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THE TESTING OF ATOMIC ABSORPTION SOURCES

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The study was undertaken to compare the light sources of atomic absorption spectrometry for flame and furnace analysis. The hollow cathode lamps and boosted discharge lamps for determination of Se, As, Cd and Pb were tested. The main analytical characteristics as baseline noise, sensitivity, detection limits and linearity of calibration curves were mesured. The significant gains in measurements of noise, sensitivity and linearity of calibration for Cd and Pb for discharge boosted lamps were observed.

Introduction

Sensitivity, detection limit and linearity of calibration curves are the main characteristic criteria of atomic absorption spectrometry. The characteristic criteria rely on the light source, which provides an emission spectrum specific to the element of interest. The sensitivity of method is virtually independent of the absolute strength of the line emitted by spectral line source. 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 has a low intensity, the baseline noise is increased. If the source has a wide line width or a complex spectrum, the calibration becomes non-linear. Generally, increase of linearity has plenty of advantage:

- it widens working place
- linear calibration is essential for successful use of the standard additions technique in wider range of absorbance values. Then the precision of method increases and dilution of samples is not needed.

At present the most common are hollow cathode lamps. 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. Fig. 1a shows a schematic diagram of a conventional hollow cathode lamp.

The main disadvantages are a low intensity for some elements and also widening of spectral lines of high vapour pressure elements such as arsenic, selenium, lead ... These problems are solved by an electrodeless lamp, which emits resonance line one order more intense. Unfortunatelly, the electrodeless lamps have shorter lifetimes, need a special energy source and are more expensive.

A solution to these problems is presented by the "boosted discharge lamp", which was described by Sulivan and Walsh[1] at first. Their new type of atomic spectra lamp emited some hundred times more intensely than conventional hollow cathode lamps. This enhanced intensity was obtained without any increase in line width. The essential feature of this new lamp was the use of a discharge to produce an atomic vapour by cathodic sputtering, and the excitation of this vapour in the positive column of a second discharge, which is electrically isolated from the first discharge.

A modified version of the Sulivan- Walsh type of high intensity hollow cathode lamp was developed as a source for flame atomic fluorescence. Measurements for several elements shawed that this type of lamp in which the secondary discharge passes through the centre of the open-ended cylindrical cathode, gave fluorescence signals several times greater then conventional hollow cathode lamp.

Other authors described high intensity lamp, e.g. West and Williams[3,4] investigated the atomic fluorescence characteristic of magnesium and silver in detail with high intensity hollow cathode lamps as excitation sources. Manning and Heneage[5] used this lamp for several other elements.

The main promblems of this "boosted discharge lamp" were a very short lifetime and instability of signal. Further evolution brought the new Photron Super Lamp, whose lifetime is approximately twice that of hollow cathode lamp and the instability of signal is similar to that of the hollow cathode lamp.

The new Photron design provides a second discharge between a special emission source and the anode, passing through the cylindrical cathode. The electron produced excite the excess ground state atoms, thus increasing lamp intensity and enabling the use of higher currents without the efects of self-absorption or line broadening. The new lamp is shown schematically in Fig. 1b.

