



Applied Speciation and Consulting, LLC

Hydride Generation vs. IC-ICP-MS for Selenium Speciation Analysis A side-by-side comparison

The dissemination of information regarding the toxicity associated with different selenium species has significantly increased the demand for selenium speciation analysis. Historically, scientists and industrial experts have relied heavily on older methodologies (hydride generation) which retained considerable interferences and limitations. This brochure is intended to present the facts associated with two different analytical methods for selenium speciation currently applied to real world samples.

	HG-AAS/AFS	IC-ICP-MS
1)	Each species is “identified” by the hope/belief that the underlying chemistry works for each Se species in every matrix	One distinct signal for each species in every matrix
2)	Quantification by difference increases uncertainty due to propagation of error	Excellent accuracy for all species
3)	Requires several labor intensive chemical treatments	No additional reagents and no sample prep since it is a direct injection method
4)	Multiple successive measurements (Se(IV) and TotSe)	One analysis for all species
5)	Unanticipated species can not be accounted for and produce false positives	Unanticipated species can be detected and reported
6)	Matrix components (transition metals, salinity, DOC, etc.) interferes with the chemistry used to convert species to the measurable form	Matrix can cause chromatographic interferences which can be identified and separated if necessary
7)	Low detection limits due to large sample sizes	Low detection limits due to better sensitivity of ICP-MS
8)	Limited linearity of the calibration (an order of magnitude)	3 - 4 orders of magnitude dynamic linear range

- 1) With HG-AAS/AFS, selenium speciation requires two separate analyses, selenite [Se(IV)] and total reducible selenium. Selenate determination is accomplished via subtraction of the selenite result from total reducible selenium. Selenium speciation via IC-ICP-MS generates discrete, quantifiable, peaks for each selenium species.
- 2) Statistics dictates the calculation associated with selenate determination via HG-AAS results in increased variability and decreased precision compared to direct quantification. The concentration of selenate is obtained by simple algebra: $[Se(VI)] = [TotSe] - [Se(IV)]$. If the concentration of one species is considerably greater than the other (~ 10X), the propagation of error significantly reduces the confidence of the results.

Example:

The total selenium concentration is 100 ppb with 2% error (+/- 2ppb), The Se(IV) concentration is 90 ppb with 2% error (+/- 1.8ppb). The calculated selenate concentration would be 10ppb +/- 3.8ppb (38% margin of error). Without direct application of the uncertainty associated with the total selenium and Se(IV) analysis to the Se(VI) results considerable biases may be overlooked.

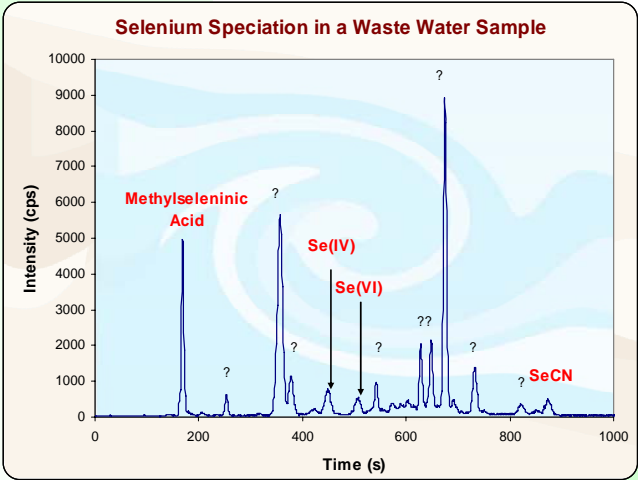
With IC-ICP-MS, on the other hand, the error for each species is not inflated by any equations so the precision and accuracy is excellent even if the concentration of one species is 1000 times the other one.

- 3) Preparation of the samples for total selenium analysis requires various chemical treatment steps to convert all selenium species to Se(IV) before analysis. As the chemistry associated with sample pretreatment increases in complexity the variability and anticipated bias associated with the final results increases proportionately. IC-ICP-MS analysis requires only filtration of the sample before injection onto the analytical column which reduces error propagation from sample preparation.

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- 4) Two different analyses are required to obtain speciation information from the HG-AAS/AFS method while a single injection of the sample provides data for each species.
- 5) This is probably the most important flaw of the HG-AAS/AFS method. If the sample contains different selenium species such as organic selenium or selenocyanate, these species may be included in the total selenium results which ultimately produces false positives for Se(VI). All unanticipated species are resolved and quantified with the IC-ICP-MS method which produces the maximum amount of information so the end user can make better educated decisions. See Figure 1.

Figure 1. Water sample from an industrial wastewater treatment plant was analyzed by IC-ICP-MS. Sum of Se(IV) and Se(VI) concentrations was less than 10% of total selenium in the sample. Unknown selenium peaks were confirmed by their isotopic abundance patterns.



- 6) Hydride generation is a chemical reaction; therefore, variations in the sample matrices could result in changes in the reaction efficiency. The interferences from transition metals, salinity, and dissolved organic carbon are all known to cause interferences, positive and negative. Application of Se(VI), rather than Se(IV), for matrix spikes associated with total selenium quantification is imperative to properly represent the efficiency of the digestion. Incorporation of Se(IV) in matrix spikes may produce good QA/QC results but it does not represent the performance of the digestion; therefore, it is a completely unacceptable practice. It is highly recommended that you inquire about the application of Se(VI) in the matrix spikes associated with any historical results for Se speciation by HG-AAS. If the laboratory did not apply Se(VI) in their matrix spikes, the validity of the data is highly questionable. In addition, if Se(VI) was used, a copy of their control charts should be requested to identify systematic problems which may not have been properly communicated with the results. You may be surprised by the variability in recoveries from different analytical batches.

Salinity and transition metals can also be a problem with the IC-ICP-MS method. High salinity samples can overload the column resulting in elution of the analytes in the dead volume. Being a multi element detector, ICP-MS allows for monitoring of common anions (Chloride, sulfate, phosphate, etc) to identify column overloading and assist in recognizing appropriate dilutions to reduce the analytical impacts of the interferences. If the sample matrix is highly oxidizing or reducing the matrix spikes may be out of specifications; however, since all species are monitored separately, the species conversion can be identified easily. In this instance, the quality control parameters can identify the equilibrium of the sample matrix and provide further insight into the nature of the sample. It should also be noted that transition metals may precipitate on the column due to the basic nature of the chromatographic eluant and result in loss of the Se(IV) peak. At Applied Speciation, we have developed a variety of methods that will suit different types of samples. This allows us to switch to a different column/eluant combination if a problem is identified.

- 7) HG-AAS/AFS can produce very low detection limits since the sample size is usually much higher than IC-ICP-MS. It is common to use 15 to 50 mL of sample for a single HG-AAS/AFS analysis to achieve ~ 10-20 ng/L detection limits compared to 0.1 mL for IC-ICP-MS with 5-10 ng/L detection limits. Still, some samples may need to be diluted before analysis to avoid problems, as previously mentioned.
- 8) In cases where the concentration of one of the analytes exceeds the calibration curve, linearity can not be assumed for HG-AAS/AFS since the dynamic linear range of these methods are very limited. ICP-MS has a dynamic linear range of 6 orders of magnitude and the calibrations with IC-ICP-MS analysis usually covers 3-4 orders of magnitude.