

AAS

APPLICATION NOTES

The determination of arsenic, selenium and mercury levels in U.S. EPA quality control samples using the GBC HG3000 continuous-flow hydride generator

AAS



Introduction

Vapour generation has now been used successfully for atomic absorption analysis of Hg and the hydride-forming elements (As, Bi, Pb, Sb, Se, Sn, Ge and Te) for a number of years. The success of this technique stems largely from two features:

- it effectively separates the analyte element from its chemical matrix, eliminating matrix interference effects in the atomisation process and minimising background absorption; and
- it provides a far more efficient means of atomisation for these elements than conventional flame methods.

Recently, the growing demand for increased sample throughput has prompted the development of continuous-flow hydride vapour generation systems to replace the more tedious and time consuming batch methods.

This report describes the application of the GBC HG3000 continuous-flow automatic hydride generator to the analysis of United States Environmental Protection Agency (U.S. EPA) Water Supply Quality Control Samples for the environmentally significant elements arsenic, selenium and mercury.

Experimental

Instrumentation

The analyses were performed using a GBC automatic multi-element atomic absorption spectrophotometer in conjunction with the GBC HG3000 hydride generator. The GBC AAS operating software provides the facilities for data collection and storage as well as the storage of all associated signal graphics. A GBC autosampler accessory was used to perform automated analyses.

Since arsenic and selenium Super Lamps were available they were used for determining these analytes. The narrower line width and greater brightness of Super Lamps compared to standard hollow cathode lamps results in lower baseline noise and increased sensitivity.¹

Reagent preparation

Analytical-reagent grade chemicals were used throughout.

De-ionized water

Type 1 ultra-pure water was obtained using a reverse osmosis, mixed bed de-ionizing unit.

Sodium borohydride solution

0.6% w/v, prepared by dissolving 3.0 g of NaBH₄ powder together with 3.0 g of NaOH pellets in de-ionized water. The solution was made up to 500 mL and filtered into the HG3000's sodium borohydride reagent bottle.

NOTE:

This solution is unstable and slowly decomposes during storage. Reagent solutions more than 3 to 4 days old should not be used.

Acid solution

The HG3000's acid reagent bottle was filled with 500 mL of concentrated (approximately 36%) HCl.

Working standards

Three composite working standards containing the three analytes (Table 1) were prepared from commercial 1000 µg/mL stock solutions by dilution in 1M HCl and 0.1% HNO₃.

Standard	As*	Se	Hg
1	5	3	1
2	10	6	2
3	15	9	3

* 0.1% w/v KI was added to standards prior to As analysis.

Table 1: Analyte concentration (µg/L) for working standards

U.S. EPA quality control sample preparation

Two water sample concentrates for trace metals, designated Water Supply Quality Control Sample WS378 (numbers 2 and 13), were prepared according to the instructions supplied by the U.S. EPA.² 10 mL of concentrate was pipetted into a 1 L volumetric flask containing 100 mL of concentrated HCl and 1 mL of concentrated HNO₃ then made up to volume with de-ionized water.

Sample treatment

In most cases maximum analytical sensitivity for hydride generation is obtained when the analyte is present in a particular oxidation state. It was therefore necessary to treat the water samples and standards prior to analysis to convert the analyte to the appropriate chemical form. This treatment varied for the different elements of interest as outlined below.

Mercury

Mercury must be present in ionic form for analysis, and the sensitivity is improved in acidified solution. For this work the samples and standards used for Hg analysis were acidified with concentrated HCl to give an approximately 3 molar solution.

NOTE:

Stannous chloride, often used as a reducing agent for Hg vapour analysis, is not recommended for use with the HG3000 as contamination of the system by tin can interfere strongly with the analysis of other elements.

A 10 µg/L Hg solution should give an absorbance reading of approximately 0.1.

Selenium

Maximum analytical sensitivity for selenium is obtained only for the tetra-valent oxidation state. To ensure that all Se^{VI} present was reduced to se^{IV} the samples and standards were acidified with concentrated HCl to give an approximately 7 molar solution, and warmed gently to 70°C for 30 minutes. The samples were cooled to room temperature before analysis.

A 10 µg/L Se^{IV} solution should give an absorbance reading of approximately 0.3.

Arsenic

Arsenic is normally present in both the tri- and penta-valent oxidation states. The analytical sensitivity of As^{III} is approximately twice that of As^V using the hydride technique. Before measurement, all As^V present was reduced to As^{III} by acidifying the samples with concentrated HCl to give an approximately 2 molar solution and adding 0.1% w/v KI. Approximately one hour was allowed for the reduction to proceed to completion at room temperature.

NOTE:

Since KI acts as a strong interferant during Se analyses, samples treated in this way cannot be analysed for selenium. If it is necessary to determine both As and Se concentrations from a single sample, for instance during an automated multi-element analysis, use concentrated HNO₃ to convert all As^{III} present to As^V and perform a calibration using this oxidation state.

A 10 µg/L As^{III} solution should give an absorbance reading of approximately 0.5.

Instrument settings and procedure

A printout of instrument settings for the GBC atomic absorption spectrophotometer (AAS) used for determining arsenic appears in Figure 1. A summary of specific parameters for all three analytes is given in Table 2.

