

## Atomic Absorption

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## Determination of As, Se and Hg in Waters by Hydride Generation/ Cold Vapor Atomic Absorption Spectroscopy

### Introduction

Contamination of industrial and municipal water supplies with arsenic (As), selenium (Se), and mercury (Hg) can occur from natural deposits, industrial discharge, runoff from mining, landfill and agricultural operations. Consumption of contaminated water can cause skin damage (As), kidney and nervous system damage (Hg) and numbness in the fingers and toes (Se).<sup>1</sup> The U.S. Environmental Protection Agency (EPA) and the Canadian Council of Ministers of the Environment (CCME) have guidelines on the concentration of As, Se and Hg for the protection of marine

and freshwater aquatic life and the protection of agriculture.<sup>1,2</sup> Due to the low levels of these guidelines for As, Se, and Hg, it is important to have analytical measurements that are precise and accurate with low amounts of noise.

Hydride generation (HG) is a very effective analytical technique developed to separate hydride forming metals, such as Se and As, from a range of matrices and varying acid concentrations. The heated quartz tube atomizer is particularly useful for the determination of arsenic and selenium because the absorption wavelengths for these elements are below 200 nm in an area subject to intense interference from flame radicals that can significantly affect detection limits. Mercury can be easily reduced in solution to generate elemental mercury, otherwise known as cold vapor (CV). This technique is also effective at separating mercury from a range of matrices. These analytical techniques can improve detection limits by a factor of approximately 3000 times that of flame detection limits and typically have less interference than graphite furnace techniques.

Separating the analyte from the matrix can improve the sensitivity of the atomic absorption technique and avoids physical, matrix and spectral interferences. The separation of the hydride from the matrix allows for high efficiency of analyte introduction into the atomic absorption spectrophotometer (AAS). The concentration effect and added sensitivity of these techniques ultimately enables laboratories to meet the lower detection limits required for environmental regulations.

## Experimental Conditions

### Instrumentation

The measurements were performed using a PerkinElmer® PinAAcle™ 900T atomic absorption spectrophotometer (Shelton, CT, USA) equipped with the intuitive WinLab32™ for AA software, which features all the tools to analyze samples, report and archive data and ensure regulatory compliance. The PinAAcle spectrometer was coupled to a FIAS 400 flow injection analysis system that incorporates two peristaltic pumps, a 5-port flow injection valve and a regulated gas supply. Default parameters found in the software were used for all three elements: As, Se, and Hg.

Using a FIAS-AAS system, a sample loop on the flow injection valve is filled with the acidified sample, blank, or standard. The valve is automatically switched to the inject position and the sample is mixed with a pumped stream of reductant, sodium borohydride for hydrides or stannous chloride for mercury to produce the gaseous vapors. At the point of reaction with the reductant, arsenic or selenium hydrides or elemental mercury vapor are produced, along with hydrogen from the sodium borohydride, resulting in a two-phase mixture: vapor with the analyte in it and the used-up reductant. A flow of argon is added to this mixture and the vapors are carried through a gas/liquid separator. This allows the gaseous phase which contains the analyte vapor to enter the quartz cell on the AAS for analysis while the remaining liquids are pumped to a waste container. Refer to Table 1 for the FIAS parameters and Figure 1 for a schematic of the FIAS system.

**Table 1. FIAS pump and valve timing.**

Step #	Time	Pump 1 (rpm)	Pump 2 (rpm)	Valve Position		Read Trigger
				Fill	Inject	
Prefill	15	100	120	X		
1	10	100	120	X		
2	15	0	120		X	X
3	1	100	120	X		

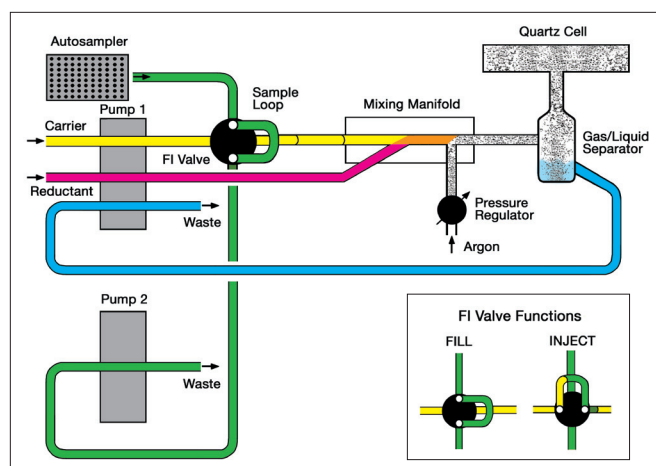


Figure 1. Schematic diagram of FIAS 400 system for automated hydride generation.

