Practical Multi-Element Hollow Cathode Lamps for Atomic Absorption Spectrometry

Application Note

Atomic Absorption

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Introduction

Multi-element hollow cathode lamps have traditionally been considered inferior to single-element lamps for spectrochemical analysis by atomic absorption (AA). This publication examines some analytical figures of merit for selected elements in a variety of lamp combinations using flame atomic absorption spectrometry. The same elements are determined in a number of steel reference materials and samples, with similar results. Evidence is presented that well-designed multi-element lamps can give analytical performance at least as good as that of single-element lamps.

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What is a Hollow Cathode Lamp?

The primary requirement of a hollow cathode lamp is to generate a narrow emission line of the element that is to be measured. This line should be of sufficient spectral purity and intensity to achieve a linear calibration graph and low level of baseline noise [1].

A typical hollow cathode lamp construction appears in Figure 1.

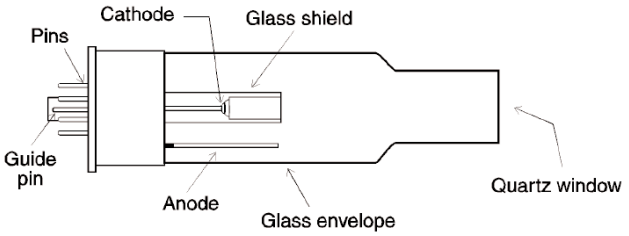

Figure 1: A typical hollow cathode lamp.

When a discharge occurs between two electrodes through a gas at low pressure, the cathode is bombarded by energetic, positively charged gas ions for example, ionized filler gas atoms. The energy of these ions is such that atoms of the cathode material are ejected or "sputtered" into the plasma. Here they may collide with other high-energy particles. These collisions result in a transfer of energy causing the metal atoms to become excited. The excited atoms relax back to their ground state, emitting radiation at the characteristic wavelengths of that element. For most elements, more than one analytically useful spectral line is generated [2].

Cathode Construction

The cathode is made from, or contains, the element of interest. If the metal is stable in air and has a high melting point, the pure metal may be used (for example Al, Cu, Ni, Fe). If it is brittle, a sinter of pressed metal powder is used (for example Mn, W) [2].

Single-Element?

The examples given have all been pure metals. If, however, a metal is reactive in air then the metal oxide or halide can be used (for example the Group IA and Group IIA metals). A metal with a relatively low boiling point or a relatively high vapor pressure (for example Hg, Cd, Pb, Zn) is usually alloyed with another metal.

Thus a number of lamps labeled as single-element lamps in fact contain more than one element. They are actually multi-element lamps.

Single-Element and Multi-Element

A common misconception is that single-element lamps always have a superior performance when compared with multi-element lamps, despite the fact that many "single-element" lamps are actually multi-element.

There are some reasons why this misconception may have arisen. The copper emission from a brass lamp, for instance, may not be quite as bright as that from a copper lamp. Another, more likely, explanation is spectral interference. Spectral interference is the overlap of an emission line of one element with the analytical emission line of another element. Examples are shown in Table 1. Constructing a "precious metals" lamp is clearly impractical. Even a relatively simple "electrum" lamp with just gold and silver would not be satisfactory. Emission lines from silver interfere with the analytical line of gold and, in turn, gold emission lines interfere with the silver analytical line. Such mutual interference is rare, usually only one element displays interference. The effect of spectral overlap is a calibration graph that is distinctly more curved than one generated using a lamp with no spectral interference.

*Table 1: Spectral Interferences in a Potentially Useful Combination of Elements [3] Bold: Analytical Line; Light Face: Spectral Interference(?); *: Ion Line*

Copper	Silver	Gold	Platinum	Palladium
324,754	324,755			
327,396	327,444			327,256*
	328,068	328,293	328,197	
242,444*	242,964*	**242,795**	242,820	
			242,804	
		267,595	267,715	267,958*
			267,457	
		265,943	**265,817**	265,872*
299,736		299,482*	**299,797**	
299,838				
	247,624*	247,604*		**247,642**
	244,973*			**244,791**

Why Use Multi-Element Lamps?

There are a number of reasons to use multi-element lamps. A laboratory that can consolidate its suite of analytical elements into a reduced number of lamps can achieve cost savings. It does not have to carry as many lamps either for operation or as spares. For example, it is possible to get as many as 15 elements (Co, Cr, Cu, Fe, Mn, Ni; Al, Ca, Mg; Na, K; Ag, Cd, Pb, Zn) in just four lamps.