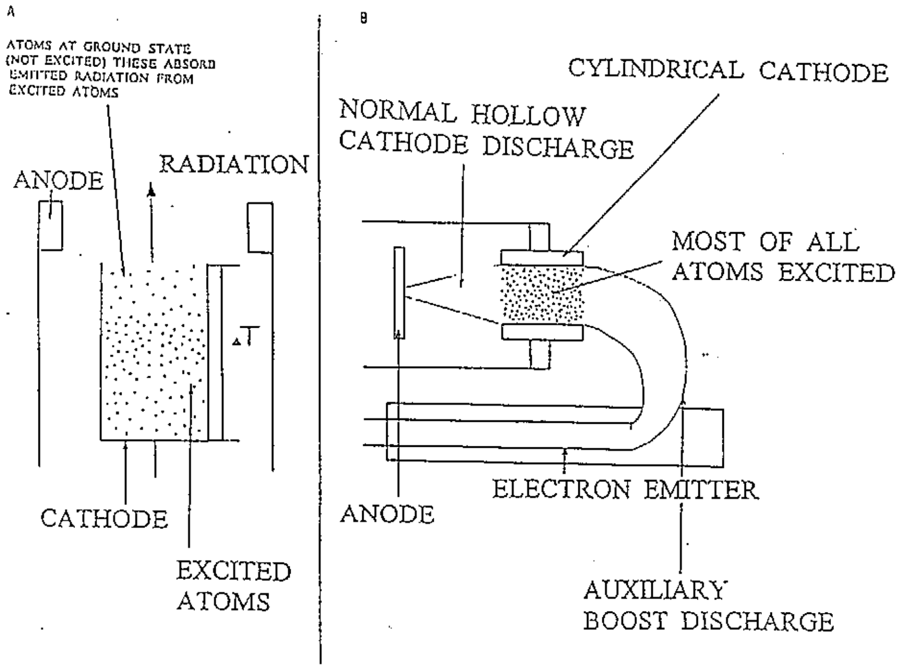

Fig. 1 Schematic diagram of a conventional hollow cathode lamp (a) and a Photron Super Lamp (b)

Experimental

Instrument Parameters

The atomic absorption spectrophotometer AAS3 (Carl Zeiss Jena, Germany), equipped with ETA EA3 (Carl Zeiss Jena, Germany), pyrolytical coated furnace

(VEB Electrokohle Lichtenberg, Germany) were used. GBC 906AA Elite spectrometer was used for comparison determination of lead.

Hollow cathode lamps (HCL) for Pb, Cd (Narva, Germany), As (SpectrAA Lamp Varian, Australia), Se (Rank Hilger, U.K.) in comparison with Photron Super Lamp As, Se, Cd, Pb (Australia) were used.

Reagents

Stock standard solutions As, Se, Cd, Pb (Analytica 1.000 g/l, Czech Republic). Matrix modifier for arsenic and selenium was prepared from standard nickel nitrate (Analytica 1,000 g/l, Czech Republic).

All stock standard solutions were diluted stepwise to obtain working standard solutions and these solutions were acidified to obtain a medium of 0.2 mol dm^{-3} HNO_3 (Suprapur Merk, Darmstadt, Germany). Water was purified using MilliQ+ water purification system (Milipore, Bedford, USA).

Parameters of analysis

Hollow cathode lamp and Super Lamp were operated at the wavelengths of 228.8 nm (Cd), 217 nm (Pb), 196 nm (Se), 193.7 nm (As) with spectral bandpass 0.2 nm (Cd), 0.3 nm (Pb), 0.3 nm (Se), 0.3 nm (As).

The Cd and Pb lamps were tested by flame analysis (acetylene-air flame, integration time 2 s).

The Se and As lamps were tested by the graphite furnace analysis. The thermal program was optimized for Ni modifier and the optimum conditions are summarized in Table I.

Table I The optimum conditions for electrothermal atomizer EA3

Parameter	Arsenic	Selenium
Charging temperature, °C	800	900
Atomizer temperature, °C	2200	2300

Results

It was necessary to optimize the working conditions to test the parameters of measurement, because there is not much information about these Super Lamps in literature.

Intensity

The super Lamp provides a high intensity output without any increase in line width. Table II shows the relative intensity gains of the Super Lamp over a standard hollow cathode lamp. The ratio of intensity is different from element to element. The maximum increase of intensity was observed with Super Lamp for cadmium.

Table II Intensity of HCL and Super Lamp

	Curremt, mA HCL	Current, mA SuperL	Intensity improvement HCL/SuperL
Cd	3	10/15	73
Pb	4	10/20	47.5
Se	13	18/50	15
As	10	25/50	7.5

Long-term Stability - drift

The drift was tested during a two-hour interval, the measurement was repeated each minute and the later each 10 minutes. In Fig. 2 we can see that the long stability of Super Lamp and standard hollow cathode lamp are similar.

