AAS
APPLICATION NOTES

An evaluation of the performance characteristics of super lamps

GBC

Introduction

Analytical precision and sensitivity are the two main criteria that have enabled atomic absorption spectrophotometry to enjoy its current widespread acceptance in the marketplace. The technique relies on a light source, the most common being a hollow cathode lamp (HCL), to provide an emission spectrum specific to the element of interest. If the emission is of high intensity, with a narrow line width and a clean spectrum, good precision and linearity are obtained. If the emission is of low intensity, baseline noise is increased. If the source has a wide line width or a complex spectrum, the calibration becomes non-linear. These undesirable traits are common to high vapour pressure elements such as arsenic and selenium.

Conventional lamps consist of an anode and a hollow cathode, the latter typically constructed from the ultrapure metal, an alloy of the metal, or a metallic compound. These electrodes are sealed in a glass envelope containing argon or neon at a reduced pressure. When a voltage is applied to the electrodes, the fill gas is ionized and the ions accelerated within the envelope. The fill gas ions then collide with the cathode material, causing the release and excitation of the metal component. The release of the metal atoms is termed "sputtering". As the excited metal atoms fall to the ground state, they emit radiation at a characteristic wavelength, specific to the element. If the current is increased past the optimum, more sputtering occurs but with little increase in excitation, leaving a cloud of ground state atoms outside the cathode.

This ground state atom cloud absorbs the radiation from the excited atoms, thus reducing the output intensity of the lamp and broadening the line width. Figure 1 shows a schematic diagram of a conventional hollow cathode lamp.

The boosted discharge lamp was first described by Sullivan and Walsh[1], then later by Lowe[2]. The Super Lamp design provides a second discharge between a special emission source and the anode, passing through the cylindrical cathode. The electrons produced excite the excess ground state atoms, thus increasing lamp intensity and enabling the use of higher currents without the effects of self-absorption or line broadening. The Super Lamp is shown schematically in Figure 2.
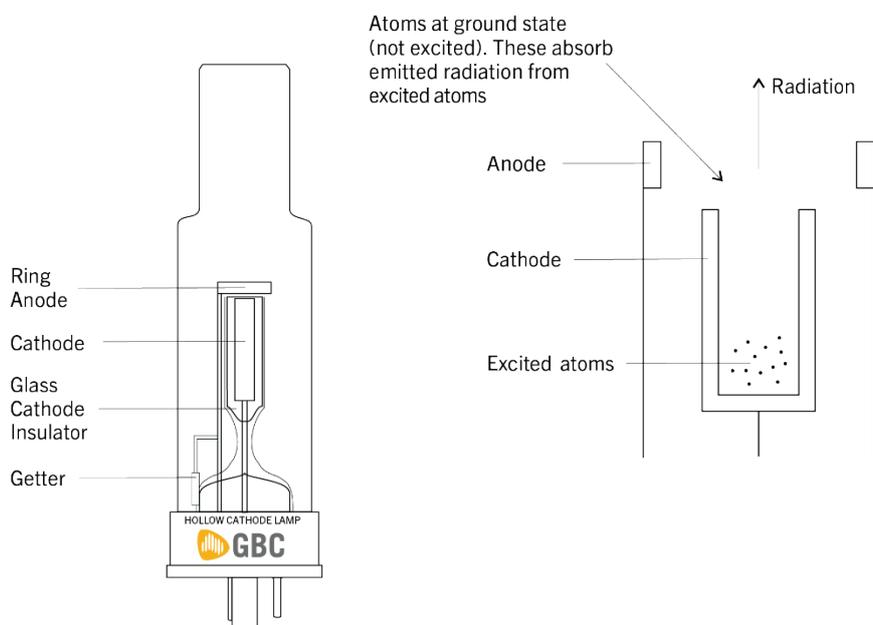