	Wavelength (nm)	Spectral Bandpass (nm)	Lamp Current (mA)	Lamp Type	Flame Conditions
As	193.7	2.0	20	Super Lamp	Oxidising
Se	196.0	2.0	18	Super Lamp	Oxidising
Hg*	253.7	0.5	4	Std HC Lamp	No Flame

* Mercury analyses were performed using a closed quartz cell.

Table 2: AAS instrumental conditions for the determination of arsenic, selenium and mercury

Instrument Parameters	
System Type	Flame
Element	As
Matrix	Aqueous
Lamp Current (mA)	20.0
Wavelength (nm)	193.7
Slit Width (nm)	2.0
Slit Height	Reduced
Instrument Mode	Absorbance BC On
Sampling Mode	Auto Sampling

Gas Control Parameters	
Flame Type	Air-acetylene
Acetylene Flow	1.10
Air Flow	10.5

Flame Sampler Parameters	
Micro Sampling	No
Delay Time (s)	60
Rinse Time (s)	10
Recalibration Rate	0
Rescale Rate	0
Rescale Std No.	1
Probe Height (mm)	0

Data Collection Parameters	
Read Time (s)	3.0
Time Constant (s)	1.0
Expansion Factor	1

Figure 1: AAS operating parameters for determining arsenic by hydride vapour generation

Results

Figure 2 shows the signal graphics trace for arsenic calibration standards and samples. The arsenic calibration curve is reproduced in Figure 3. Printouts for selenium and mercury were similar to those for arsenic.

The results for the analysis are presented in Table 3 along with sample data supplied by the U.S. EPA.

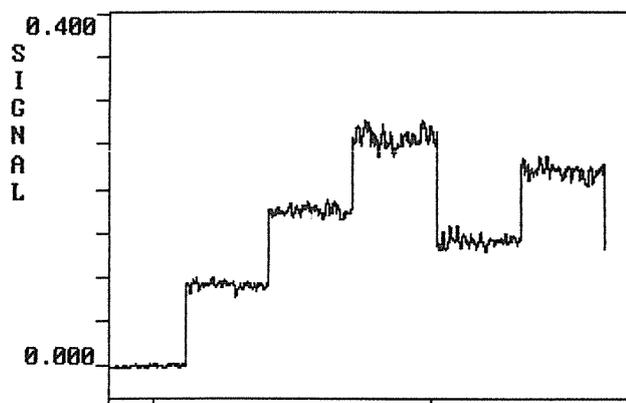


Figure 2: Signal graphics for arsenic calibration and samples (solutions diluted 1 + 2 with water)

Concentrate	Element	True Value	Measured Value	95% Confidence Limits*
2	Se	6	6.1	3.6 – 7.8
	As	27	24.2	20.4 – 32.4
	Hg	1.8	1.7	1.4 – 2.2
13	Se	7.6	7.4	4.7 – 9.7
	As	43	40.4	34.2 – 50.6
	Hg	1.4	1.3	1.0 – 1.7

* The 95% confidence limit represents the mean recovery plus or minus 2 standard deviations, and was determined from Performance Evaluation Studies carried out by the U.S. EPA.²

Table 3: Comparison of HG3000 results ("measured value") with Performance Evaluation Data (all values in µg/L)

Table 3 shows that measured results for each analyte were close to U.S. EPA true values and well within the 95% confidence limits.

Conclusion

Continuous-flow hydride generation using the GBC HG3000 and GBC AAS provides a fast and accurate means of analysing mercury, selenium and arsenic. Once optimised, the system is capable of analysing up to 360 samples per hour for several different elements with minimal operator intervention. Sensitivity and measurement precision are superior to those obtained using conventional batch methods.

NOTE:

Actual analytical detection limits are dependent on the purity of the reagents used.

References

1. An Evaluation of Performance Characteristics of Super Lamps, GBC AAS Application Note.
2. Instructions For Trace Metals Analyses, Environmental Monitoring and Support Laboratory, U.S. EPA, Cincinnati, OH, USA.
3. HG3000 Operation Manual, GBC Scientific Equipment Pty Ltd, Braeside, Victoria, Australia.

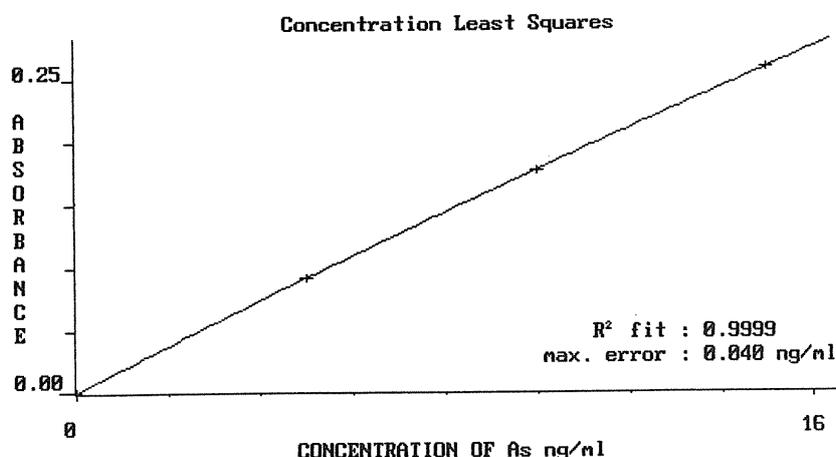


Figure 3: Calibration curve for arsenic (standards diluted 1 + 2 with water)