Design Criteria for Multi-Element Lamps

For a designer of hollow cathode lamps, there are four main criteria to consider. The first, and foremost, is whether it satisfies a market need. The Ag/Cd/Pb/Zn lamp is useful for the environmental market, and the Co/Cr/Cu/Fe/Mn/Ni lamp meets the needs of the base-metal market.

The next condition is whether the proposed lamp displays spectral overlap. Proposed Al/Mo/Si/V and Ag/Au lamps failed in this regard and were not taken to the next stage.

The third criterion is whether the elements are compatible. Can they co-exist in the same cathode without undesirable side effects? This is not easy to predict. A further complication is that the cathode may initially appear suitable but not pass the life-time requirements. Lamp lifetime is guaranteed for 5 000 mA-hours, and to ensure this requirement is met prototype lamps must exceed this by at least 50%.

Finally, is the intensity of emission acceptable? Each analytical line has to be of a sufficient intensity to give acceptable levels of baseline noise.

The last two criteria can require iterative evaluations using prototype lamps. The cathode materials and their relative ratios require careful adjustment to get an optimum design lamp.

Case Studies

One compromise is the intensities of analytical lines from each of the elements in the lamp. The respective emissions of each element in the Co/Cr/Cu/Fe/Mn/Ni lamp are certainly less compared with each of the corresponding single-element lamps.

The Ag/Cd/Pb/Zn lamp does not compromise on intensity. Cd, Pb and Zn are present in the same amount as they are in the corresponding single-element lamp, and so the respective intensities are the same. The Ag is reduced but as its emission lines are very bright anyway, the reduction in intensity compared with the single-element equivalent is acceptable.

Both lamps do have minor spectral interferences. The benefits clearly out-weigh any effect of interference, to judge by the commercial success of each lamp.

Overcoming Interferences

Do the reduced emission and potential spectral interference effects have to be tolerated in multi-element lamps? The answer, perhaps surprisingly, is no they do not.

Applying a secondary discharge can enhance the performance of a hollow cathode lamp [4]. The discharge preferentially enhances the main analytical lines of the elements present in the lamp cathode. One such lamp design is shown in Figure 2.

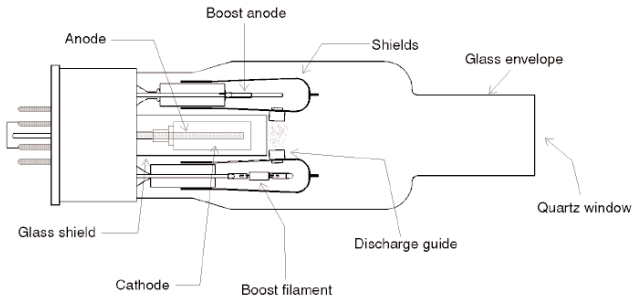

Figure 2: Design of a boosted discharge hollow cathode lamp (UltrAA).

There are a number of benefits with the boosted discharge lamps. The main one is that the respective element emission intensities are enhanced, especially the less intense Fe and Ni lines. As these lines are enhanced compared with other emission lines, calibration curvature is reduced. There is also an opportunity to use a wider slit, although this was not done in this study.

Experimental

The study was divided into two parts. First the lamps were all characterized for the elements under study using the main resonance lines and the respective recommended operating lamp currents.

Multi-element lamps are generally recommended for use with the main resonance line only. The steel samples could be measured using alternate lines for Cr, Mn and Ni. This allowed the performance of these lines also to be judged.

All reagents were supplied by BDH (Poole, England). Acids were AR grade.

Equipment

For this study, the following equipment was used:

- SpectrAA 220FS atomic absorption spectrometer
- UltrAA lamp control module
- SPS-5 Sample Preparation System with diluter

Sample Preparation

Two reference steel samples were used. These were NIST-348a (National Institute of Science and Technology, Gaithersburg, MD, U.S.A.) and BCS-336 (British Chemical Standards, Bureau of Analysed Samples Ltd, Teesside, England).

Steel turnings were sampled from Agilent Technologie's machine shop. These were 316 stainless steel and mild steel respectively. All samples were analyzed in duplicate and results averaged.

The samples were dissolved using a general method [5–8]. Each sample (0.1000 g) was accurately weighed into a beaker and 2 mL concentrated hydrochloric acid (32%) and 1 mL concentrated nitric acid (76%) added. When the reaction subsided, 2 mL of concentrated perchloric acid (70%) was added and the solution warmed until white fumes of perchloric acid appeared and the solutions became reddish-brown.