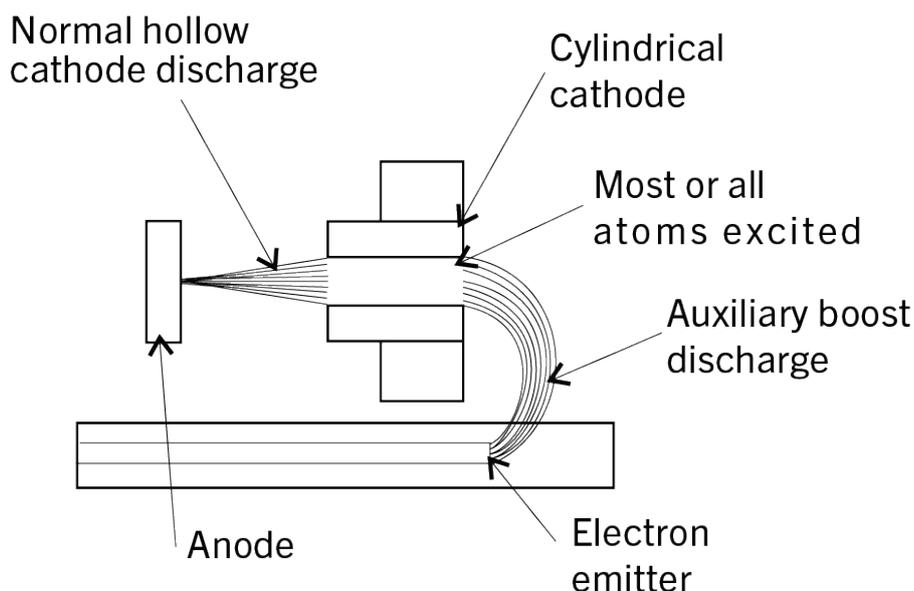**Figure 1: Schematic diagram of a conventional hallow cathode lamp**

Figure 2: Schematic diagram of a Super Lamp

Experimental

Instrument parameters

A GBC atomic absorption spectrometer and GBC automated graphite furnace system were used. The graphite furnace system consists of the graphite furnace power supply (GF) and programmable automatic sample loader (PAL).

GBC Super Lamps and hollow cathode lamps were used throughout this work.

Reagents

1000 µg/mL standard solutions were used to prepare the following working solutions: 1 µg/mL arsenic, 40 µg/L selenium, 5 µg/L lead, 10 µg/L arsenic, 0.5 µg/mL selenium, and 0.2 µg/L zinc.

Working solutions were prepared daily in 1% Aristar nitric acid.

1000 µg/mL nickel nitrate was used for matrix modification of arsenic and selenium working standards.

All standard solutions were prepared in Type 1 ultrapure water, supplied from a reverse osmosis, mixed bed de-ionizing unit.

1% nitric acid was also used in the PAL rinsing solution to provide more efficient cleaning of the capillary.

Results and discussion

Line width

To determine the emission line widths of the two lamps a 2.54 m scanning Czerny-Turner monochromator was used. This allowed for extremely high resolution study of the emission lines, which are typically in the order of 6×10^{-4} nm in width.

Figure 3 shows emission peaks from an arsenic hollow cathode lamp. As the lamp current is increased, the emission line broadens. At higher currents a distortion of peak maxima indicates the effect of self-absorption. (Note that the intensity has been normalised for these plots).
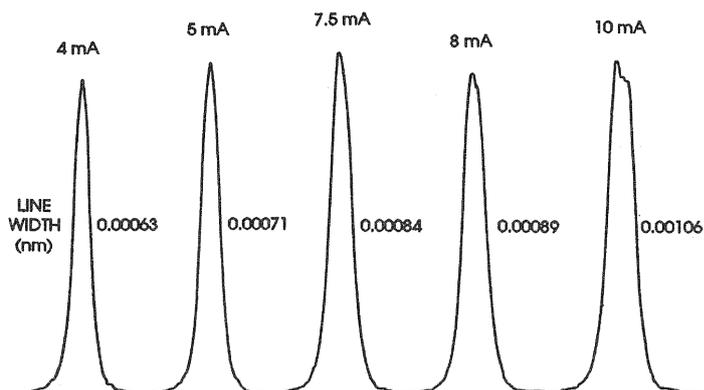
Figure 3: Emission peaks from an arsenic hollow cathode lamp

