

# AAS

## APPLICATION NOTES

The determination of arsenic and selenium in environmental samples using the GBC graphite furnace system

AAS



## Introduction

There is a worldwide concern about water pollution and many countries specify a maximum of 50 ng/mL arsenic and 10 ng/mL selenium in domestic water supplies. Both arsenic and selenium are naturally occurring elements and are abundant in many areas. Elevated levels can be detected in surface and ground waters, particularly near mine discharge sites.

In this study, three water samples were analysed – two river samples (S1 and S2) and one bore water sample (S3) from the mining district of Northern Victoria, Australia. Two USEPA quality control samples were also analysed as a check on the method. These were:

WS378 Water Supply Quality Control Sample

WP386 Water Pollution Quality Control Sample

## Experimental

### Instrumentation

The GBC atomic absorption spectrophotometer and the GBC automated graphite furnace system was used. The GBC graphite furnace system comprises the graphite furnace (GF) and programmable automatic sample loader (PAL). This combination of equipment is particularly suited to trace analysis since the GBC graphite furnace system can automatically prepare a range of standards from a single stock solution, inject chemical modifier and even automatically prepare a series of standard additions. Complete outputs of the operating parameters for the spectrophotometer, furnace and sampler are shown in Figures 1 and 2.

Element	As
Beam Mode	Double Beam
Wavelength	193.7 nm
Slit Width	2.0 nm
Atomization	Furnace
Lamp Current	8.0 mA
EHT (gain)	– 384 V
Scale Expansion	1.000
Integration Time	0.02 s

Graphite Furnace Parameters					
Step No.	Final Temp °C	Ramp Time (sec)	Hold Time (sec)	Gas Type	Read On
1	80	5.0	1.0	Inert	No
2	110	30.0	10.0	Inert	No
3	700	10.0	10.0	Inert	No
4	700	0.2	1.0	None	No
5	2500	0.9	3.0	None	Yes
6	2600	1.0	2.0	Inert	No

Autosampler Details	
Sample Volume (µL)	20.0
Modifier Volume (µL)	10.0
No. of Multiple Injections	1
No. of Sample Repeats	3
Dry Steps for Multiple Injections	1
Inject on Step Number	1

Standards Details	
No. of Standards	4
Standard 1 (5 µL) Concentration	25
Standard 2 (10 µL) Concentration	50
Standard 3 (15 µL) Concentration	75
Standard 4 (20 µL) Concentration	100
Recalibration Rate	0
Recalibration Standard	0

**Figure 1: Operating parameters for arsenic**

Element	Se
Beam Mode	Double Beam
Wavelength	196.0 nm
Slit Width	2.0 nm
Atomization	Furnace
Lamp Current	18.0 mA
EHT (gain)	- 332 V
Scale Expansion	1.000
Integration Time	0.02 s

Graphite Furnace Parameters					
Step No.	Final Temp °C	Ramp Time (sec)	Hold Time (sec)	Gas Type	Read On
1	80	1.0	1.0	Inert	No
2	100	30.0	10.0	Inert	No
3	700	20.0	5.0	Inert	No
4	700	0.2	1.0	None	No
5	2500	1.0	3.0	None	Yes
6	2700	1.0	2.0	Inert	No

<b>Autosampler Details</b>	
Sample Volume ( $\mu\text{L}$ )	20.0
Modifier Volume ( $\mu\text{L}$ )	10.0
No. of Multiple Injections	1
No. of Sample Repeats	3
Dry Steps for Multiple Injections	1
Inject on Step Number	1

<b>Standards Details</b>	
No. of Standards	4
Standard 1 (5 $\mu\text{L}$ ) Concentration	25
Standard 2 (10 $\mu\text{L}$ ) Concentration	50
Standard 3 (15 $\mu\text{L}$ ) Concentration	75
Standard 4 (20 $\mu\text{L}$ ) Concentration	100
Recalibration Rate	0
Recalibration Standard	0

**Figure 2: Operating parameters for selenium**

Super Lamps were used in preference to normal hollow cathode lamps.

The Super Lamp is a type of boosted hollow cathode lamp. The output of a Super Lamp has a narrow line width and is significantly brighter than that of a normal hollow cathode lamp. This results in better sensitivity, more linear calibration curves, lower baseline noise and improved detection limits. The narrow linewidth also allows wider slits to be used, giving even lower baseline noise, without loss of sensitivity. Figures 3 and 4 compare calibration curves obtained with Super Lamps and hollow cathode lamps for arsenic and selenium. Figures 5 and 6 show peak graphs obtained from the GBC automated graphite furnace for arsenic and selenium using both Super Lamps and hollow cathode lamps. Note that the base line is significantly less noisy and the sensitivity is better with the Super Lamps. This means that the detection limit will be better.

