

Evaluation of High Intensity Lamps for AAS

Application Note

Atomic Absorption

Authors

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Introduction

The trend over the three decades since atomic absorption spectrometry (AAS) was introduced as a very successful analytical technique [1] has been to measure ever lower concentrations of trace metals. This is especially true for the priority pollutant metals (As, Se, Sb, Pb, Cd and Tl) in the environment. An improvement in light throughput of the AA spectrometer gives a more stable baseline, and hence a lower limit of detection. Three areas need to be considered:

- Monochromator
- Photomultiplier tube
- Light source

Modern monochromator and photomultiplier tube designs have been refined to the point where further significant improvements are unlikely. An important component, the hollow cathode lamp (HCL) [2], can be modified to give better spectral characteristics and hence better performance. A new lamp design is described and characterized in this report.

The requirement is to increase the emission intensity of a HCL without broadening the emission line. The characteristics of some arsenic and selenium hollow cathode lamps, in particular, can vary widely [3], which suggests their operating conditions are critical. A broadened emission line generally results in lower absorbance, poorer signal-to-noise ratio and greater calibration graph curvature.

Considerable research has gone towards developing more intense emission sources, either by increasing the output from the hollow cathode lamp (high intensity, or boosted, hollow cathode lamps) or by developing alternative emission sources to the hollow cathode lamp (electrodeless discharge lamps-EDL).



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The EDL works on a very different principle from the HCL. The iodide salt of the element of interest is sealed with a noble gas at reduced pressure in a quartz tube. Radiofrequency (rf) energy is used to form a plasma in the gas. The temperature of this plasma evaporates some of the salt which then dissociates to give atoms. The metal atoms are excited and emit light. The light emission is significantly higher than that of a standard HCL but there are some significant practical disadvantages:

- The lamps are difficult to stabilize
- Long warm up times are required
- The lamp current must be optimized manually
- A complex (and expensive) additional power supply is required

The rf generator the EDL requires is usually external to the instrument. The internal power supply for the conventional lamps is not used.

Two modifications to the conventional hollow cathode lamp design by Walsh and Sullivan increase the emission intensity by separating the sputtering process from the excitation process [4] within the lamp. A boosting discharge passes a stream of electrons and ions through the sputtered atom cloud to increase the photon output by exciting more atoms. A separate power supply provides the boosting current. Two circuit configurations have been commercialized. One configuration (as modified by Lowe) uses an anode common to both circuits. In this design, the boosting current passes directly through the region of the sputtering discharge and lowers the number of sputtered atoms available for excitation. Hence each lamp has its own optimum boosting current which must be determined by the operator. This is obviously not amenable to automation.

The other design (commercialized as "UltraA") is shown in Figure 1. UltraA lamps have an electron source and a secondary anode in addition to the anode and cathode of a conventional lamp. The hollow cathode current is supplied by the instrument in the normal manner. The boosting current is fixed. This two anode lamp design has a number of advantages:

- The sputtering and excitation processes are separated
- The same boosting current may be used for every lamp
- The instrument can fully control the lamp's operation

UltraA lamps are installed in the lamp turret in the same way as are conventional (SpectrAA) lamps, and have lamp recognition so the instrument can automatically select the lamp and set the correct lamp current. The external module supplying the required boost current is able to power two lamps at the same time.

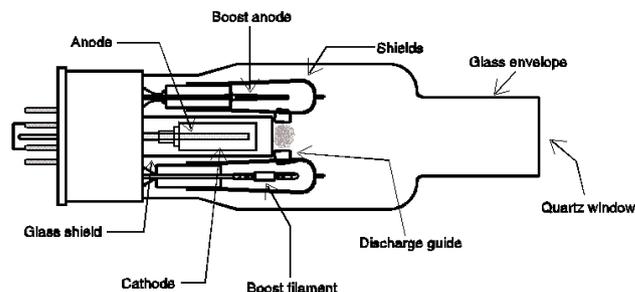


Figure 1. Schematic of UltraAA lamp.

Experimental

Instrumentation

An Agilent SpectrAA-880Z atomic absorption spectrometer with Zeeman background correction, fitted with a PSD-100 sampler, was used. The instrument was modified so both the UltraAA control module and a module for the commercial common-anode lamps could be connected. All lamps were new. Atomization was from the wall of a pyrolytic graphite coated partition tube. The inert gas was argon. Instrument parameters are the default settings for each element. The only changes were that the ash time was increased from one second to 10 seconds and 10 μL of chemical modifier was added to the sample.

Standards

Calibration standards were diluted from 1000 mg/L commercial standards (Merck) in Type I water with either dilute (0.1 M) hydrochloric acid (As, Se) or nitric acid (Pb). A working concentration of 50 $\mu\text{g/L}$ solution was prepared daily for As and Se.

Characteristic concentrations and limits of detection were determined using a 15 $\mu\text{g/L}$ solution. The working concentration of lead was 20 $\mu\text{g/L}$, and a 10 $\mu\text{g/L}$ solution was used when calculating characteristic concentrations and limits of detection.