Figure 4 shows emission peaks from an arsenic Super Lamp. Only a marginal change in line width can be seen as the lamp current is increased for the Super Lamp. Even at the highest currents, self-absorption is non-existent.
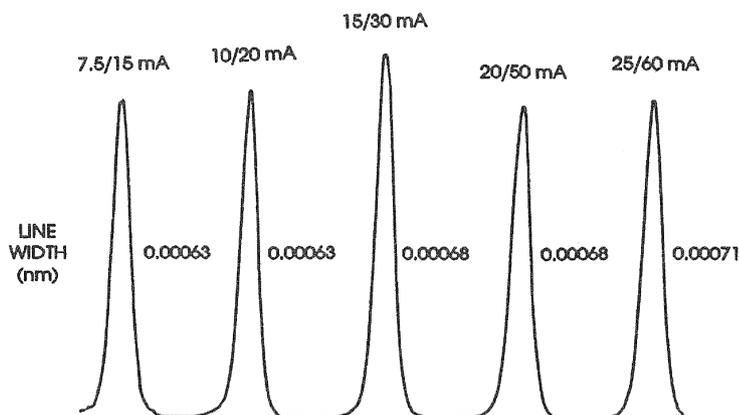
Figure 4: Emission peaks from an arsenic super lamp

Intensity

With no self-absorption present, the Super Lamp is free to provide a high intensity output with only a minor increase in line width. Table 1 shows the relative intensity gains of the Super Lamp over a standard hollow cathode lamp. A range of intensity gains is listed for each element, since both Super Lamps and conventional hollow cathode lamps show some variation in intensity from lamp to lamp.

	Super Lamp / Standard HCL
Arsenic	5–10
Selenium	10–15
Lead	25–50
Zinc	15–25

Table 1: Super lamp elements and their relative intensity gains

As the intensity of the resonance line is increased, the ratio to associated non-absorbing lines becomes greater. This often enables an opening of the bandpass with the Super Lamp without subsequent loss of sensitivity. The ability to use a higher bandpass lead to even greater intensity with the Super Lamp.

Detection limit (flame)

A comparison of detection limits for flame analysis can be seen in Table 2. The Super Lamp produced significantly lower detection limits for arsenic and selenium.

Results in Table 2 were obtained using a 1 µg/mL arsenic solution and a 0.5 µg/mL selenium solution. A nitrous oxide-acetylene flame and HYPER-PULSE background correction[3] were used for both elements, and the absorbance readings were scale expanded by a factor of 10 to provide better resolution of the signal.

	Standard HCL (µg/mL)	Super Lamp (µg/mL)	Detection Limit Improvement
Arsenic	0.5	0.1	5.0x
Selenium	0.4	0.06	6.7x

Table 2: Detection limits for flame analysis

Characteristic mass (graphite furnace)

Table 3 shows characteristic mass values for both Super Lamps and standard hollow cathode lamps. These values are calculated for the corresponding peaks shown in Figures 6, 7 and 8.

	Standard HCL (pg)	Super Lamp (pg)	Improvement (%)
Arsenic	4.7	4.1	13
Selenium	16.6	13.4	19
Lead	3.8	3.2	16
Zinc	0.31	0.25	19

Table 3: Characteristic mass values for furnace analysis

The spectral purity of the Super Lamp provides a higher absorbance for a given concentration, that is, improved sensitivity. This is reflected in Figure 5 where analyte peak results show a significant increase in height when using the Super Lamp.

Signal-to-noise (graphite furnace)

In graphite furnace analysis, low level peaks are often lost or masked by baseline noise. The improved intensity of the Super Lamp has enabled detection to significantly lower levels by reducing this noise. Graphical comparison of baselines and analyte peaks for the arsenic and selenium lamps are shown in

Figure 6. Obvious gains in baseline stability and sensitivity can be seen. The results shown in Figure 5 also show significant improvements in precision with the Super Lamp.

Figures 7 and 8 display baselines and peaks for lead and zinc respectively. Graphs of the midrange absorbance peaks clearly depict gains in sensitivity. It should be noted, however, that baseline noise has little effect at this level.