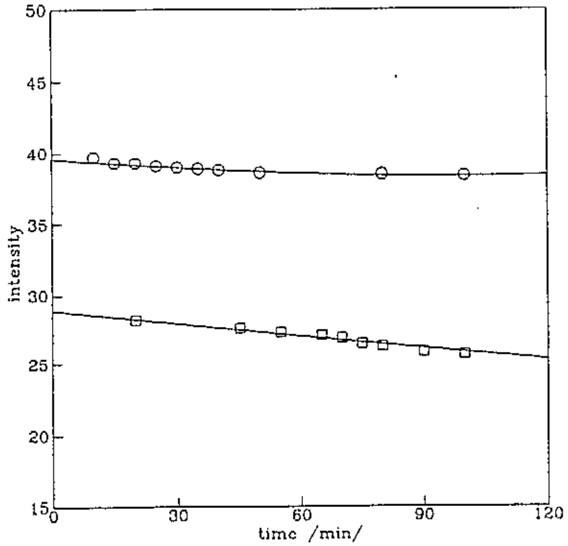

Fig. 2 Long-term stability of hollow cathode lamp (□) and Super Lamp (○)

Short-term Stability - noise

A noise of signal of absorbance has a great influence on quality of results, especially on the detection limits.

Table III shows the great improvement achieved in the determination with the Zeiss spectrometer where there is a significant loss of light. The maximum improvement was in the measurement of lead (this is connected with the wavelenght of measurement). The improvement of measured value of lead is lower with the GBC spectrometer which is connected with a small loss of light in optics of spectrometers. That means that the increase of intensity has no significant influence on the noise.

Table III Relative standard deviation: integration time 0.5 s and n = 250

	Current, mA HCL	Current, mA SuperL	RSD HCL	RSD SuperL	RSD improvement HCL/SuperL
Cd	3	10/15	5.5	2.19	2.5
Pb /1/	4	10/20	6.3	0.19	33
Pb /2/	4	8/15	0.84	1.44	1.7
Se	13	18/50	4.37	1.3	3.3
As	10	25/50	5.5	1.5	3.8

A critical situation is encountered in the determination of arsenic by electrothermal atomization with double beam spectrometers. A graphical comparison of analyte peaks of 100 pg As, which were measured with HCL (A) and Super Lamp (B) is shown in Fig. 3 and can demonstrate magnificent influence of Super Lamp.

Calibration

The calibration measurements were carried out in the largest possible interval of absorbances (limited by the apparatus output). The linear region of calibration was obtained with the use of statistic F-test (p = 0.95) for the respective squared values of parameter s_{xy} (program ADSTAT). The testing was based on comparison of the parameter s_{xy} for linear and non-linear insets calibrations with gradual cut of points. The linear part can be used when the parameter s_{xy} of calibration linear regression equation is statistically in agreement with the parameter s_{xy} which was obtained with quadratic polynomial regression equation.

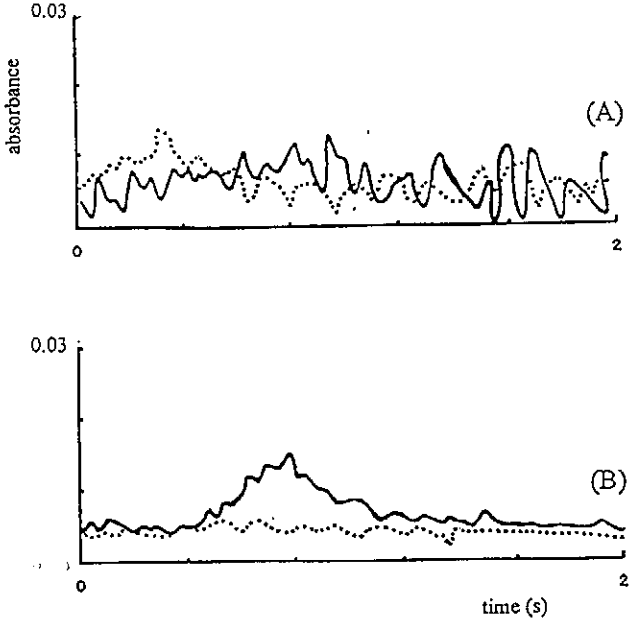

Fig. 3 Graphical comparison of analyte peaks of 100 pg As for HCL (A) and Super Lamp (B)

