Application Note

A Comparison between Flame-Heating and Electrical-Heating Trace-Level Hydride Analysis

Introduction

Flame-heated absorption cells have been used for many years for analysing the hydride-forming elements. An air-acetylene flame at 2000—2300 °C has been used as a reliable heat source.[1] However, the thermal energy from a flame can only be controlled marginally by varying the fuel/oxidant mixture, so there is little scope for optimizing the cell temperature.

The GBC EHG3000 hydride cell heating controls the heating of the quartz cell over a temperature range from ambient to 1000 °C. This permits optimization of the cell temperature and allows improvements in analytical performance. In this study, detection limits and characteristic concentration values were compare for six elements using the flame-heated and electrically-heated hydride generation techniques. Arsenic and selenium were determined using the EHG3000 in USEPA certified quality control water samples supplied by Spex Industries (Edison, New Jersey, USA).

Experimental

Instrumentation

A GBC 906 automatic multi-element atomic absorption spectrophotometer, in conjunction with the GBC HG3000 continuous-flow hydride generator and the GBC EHG3000 hydride cell electrical heater was used to perform all analyses. Superlamps (Photron Pty Ltd Australia) were used for arsenic and selenium analyses, as a narrower line width and increased intensity produced lower baseline noise levels and improved sensitivity.[2]

Reagent Preparation

Chemicals used throughout were analytical reagent grade (BDH Chemicals, Australia) except for hydrochloric acid which was "Normatom" 30% w/v (Prolabo, France).

Deionized water: Type 1 ultra-pure water was produced using a reverse osmosis, mixed bed de-ionizing unit (Modulab, Reagent Grade Model Water Systems, Continental Water Systems, Australia).

Sodium borohydride solution: 0.6% w/v solution was prepared by dissolving 3.0 g of $NaBH_4$ pellets and 3.0 g of NaOH pellets in de-ionized water. The solution was made up to 500 mL and then filtered into an acid-washed 500 mL HG3000 reagent bottle using a GF/A glass micro fibre filter (Whatman International Ltd.).

> **Note:** Sodium borohydride solutions slowly decompose during storage. Solutions older than 3 to 4 days will severely degrade analytical sensitivity and should not be used.

Acid solution: The HG3000 acid reagent bottle was filled with 500 mL concentrated HCl (approximately 36% w/v).

Working standards: Three composite working standards were prepared containing two analytes (Table 1), using commercial 1000 µg/mL stock solutions. Diluents comprising 1M HCl and 0.1% HNO_3 were used.

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

* 0.1% Kl was added to standards and left for one hour prior to As analysis

Table 1: *Analyte concentrations (mg/L) for working standards.*

Quality Control Sample Preparation

Two USEPA water samples, namely Trace Metal—AA (Lot #1-1 TMAA-1) and Trace Metal—Water Supply (Lot #1-1 TMWS) supplied by Spex Industries (Edison, New Jersey, USA) were prepared according to the manufacturers instructions. 10 mL of concentrate was pipetted into a 1 litre flask containing 900 mL of de-ionized water. One mL of concentrated HNO3 was added and the flask was made up to volume with 100 mL of concentrated HCl and de-ionized water.

Sample treatment

To obtain maximum analytical sensitivity, the analytes need to be in a particular oxidation state for hydride analysis. It was therefore necessary to treat the samples prior to the analysis to convert the analytes into an appropriate chemical form.

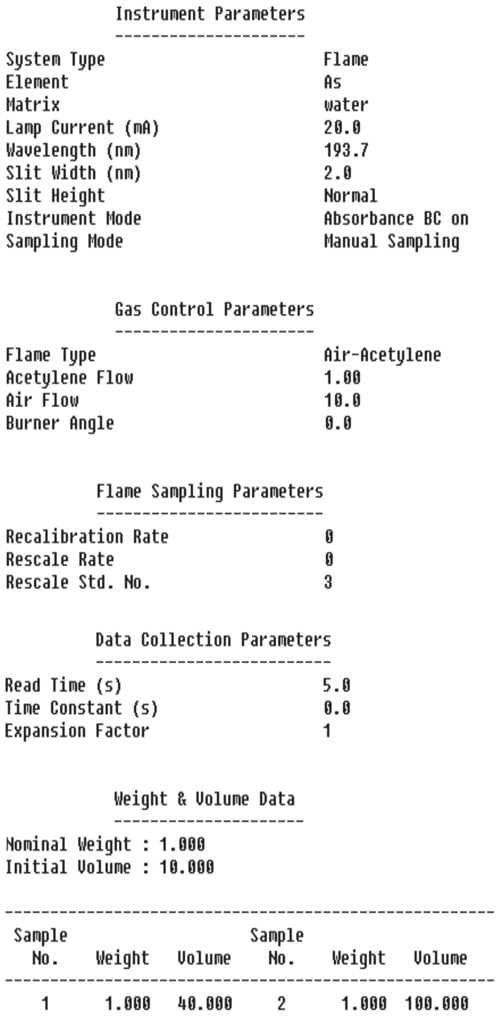
Arsenic: This analyte is normally present in both the tri-valent and penta-valent oxidation states. As^{3+} has approximately twice the sensitivity of As^{5+}. The As^{5+} in all samples was reduced to As^{3+} by the addition of concentrated HCl to give an approximately 2 molar solution followed by 0.1% w/v KI. Samples were then allowed to stand for 1 hour prior to the analysis to allow time for complete reaction.