ARSENIC

A

Sample Number 1	
Reading 1	0.098
Reading 2	0.098
Reading 3	0.091
Reading 4	0.094
Reading 5	0.083
Reading 6	0.094
Reading 7	0.097
Reading 8	0.094
Reading 9	0.083
Reading 10	0.109
Mean of 10 Pts	**0.094**
RSD	**7.96%**

B

Sample Number 1	
Reading 1	0.113
Reading 2	0.109
Reading 3	0.111
Reading 4	0.103
Reading 5	0.107
Reading 6	0.110
Reading 7	0.107
Reading 8	0.103
Reading 8	0.110
Reading 10	0.100
Mean of 10 Pts	**0.107**
RSD	**3.77%**

SELENIUM

A

Sample Number 1	
Reading 1	0.105
Reading 2	0.102
Reading 3	0.112
Reading 4	0.101
Reading 5	0.109
Reading 6	0.104
Reading 7	0.112
Reading 8	0.125
Reading 9	0.096
Reading 10	0.098
Mean of 10 Pts	**0.106**
RSD	**7.83%**

B

Sample Number 1	
Reading 1	0.132
Reading 2	0.129
Reading 3	0.132
Reading 4	0.132
Reading 5	0.128
Reading 6	0.132
Reading 7	0.127
Reading 8	0.129
Reading 8	0.134
Reading 10	0.134
Mean of 10 Pts	**0.131**
RSD	**1.90%**

Figure 5: Results of ten peak height readings for 100 pg of arsenic and 400 pg of selenium for a standard hollow cathode lamp (A) and super lamp (B)
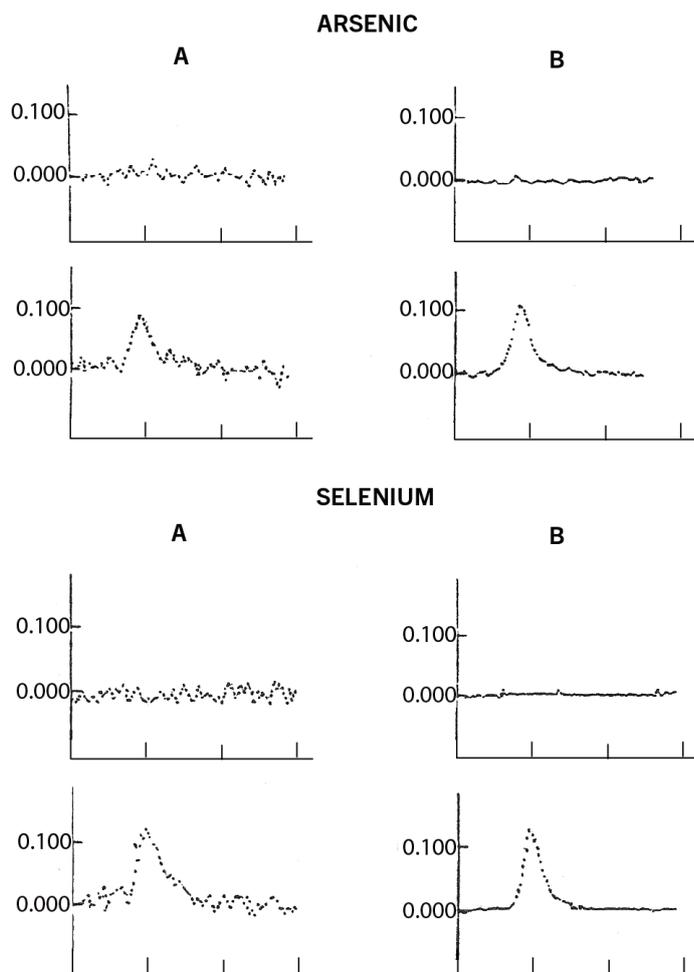
ARSENIC