For the determinations, a multi-element standard (Inorganic Ventures, Lakewood, NJ, U.S.A.) diluted to 100 $\mu\text{g/L}$ was used. A 10 $\mu\text{g/L}$ standard was included with the samples.

Samples

The samples were certified reference materials and are summarized in Table 1. They were chosen because they are supplied in liquid form and no digestion is required.

Table 1. Certified Reference Materials Used, and Their Sources

Certified reference materials

National Institute of Standards and Technology, Gaithersburg, MD, U.S.A. - SRM 1643c Trace elements in water
 High Purity Standards, Charleston, SC, U.S.A. - CRM-TMDW Trace metals in drinking water
 CRM-TMF Trace metals in fish

Modifiers

Chemical modifiers were used to stabilize the volatile elements. Reduced palladium (500 mg Pd/L with 2% w/v citric acid) was used for arsenic and selenium. Diammonium hydrogen orthophosphate (2 g/100 mL solution) was used for lead.

Results and Discussions

Typical signal graphics for the UltrAA lamp are compared with those from a conventional lamp in Figure 2. The performance of the UltrAA lamp is compared with that of the equivalent standard hollow cathode lamp and of the common-anode design lamp, for arsenic, selenium and lead. The arsenic, selenium and lead calibration graph for peak area of the appropriate conventional lamp is overlaid with the corresponding graph of the UltrAA lamp in Figures 3, 4 and 5, respectively. For all elements the slopes of the calibration graphs from the UltrAA lamps are greater than those from the corresponding conventional lamps. Not only are the absorbances higher for the UltrAA lamps but the graphs are also more linear. The explanation for this is presumably that the analytical emission line from the UltrAA lamps is narrower. The characteristic concentration (and mass) is that which is required to give 0.0044 absorbance (1% absorption) and the smaller the concentration the better the sensitivity. The calibration graphs for arsenic and lead with the conventional lamps show marked curvature.

This means the characteristic concentrations of the conventional and UltrAA lamps in Table 2 are not as different as the higher absorbances might suggest. The performance of the UltrAA lamps overall is markedly better than that of the corresponding conventional lamps.

Table 2. Characteristic Concentrations ($\mu\text{g/L}$) for Hollow Cathode Lamp of Different Designs. Characteristic Concentration is Defined as Giving 0.0044 Absorbance. Sample Volume was 20 μL .

Element	W'length (nm)	Current (mA)	Characteristic concentrations ($\mu\text{g/L}$)		
			UltrAA lamp	Conv. lamp	Common anode lamp
As	193.7	10	0.25	0.31	0.28
Pb	283.3	5	0.15	0.26	0.27
Se	196.0	15	0.49	2.20	0.75

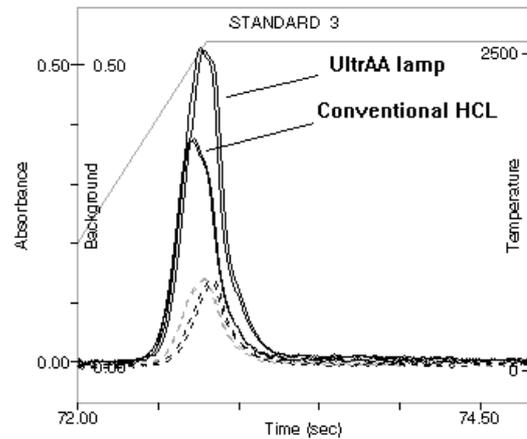


Figure 2. These signal graphics for a 75 $\mu\text{g/L}$ Se standard demonstrate the enhanced sensitivity of the UltrAA lamp compared to a conventional lamp.

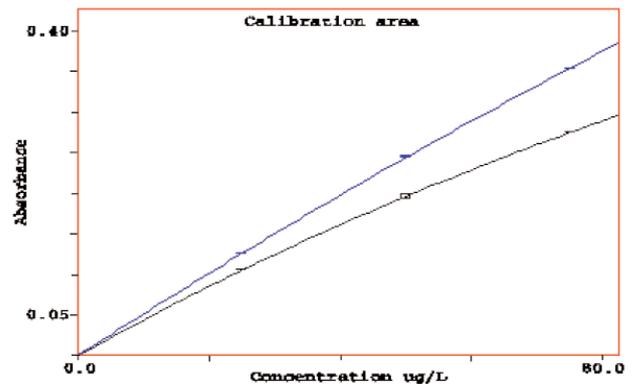


Figure 3. Comparison of arsenic peak area calibration graphs for UltrAA and conventional lamps. Upper line is for UltrAA; lower line is for conventional.