> **Note:** KI will interfere strongly with the analysis of selenium. If both arsenic and selenium are to be analysed in samples, the As^{3+} can be oxidised to As^{5+} with concentrated HNO_3 and analysis can continue after calibrating at this oxidation state. A 10 µg/L As^{3+} solution should give an absorbance reading of approximately 0.5.

Selenium: The tetra-valent oxidation state will give the maximum sensitivity for selenium. To ensure all Se^{6+} is reduced to Se^{4+}, concentrated HCl was added to give an approximately 7 molar solution. The samples were then heated at 70 °C for 30 minutes and allowed to cool before analysing. A 10 µg/L Se^{4+} solution should give an absorbance reading of approximately 0.3.

Instrument Settings and Procedure

Figure 1 shows a printout of the operating parameters for arsenic using a GBC 906 atomic absorption spectrophotometer (AAS). Table 2 shows a summary of the operating conditions used to determine arsenic and selenium in the quality control water samples. For the other elements (antimony, bismuth, mercury and tellarium), recommended parameters were used as described in the HG3000 Operation Manual.[3]



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             Instrument Parameters
             ---------------------
System Type                      Flame
Element                          As
Matrix                           water
Lamp Current (mA)                20.0
Wavelength (nm)                  193.7
Slit Width (nm)                  2.0
Slit Height                      Normal
Instrument Mode                  Absorbance BC on
Sampling Mode                    Manual Sampling


             Gas Control Parameters
             ----------------------
Flame Type                       Air-Acetylene
Acetylene Flow                   1.00
Air Flow                         10.0
Burner Angle                     0.0


           Flame Sampling Parameters
           -------------------------
Recalibration Rate                0
Rescale Rate                      0
Rescale Std. No.                  3


           Data Collection Parameters
           --------------------------
Read Time (s)                    5.0
Time Constant (s)                0.0
Expansion Factor                 1


             Weight & Volume Data
             --------------------
Nominal Weight : 1.000
Initial Volume : 10.000

-----------------------------------------------------
 Sample                      Sample
   No.   Weight   Volume      No.   Weight   Volume
-----------------------------------------------------
    1     1.000   40.000      2      1.000  100.000
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Figure 1: *Operating parameters for arsenic.*

Element	W/length (nm)	Spectral Bandpass (nm)	Lamp Current (mA)	Lamp Type	Temp. (°C)
As	193.7	2.0	20	SLamp	920
Se	196.0	2.0	18	SLamp	950

Table 2: *AAS instrument parameters for the determination of arsenic and selenium in USEPA certified quality control water samples using the EHG3000.*

The spray chamber assembly was removed from the GBC 906 AAS and replaced with the heating blanket assembly of the GBC EHG3000. A standard GBC quartz absorption cell was fitted into the blanket and aligned using the burner adjuster controls.

The temperature was preset to 1000 °C and a 10 minute warm-up time was allowed before commencing analysis. To ensure optimum performance of the HG3000 hydride system, the fluid path and atomisation cell were conditioned for each element according to the manufacturer's recommendations.[3]

Alternately blank and highest standard solutions were measured until a reproducible absorbance signal was obtained. The system was allowed to stabilize for 60 seconds after introduction of each sample. Final absorbance readings were the mean of three 3 second integrations. After the system was optimised for maximum analytical sensitivity, the EHG3000 heating blanket was allowed to cool to room temperature and then re-heated to 1000 °C while a 10 µg/L analyte solution was measured. The resulting temperature profiles for all six elements were determined to show the temperature at which the maximum analytical sensitivity was achieved. Characteristic Concentration and the Detection Limit were determined for each element.

Results

Plotting absorbance/temperature profiles for each element (see two examples in Fig. 2), allows an optimum temperature (or temperature range) to be chosen for improved performance (see Table 3). It is interesting to note that different elements respond in varying ways. For example, arsenic has a relatively narrow optimum temperature range compared to bismuth, which displays a much wider range. Also worth noting is the upper limit of the temperature range, which suggests that control at temperatures from 850–1000 °C is critical for optimum performance. Operators should appreciate the analytical benefits to be gained from adherence to the appropriate temperature range.