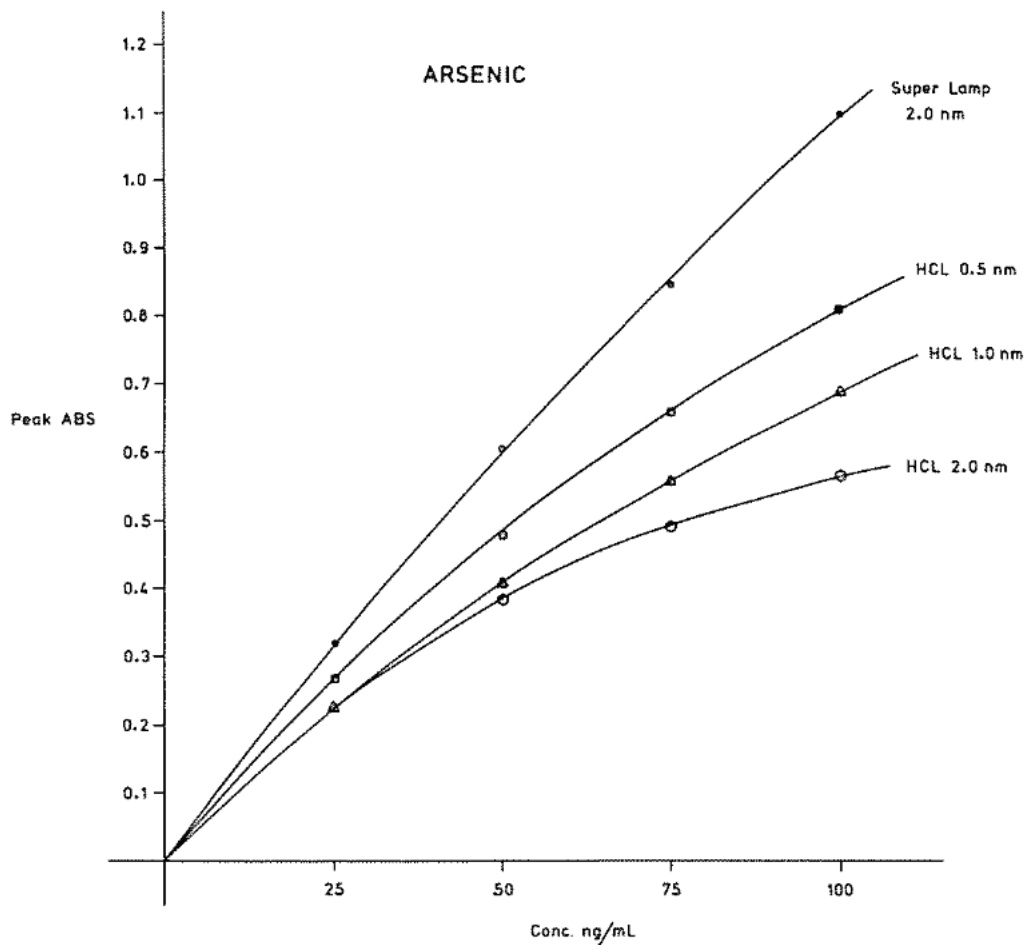


Figure 3: Calibration curves for arsenic for Super Lamp and Hollow Cathode Lamp with varying slit width