SELENIUM

Figure 6: Graphical comparison of baselines and analyte peaks for arsenic and selenium standard hollow cathode lamps (A) and super lamps (B)
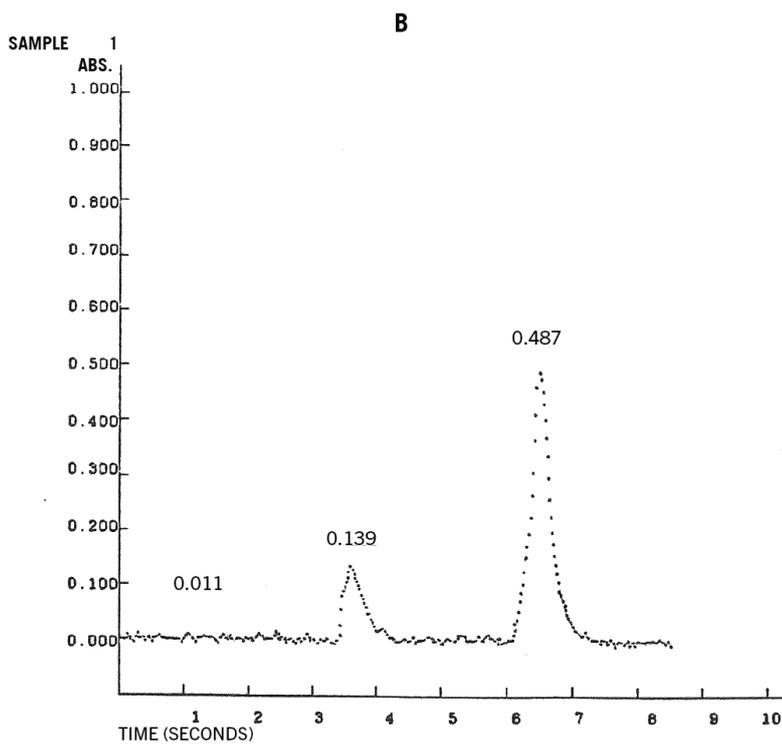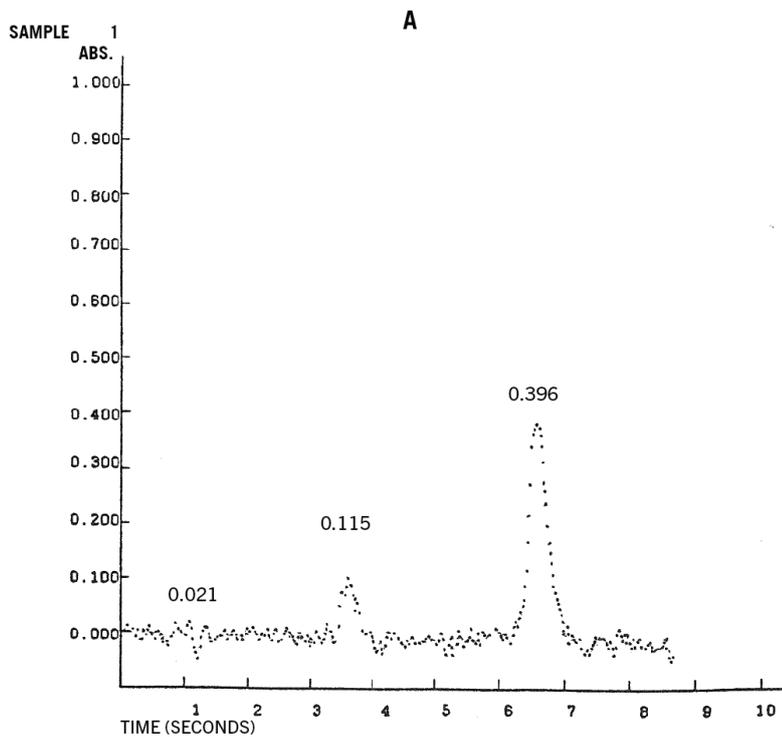
Figure 7: Graphical comparison of baselines and analyte peaks for