Warning: Observe all appropriate precautions when using perchloric acid and other concentrated acids.

Standards Preparation

The standards were prepared from stock 1000 mg/L AA standards using the SPS-5/diluter under SPS-RoboPrep software control.

Results and Discussion

All lamps used in the study of the steel samples were characterized by determining their respective limits of detection (Table 2) and characteristic concentrations (Table 3). Manufacturer's recommended operating conditions were used to make the determinations [9]. These are provided in the software.

Table 2 shows that multi-element lamps can produce, in many instances, limits of detection that are as good, if not better, than single-element lamps.

Table 2: 3σ Limits of Detection (µg/L) Measured Using Single-Element and Multi-Element Lamps
1: Ag/Cr/Cu/Fe/Ni
2: Ag/Cr/Cu/Fe/NiUltrAA
3: Co/Cr/Cu/Fe/Mn/Ni
4: Co/Cr/Cu/Fe/Mn/NiUltrAA
5: Co/Mo/Pb/Zn

		Lamp				
Element	**Single**	**1**	**2**	**3**	**4**	**5**
Co	5.1			9.9	9.9	7.7
Cr	12	33	39	22	15	
Mn	3.1			1.9	1.6	
Mo	30					17
Ni	34	22	29	15	16	

The characteristic concentrations in Table 3 show that for Co, Mn and Ni the values obtained with the single-element lamps are similar to those obtained with the multi-element lamps. There is a Mn(I) 357,788 nm line interfering with the Cr(I) 357,868 nm line [3] in the Co/Cr/Cu/Fe/Mn/Ni lamp. This is not removed or minimized by boosting the lamp. A similar effect is apparent with Ni in the same lamp (possibly a Cr 232.008 nm ion line on the Ni 232.003 nm line [3]), but in this case boosting does effectively minimize the interference.

Table 3: Characteristic Concentrations (µg/L) Measured Using Single-Element and Multi-Element Lamps
1: Ag/Cr/Cu/Fe/Ni
2: Ag/Cr/Cu/Fe/NiUltrAA
3: Co/Cr/Cu/Fe/Mn/Ni
4: Co/Cr/Cu/Fe/Mn/NiUltrAA
5: Co/Mo/Pb/Zn

		Lamp				
Element	**Single**	**1**	**2**	**3**	**4**	**5**
Co	52.7			69.7	56.5	51.8
Cr	101	95.9	71.6	141	134	
Mn	28.5			26.1	25.0	
Mo	300					245
Ni	55.9	57.7	59.2	74.4	58.9	

The instrument gains in Figure 3 can be used to compare lamp emission intensities, as intensity increases the required amplification, or gain, decreases. Relative intensities are displayed as the inverse of the photomultiplier gain, which was calculated from the displayed "% Gain" figures using proprietary conversion algorithms.

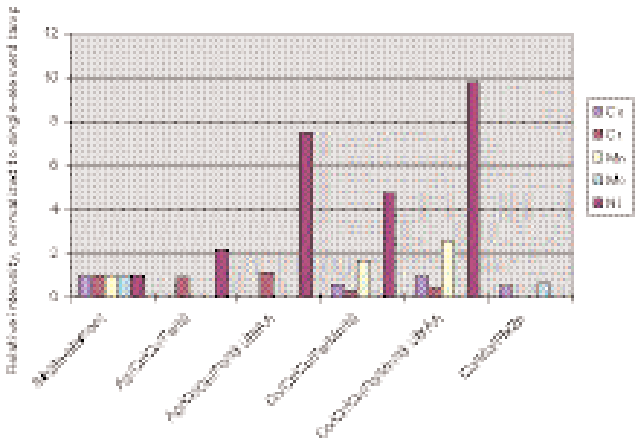

Figure 3: Instrument gain values (%) measured using single-element and multi-element lamps.

As expected, Co intensities in the multi-element lamps are lower compared with the single-element lamp. The boosted Co/Cr/Cu/Fe/Mn/Ni lamp has the same intensity as the single-element lamp.

Chromium in both the standard and boosted Co/Cr/Cu/Fe/Mn/Ni lamps has a lower intensity compared with the single-element lamp. This is interpreted as meaning the Cr emission line is not significantly enhanced by boosting. This is supported by a similar value for the standard and boosted Ag/Cr/Cu/Fe/Ni lamps. Interestingly, these values are the same as the single-element lamp.

Both Mn and Ni actually have higher emissions with the multi-element compared with the single-element lamp. In some cases this can be due to line broadening at the higher lamp current so that, although the emission is higher, the analytical performance is degraded. This does not appear to be the case here because each element shows similar characteristic concentrations for single-element and multi-element lamps.