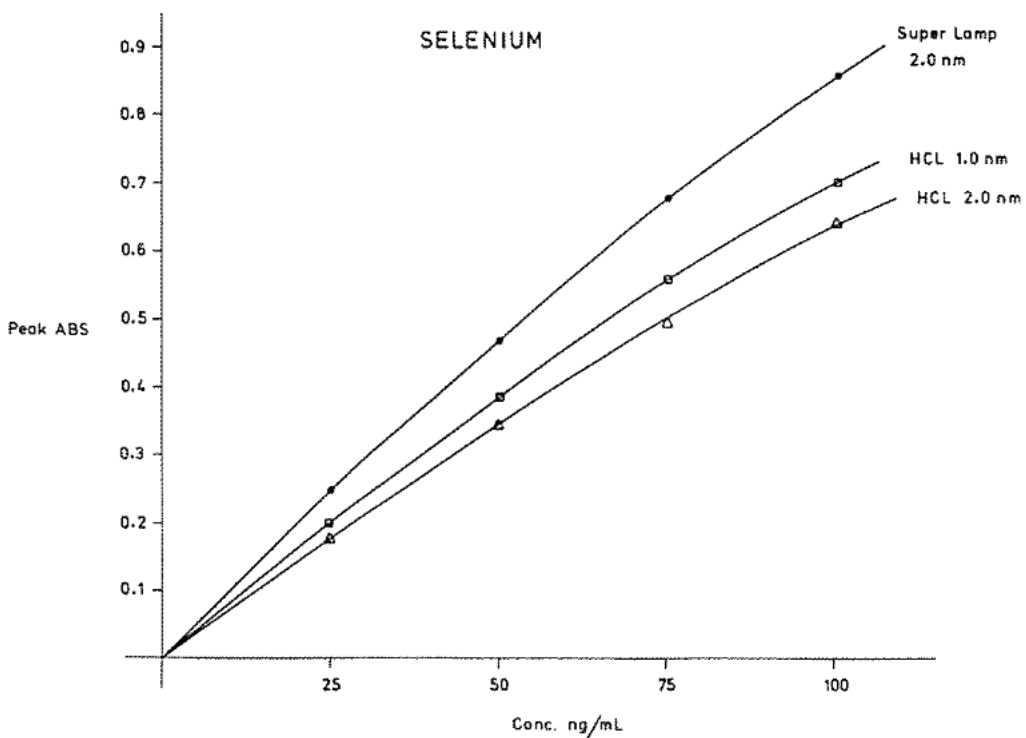
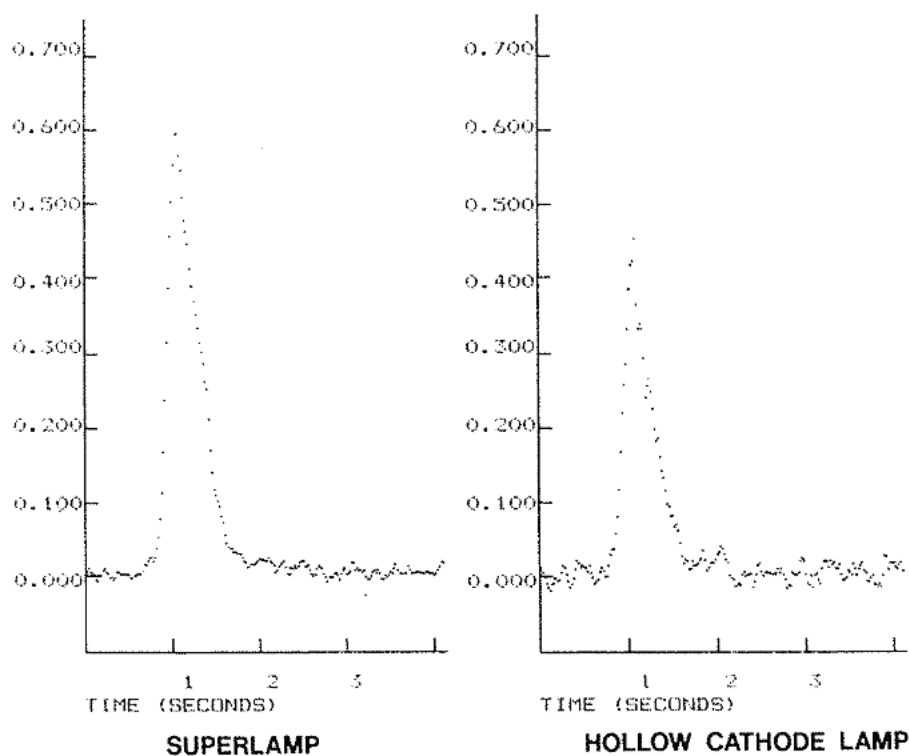