In Figs 4 - 7 we can see the calibration curves for selenium, arsenic, lead and cadmium. Generally, Super Lamp increases the linearity of calibration. In the cases of arsenic and selenium the improvement is not so great, because these elements were determined by the graphite furnace analysis with manual sampling. On the other hand, lead and at conditions different from those recommended by the manufacturer. Particularly for cadmium we obtained interesting results: the linearity of calibration extends up to the absorbance value of 2.3.

Lead was determinated on the GBC spectrometer (Fig.8) with positive results, too. In the measurement we found a lower interval of linearity of calibration, but a distinct increase of sensitivity in comparison with the Zeiss spectrometer. The difference between the results obtained with the Zeiss and GBC spectrometers is probably due to different frequences (50 and 200 Hz, respectively) of electric modulation of their lamp signals.

Sensitivity

The atomic absorption specrometry uses the quantity of characteristic concentration (for flame analysis), or mass (for electrothermal analysis) to express the sensitivity of measurement. The characteristic concentration (Table

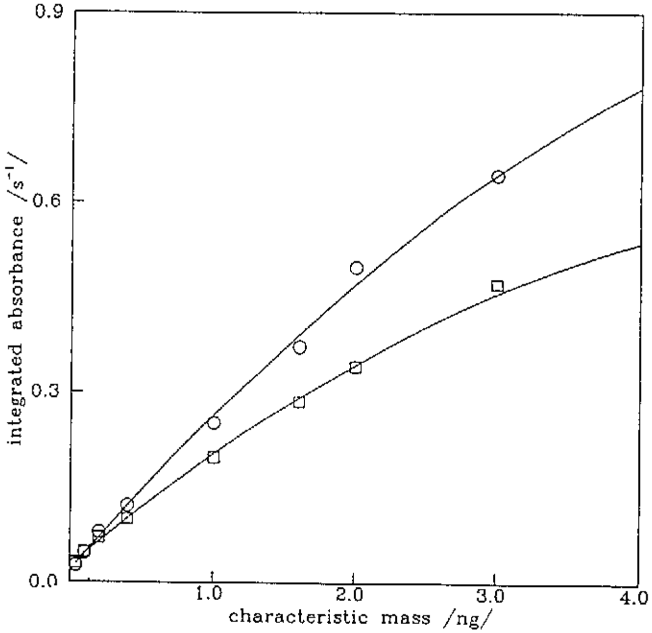

Fig. 4 Calibration curves for arsenic: current of HCL 10 mA (□), current of Super Lamp 25/50 mA (○)