The generated hydrides were decomposed and atomized in a heated quartz cell (Part No. B0507486) placed in a heating mantle (Figure 2) with adaptor (Part No. N3160162 for PinAAcle 900T, 900H, 900F models and N3160161 for the PinAAcle 900Z model) in the place of the burner assembly. The quartz cell was heated to 900 °C for the hydrides and 100 °C for mercury vapor analysis to avoid any condensation in the cell. The quartz cell used for hydride analysis was cleaned prior to use with 30% hydrofluoric acid.



Figure 2. PerkinElmer heating mantle for the PinAAcle 900T spectrometer.

High-energy electrodeless discharge lamps (EDLs) were used for all the elements (Part Nos. As: N3050605; Se: N3050672; Hg: N3050634). EDLs typically provide higher energy than the corresponding HCLs and improve sensitivity and detection limits, especially for arsenic and selenium. The sample loop size was 500 µL for all analytes and could have been increased or decreased to improve detection limits or throughput, respectively.

The carrier gas stream has a large influence on sensitivity. The objective is to have a fast enough carrier flow to obtain a sharp peak, therefore greater sensitivity. If the flow is too high, the atom or hydride cloud is dispersed too rapidly and

could be pushed out with the waste to the drain. If the flow is too low, the hydrides will come out slowly leading to a broader peak, therefore the resulting signal and sensitivity are lower. As a result, approximate flows of 50, 80 and 100 mL/min were used for the arsenic, selenium and mercury determinations, respectively. To obtain the highest sensitivity, the carrier gas flow was slightly optimized for each element prior to calibration.

### Standards, Chemicals and Standard Reference Materials

PerkinElmer Single-Element Calibration Standards for Atomic Spectroscopy were used as the stock standards for preparing the working standards (Part Nos. As: N9300180; Se: N9300182; Hg: N9300174). Working standards were prepared by serial volume/volume (v/v) dilution in polypropylene vials (Part No. B0193234). All working standard solutions were freshly prepared the day of analysis from the stock standards.

ASTM® Type I water (from an ELGA® filtration system – ELGA LLC, Woodridge, Illinois, USA) acidified to 1% nitric acid was used to make the calibration blank and standards. Micropipettes (Eppendorf®, Germany) with disposable tips were used for pipetting solutions.

The carrier solution for As and Se determination was a 10% (v/v) hydrochloric acid (HCl) solution. The carrier solution for mercury was 3% (v/v) HCl acid. The selenium hydride generation reducing agent was an aqueous solution of 0.2% weight/volume (w/v) NaBH<sub>4</sub> in a 0.05% (w/v) NaOH solution, which should be freshly prepared each day. For As, the NaBH<sub>4</sub> concentration was increased to 0.5% in order to improve sensitivity. Mercury was determined using SnCl<sub>2</sub> as the reducing agent, the reducing solution consisted of 1.1% (w/v) SnCl<sub>2</sub> (from SnCl<sub>2</sub> • 2H<sub>2</sub>O) in 3.0% (v/v) hydrochloric acid.

Standard reference material (SRM) NIST® 1640 Trace Elements in Natural Water and SRM NIST® 1643e Trace Elements in Water were used to validate the method developed. The NIST® reference materials were not certified for mercury, therefore a second source standard from SPEX CertiPrep® (Metuchen, NJ, USA) was used for validation purposes.

### Sample and Standard Reference Material Preparation

**Arsenic** – The samples and standards for arsenic analysis were pre-reduced (As<sup>+5</sup> to As<sup>+3</sup>) prior to analysis. This was achieved by adding a reducing solution containing 5% (w/v) KI and 5% (w/v) ascorbic acid. An appropriate volume of standard or sample (up to 10 mL) was placed in a 50 mL polypropylene autosampler tube. To this, 1 mL of the reducing solution and 5 mL of concentrated HCl was added. The treated samples or standards were set to stand at room temperature for 30-60 minutes prior to analysis. The tube was brought to the 50 mL mark with deionized water and

the sample was ready to run. The final dilution factor for the SRMs was 10.

**Selenium** – The samples and standards for selenium analysis were pre-reduced (Se<sup>6+</sup> to Se<sup>4+</sup>) prior to analysis by diluting 1:1 with concentrated HCl followed by heating at 90 °C for 30 minutes. The Se solutions were prepared using the PerkinElmer SPB 50-24 Block Digestion System (Part No. N9308019) with the SBP Touch controller (Part No. N9308007). The graphite blocks are PTFE coated to resist the aggressive corrosive attack that is common when pre-reducing Se solutions for hydride analysis. Following the pre-reduction, there is no risk of back oxidation (Se<sup>4+</sup> to Se<sup>6+</sup>). Therefore, the solutions were diluted to the appropriate volume and concentration for analysis. The final dilution factor for the SRMs was 10.