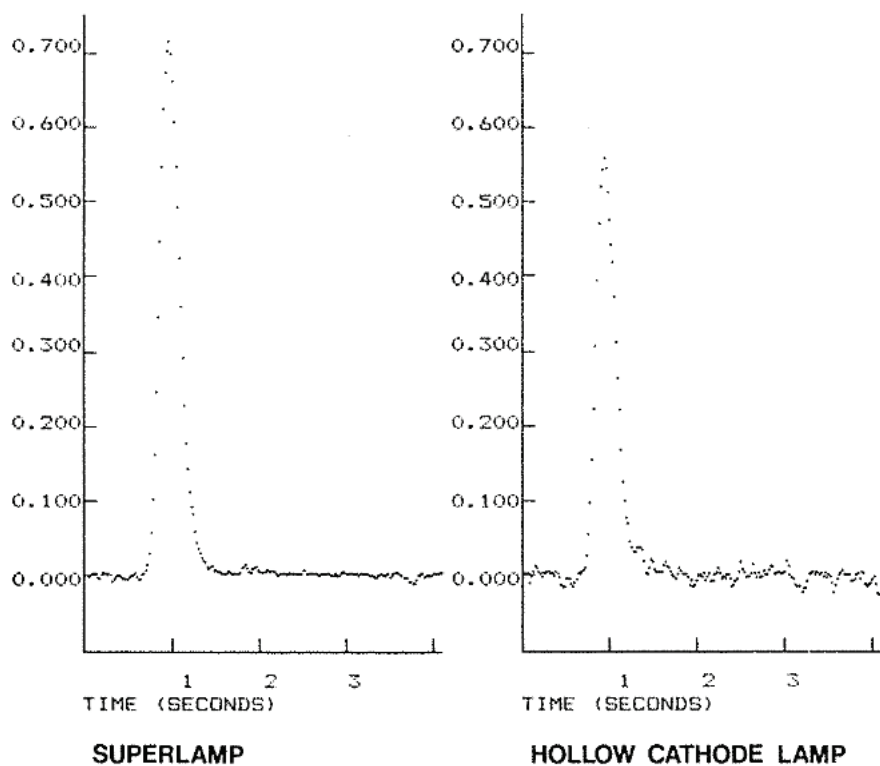
Figure 4: Calibration curves for selenium for Super Lamp and Hollow Cathode Lamp with varying slit width

**ARSENIC 2.0 nm**



**Figure 5: Peaks of arsenic with (a) Super Lamp, 2.0 nm slit width (b) Hollow Cathode Lamp, 2.0 nm slit width**

**SELENIUM 2.0 nm**



**Figure 6: Peaks of selenium with (a) Super Lamp, 2.0 nm slit width (b) Hollow Cathode Lamp, 2.0 nm slit width**

## Sample preparation

The sample preparation used was an adaption of the USEPA Methods 206.2 for Arsenic and 270.2 for selenium<sup>1</sup>. 50 mL of well mixed sample was transferred to a 250 mL beaker and 1 mL of 30% hydrogen peroxide and 1 mL of conc. nitric acid added. The sample was heated for two hours at 95°C until the volume was less than 50 mL, then cooled to room temperature and quantitatively transferred to a 50 mL volumetric flask. The USEPA methods called for addition of nickel nitrate to the samples and standards. This was performed automatically by the autosampler, thus enabling the sample preparation to be simplified. The sampler was programmed to inject 10 µL of 0.2% Ni solution.

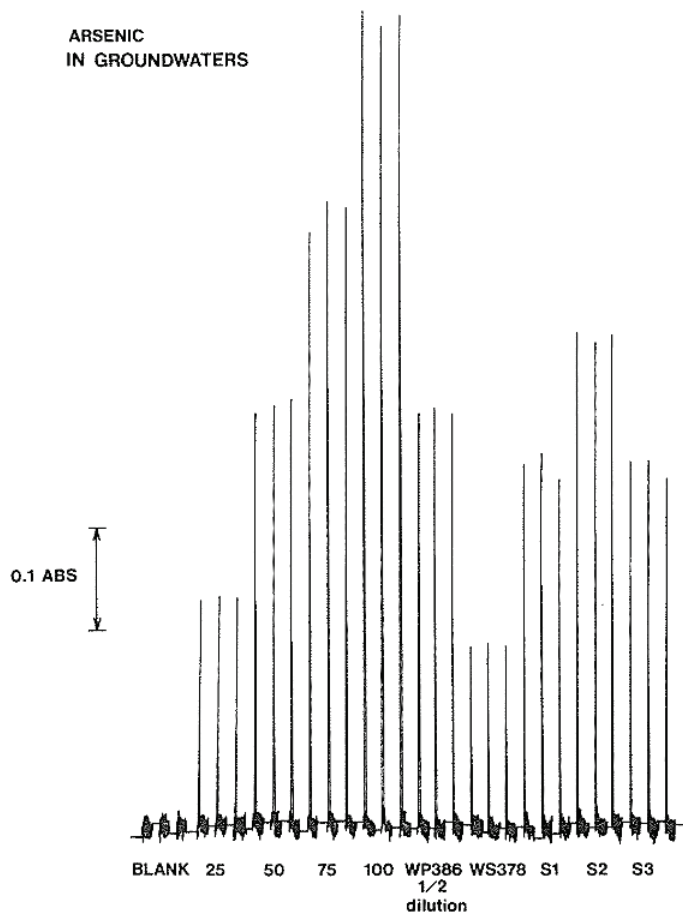
A working calibration curve was developed using four standards ranging from 25 to 100 ng/mL.

