MS instruments can suffer from various issues making trace analysis of arsenic and selenium very difficult.

Issues with As and Se Analysis by Conventional ICP-MS

Fist of all, both arsenic and selenium have much higher first ionizaztion potentials compared to most elements. This means that they are not ionized as efficiently as other elements in the plasma resulting in very low sensitivity for these two elements. Secondly, various polyatomic species can be formed in the plasma as a result of gas phase reaction between matrix components and the plasma gas, argon. Unfortunately, some of these polyatomic species are isobaric with arsenic and selenium isotopes. For instance, chlorine in the samples can form $^{40}Ar^{35}Cl^+$ and/or $^{40}Ca^{35}Cl^+$ in the plasma causing false positives for monoisotopic arsenic (m/z=75). For selenium, this type of spectral interference is more severe since the most abundant isotope of selenium (^{80}Se) is isobaric with the argon dimer ($^{40}Ar^{40}Ar^+$). Table 1. lists the typical interferences encountered for arsenic and selenium analysis. The mosty common way to get around these spectral intreferences is using correction equations. These equations are used to remove the contribution of the interferences by correlating the signal from a secondary m/z to the signal at the target m/z. For instance, $^{40}Ar^{35}Cl^+$ interference can be removed by subtracting the signal at $^{40}Ar^{37}Cl^+$ (m/z 77) from m/z 75. Unfortunately, these correction equations can complicate the analysis more than expected since $^{40}Ar^{37}Cl^+$ (m/z 77) is also isobaric with ^{77}Se. This means that the correction equation should also include ^{82}Se so that the contribution of selenium to m/z 77 is subtracted. Here is how the final equation looks like:

$$^{75}As = 75cps - 3.12 \times (77cps - (0.874 \times 82cps))$$

Where cps is the signal intensity (counts per second) for the respective masses, 3.12 is the isotopic ratio of ^{35}Cl to ^{37}Cl and 0.874 is the ratio of ^{77}Se to ^{82}Se.



This equation can still produce biased results since samples that contain bromine may produce falsely high signal at mass 82 as a result of formation of $^{81}Br^1H^+$. In addition, even though the equation may seem quite straightforward, propagation of error increases the variability of the arsenic results. This effect is more pronounced for samples with low arsenic and elevated chloride concentrations.

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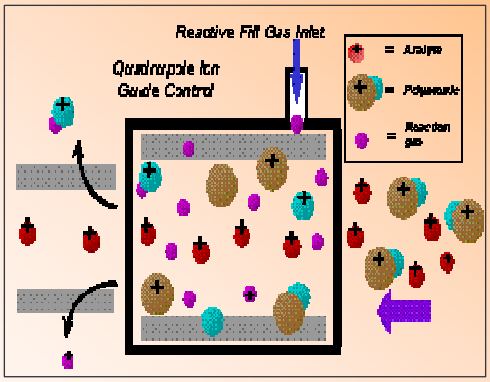
Table 1. Various analytes and common interferences that affect them.

Analyte	Interferences	Sources
Arsenic (^{75}As)	$^{40}Ar^{35}Cl^+$, $^{40}Ca^{35}Cl^+$	Chlorine, Calcium
Selenium (^{78}Se)	$^{40}Ar^{38}Ar^+$, $^{38}Ar^{40}Ca^+$	Argon (plasma gas), Calcium
Selenium (^{80}Se)	$^{40}Ar^{40}Ar^+$, $^{32}S^{16}O_3^+$, $^{40}Ar^{40}Ca^+$, $^{81}Br^1H^+$	Argon (plasma gas), Sulfur, Calcium, Bromine
Selenium (^{82}Se)	$^{81}Br^1H^+$, $^{34}S^{16}O_3^+$	Bromine, Sulfur

Trace As and Se Analysis with the Dynamic Reaction Cell Technology

Inductively coupled plasma dynamic reaction cell mass spectrometry (ICP-DRC-MS) is the identical platform as ICP-MS with the addition of a reaction gas chamber placed in the path of the ion beam (after the ionization process) and an additional quadrupole. The DRC employs specific reactive gasses to preferentially react with the target interferences or elements to produce a secondary mass to charge ratio or displaces the charge from the atom or molecule (reducing the mass to charge ratio to zero).



For arsenic analysis, oxygen is typically used as the reaction gas to generate $^{75}As^{16}O^+$ (91m/z) which separates it from the $^{40}Ar^{35}Cl^+$ interference. As a result, determination of trace levels of arsenic becomes a reality even in extremely saline solutions. For the determination of selenium, the reaction gas of choice is methane. The reaction between methane and the common interferences on Se such as $^{40}Ar^{40}Ar^+$ and $^{79}Br^1H^+$ is extremely efficient without loss of analyte signal. As a result, quantification of selenium using its most abundant isotope (^{80}Se) becomes possible.

By utilizing the DRC technology with the methods developed at ASC, detection limits in the range of 10 ng/L (ppt) for As and Se can be achieved with negligible bias.

Comparison between HG-AAS/AFS and ICP-DRC-MS

Hydride generation atomic absorption spectrometry and atomic fluorescence spectrometry (HG-AAS and HG-AFS, respectively) facilitates the reaction of sodium borohydride with reduced arsenic and selenium species (arsenite and selenite) to produce volatile hydrides which are purged from solution and detected spectrophotometrically. While these methods can produce very low detection limits (20 ng/L), they are prone to severe matrix interferences. The major issue with hydride generation methods is that they are operationally limited to the quantification of arsenite and selenite in solution; requiring pretreatment to convert all arsenic and selenium species to arsenite and selenite before analysis. Due to this inherent limitation, these methods can only provide "total reducible" arsenic and selenium and not "total" results that ICP-MS can provide. In addition, the complexity of the sample matrix can alter the efficiency of the reduction procedure or the hydride generation reaction. The interferences from transition metals, dissolved organic carbon, and salinity are very well documented and allow for significant biases associated with complex matrices, especially at trace levels. Finally, the tedious sample preparation protocols necessitate commercial laboratories to charge significantly more for this analysis compared to ICP-DRC-MS analysis.

Conclusion

ICP-DRC-MS provides interference elimination and robustness for true total arsenic and selenium analysis in any matrix. Feel free to contact us at info@appliedspeciation.com or (206) 219-3779 for a quotation or more information regarding how we can save you time and money associated with your next project.

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