Developments in Hollow Cathode Lamps

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Atomic absorption spectrometry has been an extremely popular analytical technique for the last 40 years but one of its limitations is that it is essentially a single-element technique. It is necessary to have a hollow cathode lamp for each element and to change lamps whenever a new element is to be determined.

Recently the use of multi-element single-cathode lamps has increased considerably in an attempt to reduce the number of lamps which need to be fitted to the spectrometer and to increase the speed of analysis.

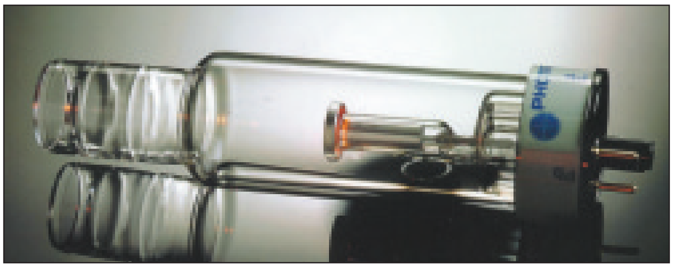

Figure 1. *Photo of single-cathode multi-element lamp*

A multi-element lamp is constructed in the same way as a single element lamp. That is, a cathode in the shape of a hollow cylinder surrounded by a glass envelope. The difference is that the cathode contains more than one element — usually between two and six. There is usually little loss of performance with two elements, but when six elements are included in a single cathode the performance loss can be significant.

Limitations of a Single-Cathode Multi-Element Lamp

Since there are far fewer atoms of each element, it is inevitable that the intensity of the light emitted by each element will be significantly less than that from a standard single-element lamp. This lower intensity leads to higher baseline noise levels and poorer detection limits.

Since there are many more spectral lines being emitted by a multi-element lamp, it is more likely that there will be interfering lines close to the analytical wavelength. Such nearby lines lead to poorer sensitivity and a less linear calibration curve. The combination of a poorer detection limit and calibration curvature has the effect of reducing the range of concentrations that can be measured.

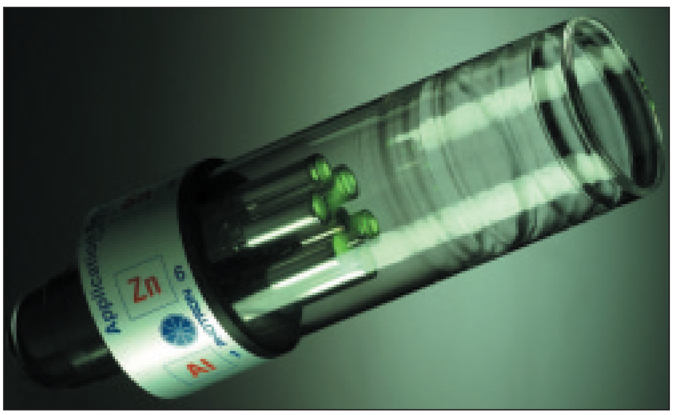

Figure 2. *Photo of six-cathode lamp*

Another limitation of the multi-element lamp is that the choice of elements is restricted. It is not possible for some element combinations to be combined in a single cathode. For example, arsenic and mercury are not compatible. In fact, most of the environmentally important toxic elements cannot be combined in a single cathode, either because of element alloy incompatibility or such low intensity due to instrument efficiency of spectral lines in the very short UV.

To retain the benefits of a multi-element lamp without the disadvantages, Photron has developed a multi-element lamp with six separate cathodes.

Each cathode is essentially the same as used in a single-element lamp and the six cathodes are housed in a single glass envelope, arranged in a circle around a common anode.

The majority of samples analysed by atomic absorption spectrometry require the determination of six elements or less.

Therefore, the major benefit of the six-cathode lamp is that most analysts will only require one lamp. The lamp can be customised for individual applications so analysts can choose which elements they require, with no restrictions whatsoever.

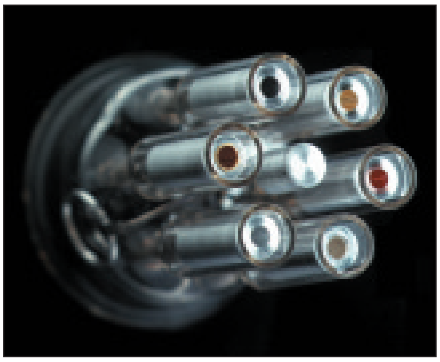

Figure 3. *Close-up photo of cathodes*

They may also select a set of dual-element cathodes providing analysis of up to 12 elements still as efficiently as a single-cathode lamp. There will be no need to change lamps and they will be able to use a lower cost atomic absorption spectrometer with no lamp turret or expensive lamp coding.

Figure 3 shows a close-up photograph of the lamp base with the six cathodes arranged in a circle around the common anode. You can see the different colours of the different elements. Starting with copper, silver, magnesium, gold, nickel and cadmium. Precise construction of these cathode electrodes means little or no optical alignment is needed. The lamp is simply rotated to each cathode.

Figure 4. *Photo showing lamp base assembly*

Figure 4 shows the lamp base vertically. Each cathode is wired separately so that power will not be applied to cathodes which are not in use. However, it is possible to have two cathodes powered so that a warm-up current can be applied to the next element in a multi-element analytical sequence.