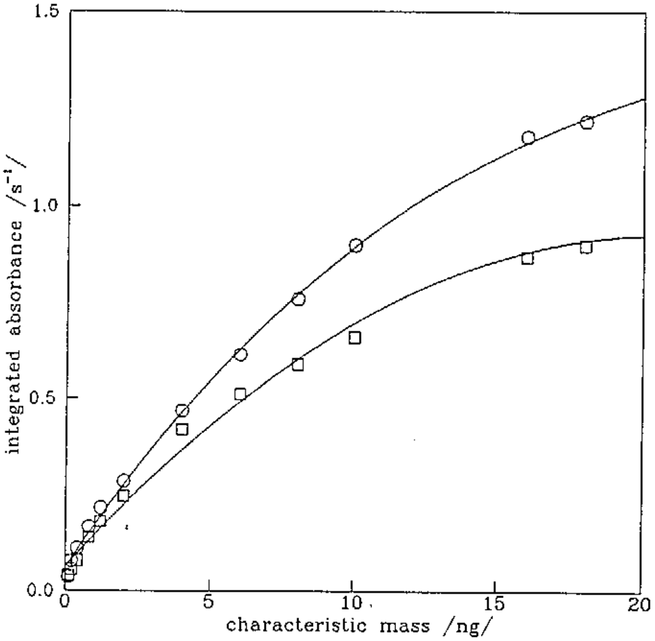

Fig. 5 Calibration curves for selenium: current of HCL 13 mA (□), current of Super Lamp 25/50 mA (○)

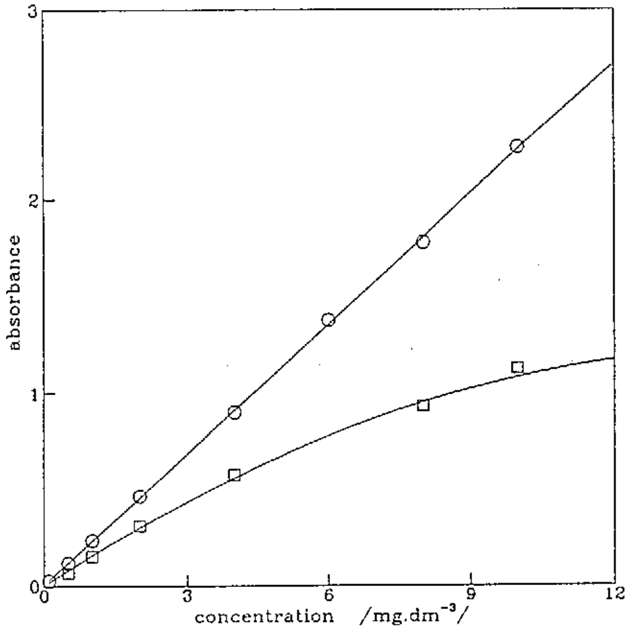

Fig. 6 Calibration curves for cadmium: current of HCL 3 mA (□), current of Super Lamp 6/20 mA (○)

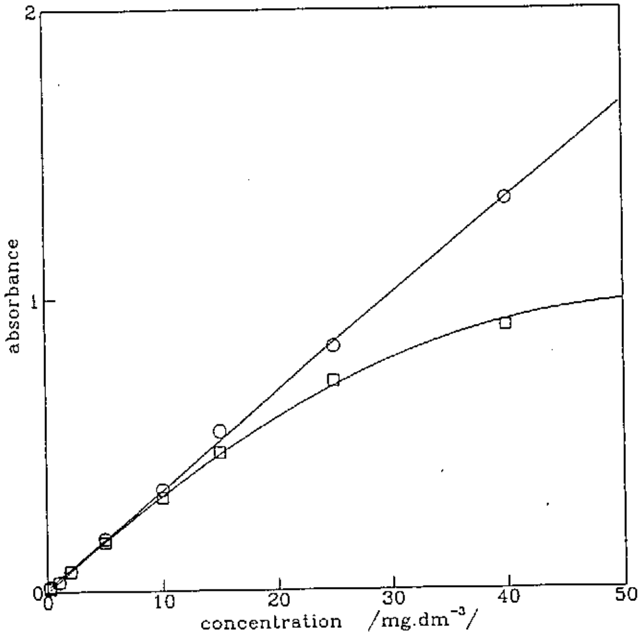

Fig. 7 Calibration curves for lead measured on the Zeiss spectrometer: current of HCL 4 mA (□), current of Super Lamp 6/20 mA (○)