two lead samples using a standard hollow cathode lamp (A) and super lamp (B)
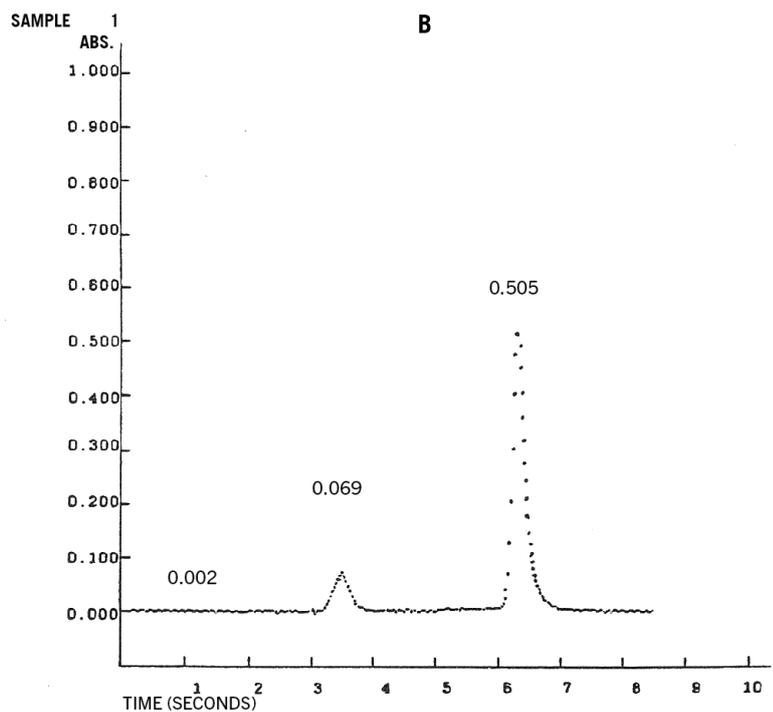
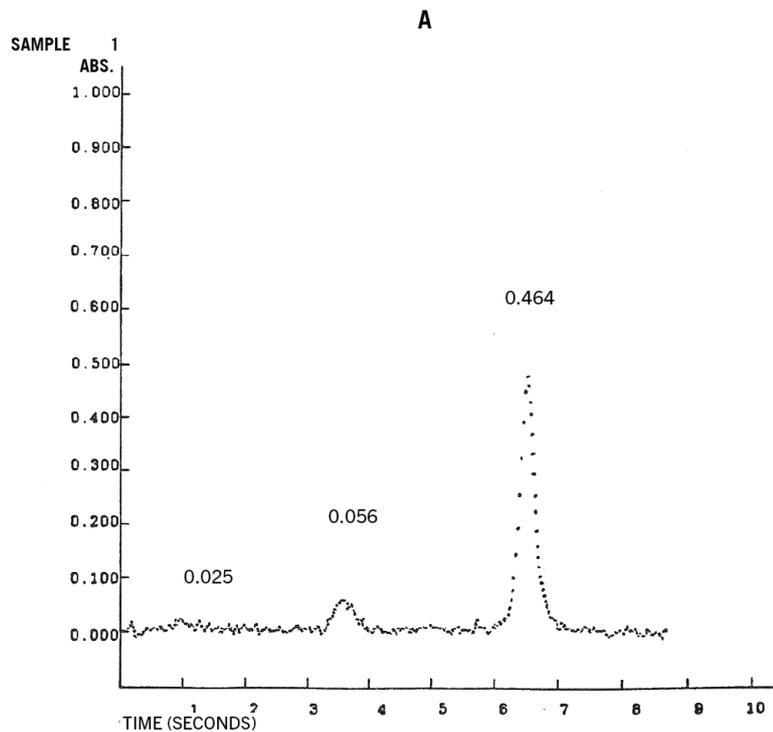**Figure 8: Graphical comparison of baselines and peaks for two zinc samples using a standard hollow cathode lamp (A) and super lamp (B)**