**Mercury** – No sample preparation was used for mercury analysis.

## Results and Discussion

### System Performance

The system performed to the specifications as described in *Recommended Conditions and General Information for Flow Injection Mercury/Hydride Analysis using the PerkinElmer FIAS 100/400* technical note and in the WinLab32™ for AA software recommended conditions.

The sensitivity and detection limits of the system were established for each element and the information is presented in Tables 2 and 3 (Page 4), respectively. The method detection limits (MDLs) were determined from 10 analyses (3 replicates each) of the blank solution that was taken through the preparation procedures described above (Table 3, Figure 3 – Page 4).

**Table 2. System sensitivity.**

Analyte	Concentration (µg/L)	Peak Height (Abs)
As	10	0.44
Se	10	0.18
Hg	10	0.10

The method detection limits obtained were sufficient to meet the U.S. EPA maximum contaminant levels (MCLs) for drinking water.<sup>1</sup> Arsenic and selenium detection limits were sufficient to meet the lowest Canadian CCME limit.

The mercury MDL obtained was sufficient for the analysis of soils as per Canadian regulations.<sup>2</sup> However, either FIMS (flow injection mercury system) or a larger sample loop is recommended for meeting the CCME mercury guideline for the protection of marine life.

**Table 3. System detection limits with U.S. EPA and CCME limits.**

Analyte	MDL (µg/L)	U.S. EPA MCL (µg/L)	Lowest CCME Limits (µg/L)
As	0.020	10	5
Se	0.027	50	1
Hg	0.035	2	0.016

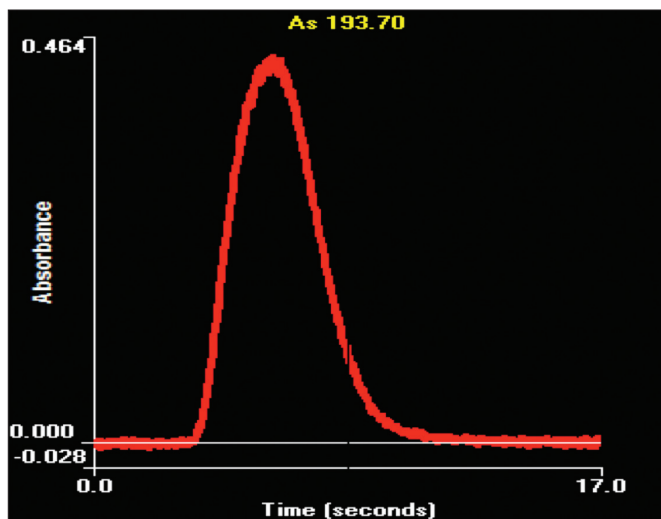


Figure 3. Three replicates of 10 µg/L As.

## Water Samples

The two NIST® SRMs and the second source standard of mercury were used to establish the accuracy and precision of the methods. The accuracy and precision determined for the validation samples for all elements was very good (Table 4). The SRM samples were diluted 10x prior to analysis.

**Table 4. NIST® SRM hydride results and mercury second source solution results.**

Reference Material	Analyte	Target (µg/L)	Average Found (µg/L)	% Recovery	N	Std Dev
NIST® 1640	As	26.71	27.76	104%	9	0.75
NIST® 1640	Se	21.99	23.61	107%	11	0.19
NIST® 1643e	As	60.45	61.30	101%	9	0.67
NIST® 1643e	Se	11.97	12.38	103%	11	0.22
Second Source	Hg	1.00	1.024	102%	10	0.007

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## Conclusions

An accurate and reliable sample pretreatment and analysis procedure for the determination of arsenic, selenium and mercury in waters using FIAS-AAS is described. Hydride generation is widely used in the determination of low levels of elements whose salts readily form hydrides with sodium borohydride. The advantage of hydride generation is that it provides a concentration step and the analyte is transported to the atomizer much more efficiently compared to that of solution nebulization systems. This enhanced transportation efficiency, combined with the heated quartz tube atomizer, results in a large increase in sensitivity over flame (as well as furnace) atomization and is valuable for very low-level determinations.

The results presented here demonstrate that the PinAAcle 900T spectrometer coupled with a FIAS 400 flow injection system can provide accurate and precise data for the analysis of arsenic, selenium and mercury in waters. The unique design of the PinAAcle 900T system allows for simple installation and optimization of the quartz cell heating mantle. This permits the user to easily switch between flame, furnace and mercury/hydride techniques. This application can be used on all of the PinAAcle spectrometer models with the appropriate adaptor kit.

## References

1. U.S. EPA: <http://water.epa.gov/drink/contaminants/#List>
2. CCME: <http://st-ts.ccme.ca/?chems=9,132,197&chapters=1,2,3,4>