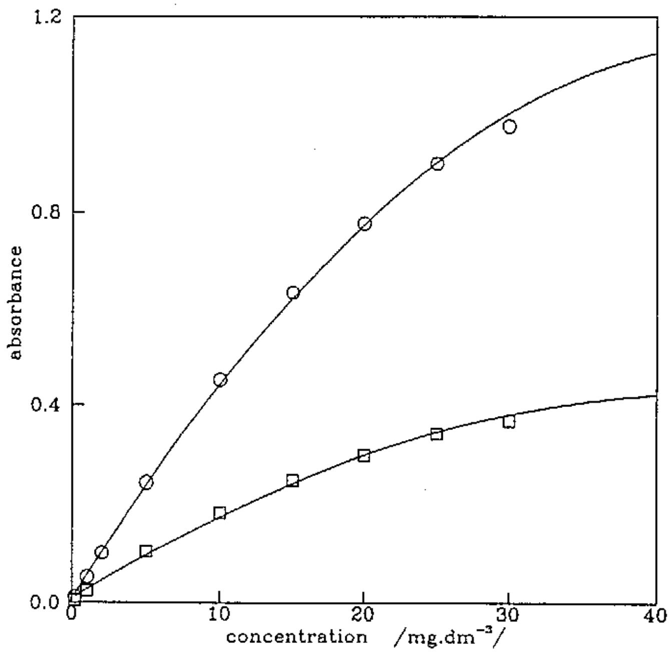

Fig. 8 Calibration curves for lead measured on the GBC spectrometer: current of HCL 4 mA (□), current of Super Lamp 7/15 mA (○)

IV) and characteristic mass (Table V) were calculated from the linear parts of calibration curves, they correspond to the absorbance value of 0.0044.

Table IV Characteristic concentration: the Cd/1/ value was measured at the optimum conditions for linearity of calibration and Cd/2/ value for the maximum sensitivity. The Pb/1/ and Pb/2/ values were measured on the Zeiss and GBC spectrometers, respectively

	Current, mA HCL	Current, mA SuperL	Sensitivity HCL	Sensitivity SuperL	Sensitivity improvement HCL/SuperL
Cd/1/	3	6/20	0.03	0.019	1.42
Cd/2/	3	2/15	0.03	0.016	1.69
Pb/1/	4	6/20	0.14	0.132	1.07
Pb/2/	4	7/15	0.22	0.092	2.35

Table V Characteristic mass

	Current, mA HCL	Current, mA SuperL	Sensitivity HCL	Sensitivity SuperL	Sensitivity improvement HCL/SuperL
Se	10	18/50	1.69	1.51	1.12
As	13	25/50	1.46	0.97	1.50

In all the casses we observed a higher sensitivity when using the Super Lamp. In the flame analysis a significant increase of sensitivity was monitored for lead on GBC spectrometer (an increase of 135%). In the case of cadmium we observed, that the change in conditions of current increases the sensitivity of measurement, but the linearity of calibration is lowered.

Detection Limit

Blanks cannot be added to the calibration curves according to statistic *t*-test. This test is based on a comparison of the standard deviation of blank and standard deviation of set of calibration points, which were not in agreement. That is why the absorbance of small concentration was used for the calculation of detection limit which is a treble of standard deviation of this concentration. Comparisons of these detection limits are shown in Tables VI and VII.

Table VI Detection limits for flame analysis: The Pb/1/ and Pb/2/ values were measured on the Zeiss and GBC spectrometers, respectively

	Current, mA HCL	Current, mA SuperL	Det. limit HCL	Det. limit SuperL	Det. limit improvement HCL/SuperL
Pb/1/	4	6/20	1.13	0.24	4.7
Pb/2/	4	7/15	0.12	0.03	4.3
Cd	3	2/15	0.03	0.02	1.5

Table VII Detection limits for furnace analysis

	Current, mA HCL	Current, mA SuperL	Det. limit HCL	Det. limit SuperL	Det. limit improvement HCL/SuperL
As	10	25/50	32.80	18.8	1.75
Se	13	18/50	68.30	64.8	1.05

Conclusion

The newly designed 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 limits 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.

The most significant contribution of this work is a finding that frequency of electrical modulation has a great effect upon the linearity of calibration.

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