Calibration linearity

Figure 9 shows calibration curves for arsenic and selenium, based on the results of earlier studies. As the bandpass is opened for the hollow cathode lamps, more non-absorbing lines are seen and curvature becomes excessive. The Super Lamp offers improved spectral purity, and therefore wider slits may be used without increasing curvature.

Improved linearity of the calibration curve allows for greater separation of absorbance units per unit of concentration. This provides more accuracy for concentration readings in the higher absorbance areas.

Linear calibration is essential for successful use of the standard addition's technique. If curvature exists, the linear regression calculation will give a falsely high result. The Super Lamp increases the working standard addition range well above that of the standard hollow cathode lamp.
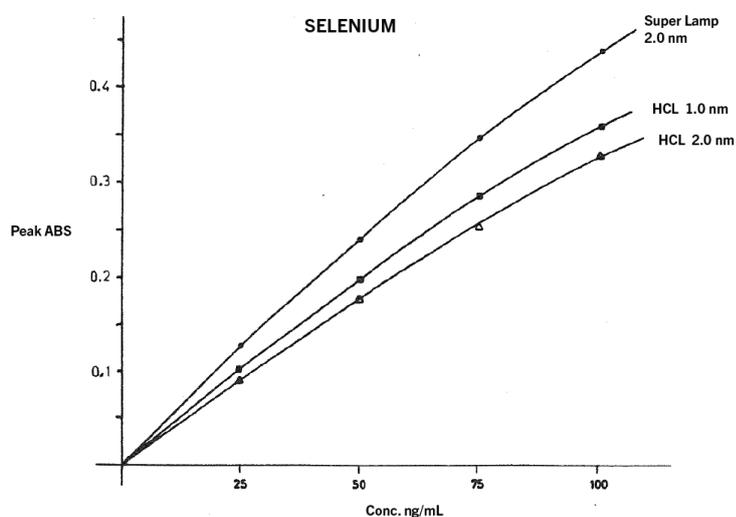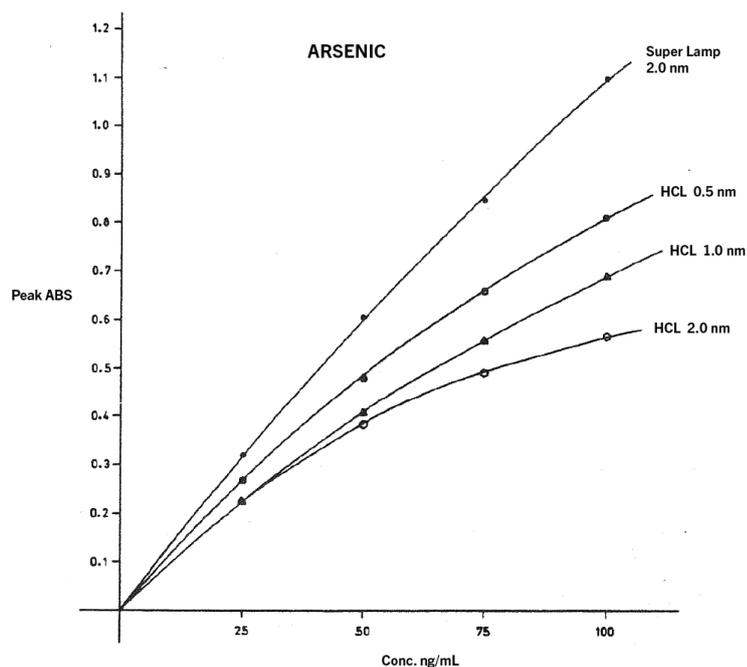

Figure 9: Calibration curves for arsenic and selenium comparing super lamps and standard hollow cathode lamps with varying slit widths

Conclusion

The boosted discharge lamp proved to be superior to its equivalent hollow cathode lamp in all areas. Significant gains were made in baseline noise, sensitivity, detection limit and linearity, thus providing a very useful tool for trace analysis of the associated element. The improved calibration linearity of the lamp enables use of standard additions over a wider absorbance range and offers the ability to calibrate with one addition anywhere in the linear region.

References

1. Sullivan, J.V., and Walsh, A., Spectrochim. Acta, 1965, 21, 721.

2. Lowe, R.M., Spectrochim. Acta, 1971, 26B, 201.

3. Liddell, P., Athanasopoulos, N., and Grey, R., American Laboratory, 1986, 18 (11), 68.