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Atomic Absorption Performance

There are many factors that affect the performance of an atomic absorption analysis, including the design of the spectrometer's optical and atomisation systems.

Performance Criteria
• Intensity • Detection Limit
• Sensitivity • Lamp Life • Cost

Table 1. *Performance criteria*

One of the factors affecting performance is the quality of the hollow-cathode lamp and the criteria listed in Table 1 should be considered when selecting a hollow-cathode lamp. The intensity of the lamp will affect the noise level and the detection limit while the spectral purity will affect the sensitivity and calibration linearity.

The cost of the lamp and the length of time it lasts are clearly also important considerations.

Intensity Comparison

There is no reason why the intensity of the six-element lamp should be different from that of a single-element lamp. The data in Table 2 shows the range of intensities for at least seven 6-cathode lamps compared with a single-element lamp set to 100%. For aluminium, the 6-cathode lamps range from 94% to 115% of the intensity of a standard lamp. The other elements are similar — each batch of lamps showing intensities ranging from slightly below to slightly above the single-element lamp. There is always some variation in intensity between lamps and these differences are not significant.

Element	Intensity of 6-cathode lamp compared with standard lamp (100%)
Al	94-115%
Ca	90-108%
Fe	94-125%
Pb	94-125%
Ni	94-105%
Zn	95-105%

Table 2. *Intensity Comparison*

Characterisation Concentration

Table 3 shows the sensitivity, or characteristic concentration, measured with the six-cathode lamp compared with the characteristic concentration measured using a standard single element lamp. For aluminium, the 6-cathode lamp shows a slightly better characteristic concentration, arsenic and gold are slightly poorer while cadmium, lead and antimony are slightly better. The small differences between the two lamps are insignificant, as expected.

Element	6-cathode lamp	Standard lamp
Al	0.47	0.55
As	0.47	0.46
Au	0.09	0.08
Cd	0.008	0.009
Pb	0.055	0.06
Sb	0.17	0.26

Table 3. *Characteristic Concentration (mg/L)*

Detection Limit

The lamp intensity is a critical factor affecting the noise level and hence the detection limit. Table 4 shows the detection limits for six elements using a six-cathode lamp designed for environmental applications compared with six conventional single-element lamps. Arsenic showed a poorer detection limit with the six-cathode lamp while cadmium, mercury, lead, selenium and thallium all showed a better detection limit.

The nature of a detection limit measurement means that there is always some variation and the differences seen here are not considered significant.

Element	6-cathode lamp	Standard lamp
As	0.17	0.11
Cd	0.0022	0.0027
Hg	0.21	0.28
Pb	0.013	0.023
Se	0.10	0.22
Tl	0.018	0.035

Table 4. *Detection Limit (mg/L)*

Calibration Curve

Figure 5 shows calibration curves for chromium plotted with a standard lamp, a six-cathode lamp and a single-cathode multi-element lamp.

Since the single-cathode multi-element lamp has many spectral lines, there is potential for interfering lines to appear within the bandwidth of the monochromator. This leads to poorer sensitivity and more curvature of the calibration, as shown in this graph. Since the composition of the cathode in the six-cathode lamp is identical to that in a standard lamp, the calibration graph is identical.

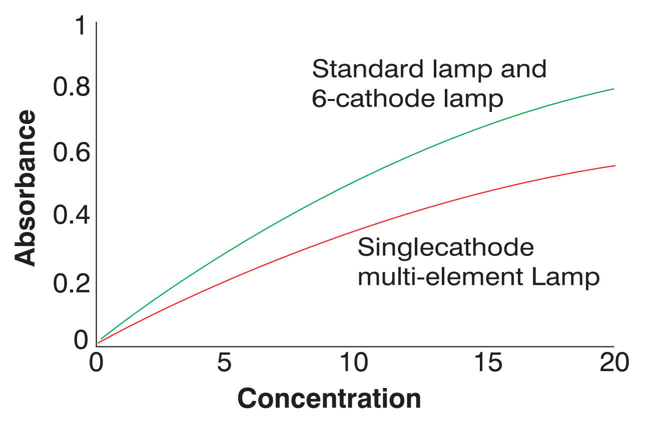

Figure 5. *Calibration graphs for Cr*

Potential Disadvantages

Photron has also investigated the possibility of increased spectral interference or cross-contamination by powering neighbouring cathodes containing elements with nearby spectral lines — aluminium/arsenic and selenium/iron. No interferences were observed. The possibility of cross-contamination between cathodes was also investigated.

There is some coating of neighbouring cathodes with the element from the operating cathode. However, this does not result in any spurious signal since sputtering occurs inside the cathode and the coating is on the outside.

Obviously any inter-element effect is insignificant compared to a single-cathode multi-element lamp where all elements are excited and are in the light path.

One obvious limitation is that the six-cathode lamp cannot be used with an existing atomic absorption spectrometer, so a new spectrometer is required.

In summary, Photron's atomic absorption light source with six cathodes in the one lamp offers benefits to the analyst including lower lamp costs, no constant changing of lamps and a lower cost spectrometer with no need for lamp turrets and coding circuitry. The new lamp offers the same performance as a single-element lamp in all respects and far better performance than a single-cathode multi-element lamp.

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