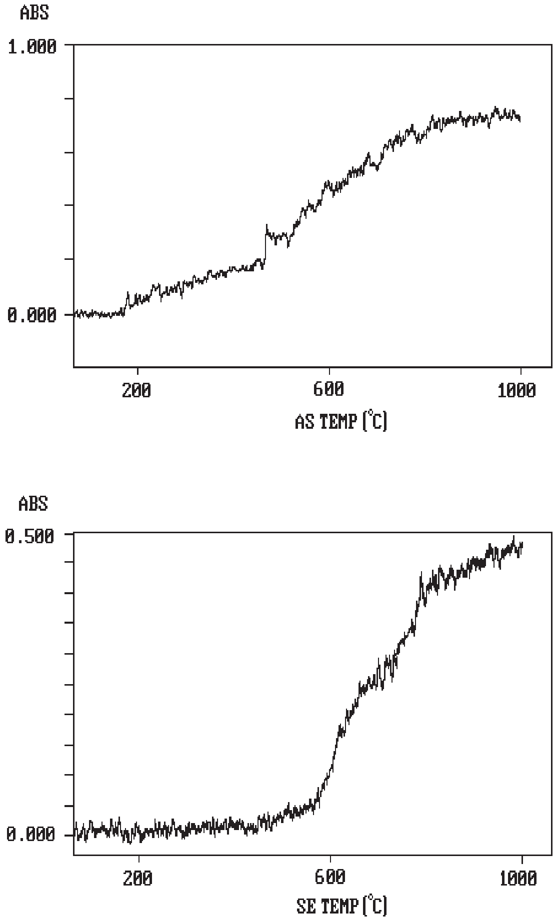

Figure 2: *Temperature profiles for arsenic and selenium.*

Element	Flame-heated cell*		EHG3000 Electrically-heated cell		Optimum Temp. Range (°C)
	C.C. (µg/L)	D.L. (µg/L)	C.C. (µg/L)	D.L. (µg/L)	
Antinomy	0.1	0.08	0.1	0.09	880–980
Arsenic	0.05	0.05	0.05	0.025	880–1000
Bismuth	0.1	0.04	0.12	0.03	650–900
Mercury**	0.3	0.05	0.29	0.036	ambient –50
Selenium	0.13	0.04	0.11	0.036	850–1000
Tellurium	0.2	0.13	0.17	0.06	700–850

C.C. Characteristic Concentration (concentration required to obtain 0.0044 absorbance units or 1% increase in light throughput).

D.D. Detection Limit is that concentration which gives an absorbance equal to twice the standard deviation of a series of measurements near the blank level (2σ detection limit).

* For flame analyses an oxidizing air-acetylene flame was used

** For mercury analysis, the cold-vapour technique (no flame-heating) was

Table 3: *Characteristic Concentration and Detection Limit comparison for flame-heated and electrically-heated (EHG3000) absorption cells, with optimum temperature ranges*

From Table 3 it is clear that the accurate temperature control provided by the EHG3000 improves detection limits for arsenic, bismuth, selenium and tellurium when compared with a flame-heating system.

For these elements at concentration levels close to the detection limit, improvements in signal noise and stability enhance the accuracy of the results. Combined with the ability to maintain or improve sensitivity for all elements, as measured by characteristic concentration, it is clear that the EHG3000 can improve analytical performance and is a more than adequate alternative to flame-heating for this type of analysis.

The measured results for the USEPA certified water quality samples (Table 4) were very close to the expected certified values for both elements and hence well within the stated 95% confidence limits. Figure 3 shows the calibration curve for arsenic.

Sample	Element	Certified Value	Measured Value	95% Confidence Limits
Lot 1-1TMWS	As	19.5	18.7	16.3–22.7
	Se	4.7	4.8	3.2–6.2
Lot 1-1TMAA-1	As	48.9	48.1	41.9–55.9
	Se	48.4	47.4	39.4–57.4

***Table 4:** Electrically-heated absorption cell results, compared with performance evaluation data (μg/L) for USEPA certified samples.*

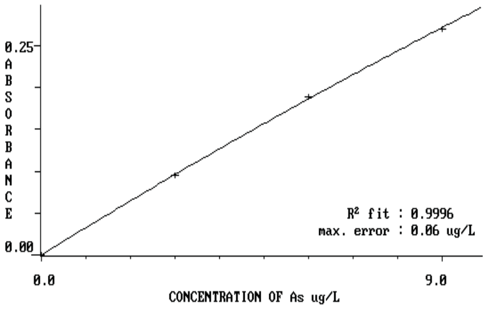

***Figure 3:** Arsenic calibration curve using an electrically-heated cell.*

Conclusion

The GBC EHG3000 Electric Heater accessory provides a useful alternative to the air-acetylene flame for absorption cell heating in trace element hydride and cold vapour mercury analysis. Accurate temperature control results in lower detection limits for some elements.

This accessory allows hydride analysis to be performed on a furnace-only instrument. Adding hydride capability to a furnace-only instrument provides an enhanced analytical capability which is particularly useful for environmental analysis.

Eliminating acetylene from hydride analysis removes an expense and also allows unattended analysis for more efficient time management.

References

1. Chapple, G. and Danby, R. The Determination of Arsenic, Selenium and Mercury Levels in USEPA Quality Control Samples using the GBC HG3000 Continuous-flow Hydride Generator. GBC AA Applications No. 17, 1990.
2. Chapple, G. An Evaluation of Performance Characteristics of Super Lamps. GBC AA Application No. 16, 1998.
3. HG3000 Operation Manual, GBC Scientific Equipment Pty Ltd, Dandenong, Victoria, Australia.