The standards were prepared by the autosampler injecting a varying amount of a single standard. The total injection volume was maintained constant by adding blank solution.

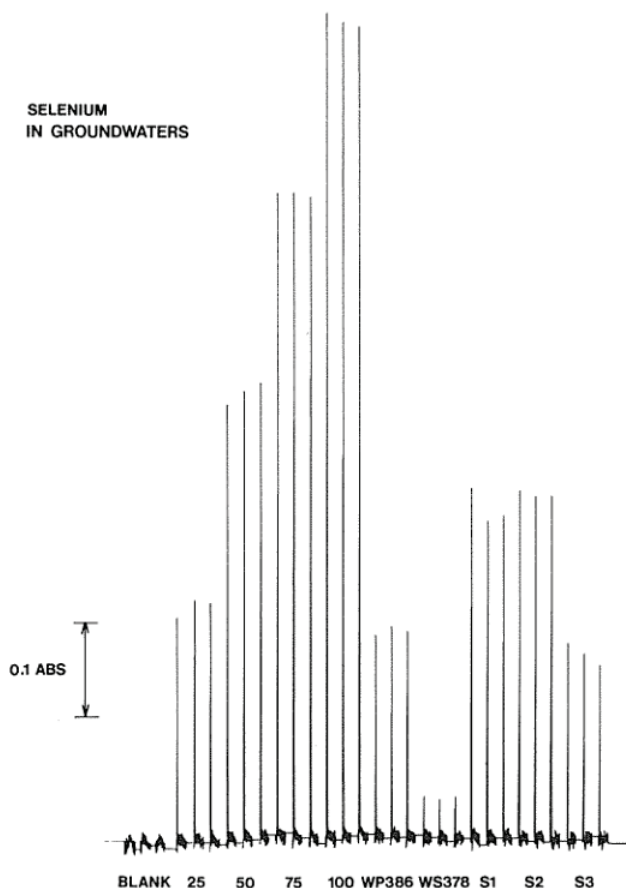
A mixed working standard of 100 ng/mL of As and Se was prepared from 1000 µg/mL standards. The nitric acid and hydrogen peroxide solution were ARISTAR grade. The standard and blank were put through the same sample preparation procedure as the samples. The EPA WP386 standard was diluted by ½ for the arsenic analysis.

## Results

Figures 7 and 8 show the outputs for the calibration standards and samples for arsenic and selenium. The automatic sampler was programmed for three replicate measurements of each solution. The relative standard deviation ranged from 1 to 5%.



**Figure 7: Output of calibration standards and samples for arsenic**



**Figure 8: Output of calibration standards and samples for selenium**

Table 1 shows the results obtained for all samples including the true values and 95% confidence interval value reported for the USEPA standards.

Sample	S1 Found	S2 Found	S3 Found	WS378			WP386		
				Found	TV	95% CI	Found	TV	95% CI
As ng/mL	42.5	59.1	42.5	19.3	20	15.1–24.3	98.4	100	77.2–121
Se ng/mL	36.9	38.2	20.0	4.1	4.0	2.4–4.9	22.6	25	15–31.2

**Table 1: Concentration of arsenic and selenium found in samples**

## Conclusion

A method for the determination of arsenic and selenium in ground waters has been developed. The method was conveniently automated by the use of the GBC atomic absorption spectrophotometer and the GBC automated graphite furnace system. This system was programmed to automatically load the sample, add modifier and automatically prepare a series of calibration standards from a single stock standard solution. The sample used was 20  $\mu\text{L}$  and this enabled measurement over a large dynamic range (1 to 100 ng/mL) for both arsenic and selenium.



The GBC automated graphite furnace system can be programmed for a 100  $\mu\text{L}$  single injection, enabling the measurement of extremely low levels. For even lower levels, multiple injections can be performed. With this technique, a sample is injected, dried and a further sample injected. (This can be repeated up to 255 times).

## References

1. USEPA Standard Methods of Examination of Water and Wastewater, 1983, Methods 206.2 and 207.2