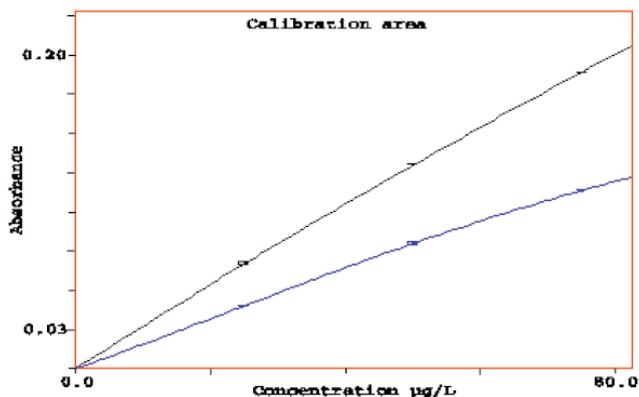


Figure 4. Comparison of selenium peak area calibration graphs for UltrAA and conventional lamps. Upper line is for UltrAA; lower line is for conventional.

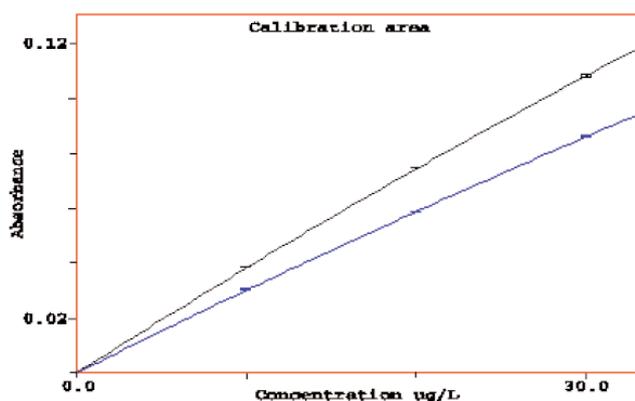


Figure 5. Comparison of lead peak area calibration graphs for UltrAA and conventional lamps. Upper line is UltrAA; lower line is conventional.

Limit of detection is defined as the concentration of a solution which gives an absorbance equal to three times the standard deviation of the blank absorbance. Thus limit of detection is a measure of noise and sensitivity. The UltrAA lamps give a higher signal-to-noise ratio for all elements and produce a better limit of detection, as shown in Table 3.

Table 3. Limits of Detection ($\mu\text{g/L}$) Measured Using Lamps of Various Types. Fifteen Blank Readings Using a Sample Volume of $20\ \mu\text{L}$ Were Made.

Element	W'length (nm)	Current (mA)	Limits of detection ($\mu\text{g/L}$)			EDL [5]
			UltrAA lamp	Conv. lamp	Common anode lamp	
As	193.7	10	0.26	1.40	1.65	1.0
Pb	283.3	5	0.18	0.80	1.75	0.15
Se	196.0	15	0.29	3.10	0.67	0.8

The certified reference material results are shown in Table 4. The UltrAA lamps are capable of producing accurate results, based on the certified values.

Table 4. Sample Results Using UltrAA Lamps for Arsenic, Selenium and Lead. Spread is Based on Sample/Duplicate Results with Two Replicates Each. Sample Volume was $10\ \mu\text{L}$.

Element	Sample	Found	Certified	Units
Arsenic	NIST 1643c	82.3 ± 0.3	82.1 ± 1.2	$\mu\text{g/L}$
	CRM-TMDW	79.8 ± 0.9	80.0 ± 0.4	$\mu\text{g/L}$
	CRM-TMF	96.9 ± 0.5	100.0 ± 0.5	mg/L
	10 $\mu\text{g/L}$	10.2 ± 0.4	10.0 ± 0.1	$\mu\text{g/L}$
Selenium	NIST 1643c	12.5 ± 0.3	12.7 ± 0.7	$\mu\text{g/L}$
	CRM-TMDW	9.4 ± 0.1	10.0 ± 0.1	$\mu\text{g/L}$
	CRM-TMF	9.4 ± 0.4	10.0 ± 0.1	mg/L
	10 $\mu\text{g/L}$	9.7 ± 0.1	10.0 ± 0.1	$\mu\text{g/L}$
Lead	NIST 1643c	36.7 ± 0.0	35.3 ± 0.9	$\mu\text{g/L}$
	CRM-TMDW	35.9 ± 0.2	35.0 ± 0.2	$\mu\text{g/L}$
	CRM-TMF	8.6 ± 0.1	10.0 ± 0.1	mg/L
	10 $\mu\text{g/L}$	9.4 ± 0.2	10.0 ± 0.1	$\mu\text{g/L}$

Summary

The UltrAA lamp design gives consistently better analytical performance than the corresponding conventional hollow cathode lamp. The linearity of the calibration graphs provides indirect evidence that the emission line characteristics are improved. The more intense emission line means there are more photons per unit time; hence the noise associated with the random arrival of photons at the photomultiplier tube is less, which in turn produces less background noise and better limits of detection. The narrower emission line enhances the sensitivity.

In addition to the benefits of improved limits of detection and enhanced sensitivity, the UltrAA lamps offer the same simplicity and ease of use as the conventional SpectrAA hollow cathode lamps.

Acknowledgments

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References

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