Table 4 shows that nitrous oxide-acetylene flame was used to measure all elements. Although not all elements required such a flame, it was still used because it tends to reduce interferences present in such a matrix. It also provides an opportunity to use the fast sequential by element (FS) measurement mode. The FS mode of operation enables all the elements to be determined in each sample before analyzing the next sample.

Table 4: Experimental Conditions Used for fhe Analysis of Steel Samples

Property	Element				
Co	**Cr**	**Mn**	**Mo**	**Ni**	
Wavelength (nm)	240.7	428.9	403.1	313.3	352.5
Slit (nm)	0.2	0.2	0.2	0.2	0.2
Flame type	N_2O-C_2H_2	N_2O-C_2H_2	N_2O-C_2H_2	N_2O-C_2H_2	N2O-C_2H_2
Concentration range (mg/L)	10	150	20	60	150

The results for the each of the elements are displayed graphically in Figure 4 to Figure 8. Error bars representing the spread of data are included. Within experimental error, the results from the different lamps are consistent.

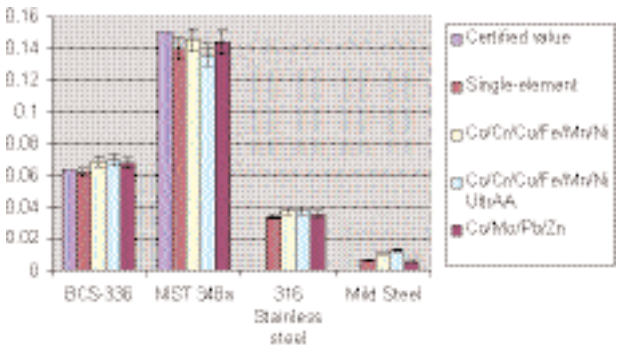

Figure 4: Concentration of Co determined in samples of steel, all values are percent by mass.

The results for Co in the reference materials agree within experimental error. The specifications for 316 stainless steel and mild steel do not have a Co value.

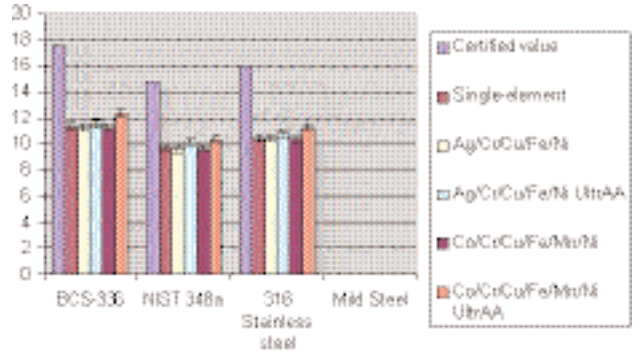

Figure 5: Concentration of Cr determined in samples of steel, *all values are percent by mass; 316 specifies 16.0–18.0%.*

The Cr results were all consistently low. Care was taken to ensure that the oxidation state of the samples and standards was chromium(VI). Chromium(III) standards were also tried with the same result. The poor recoveries indicate that the standards and samples were not matched. The same samples analyzed by the method of standard additions gave good results for Cr [5].

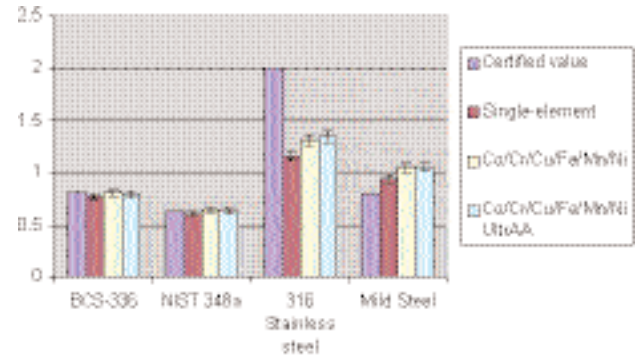

Figure 6: Concentration of Mn determined in samples of steel, all values are percent by mass; 316 specifies 2.0% maximum, mild steel 0.8–1.3%.

The Mn results are in very good agreement for reference materials and samples. The level in mild steel suggests that it is a "free cutting" steel that specifies 0.8–1.2%, or possibly a "free cutting carbon" steel that specifies 1.0–1.3%. It is not possible to give a definitive answer because the other elements specified are C, P, and S that are outside the scope of this publication.

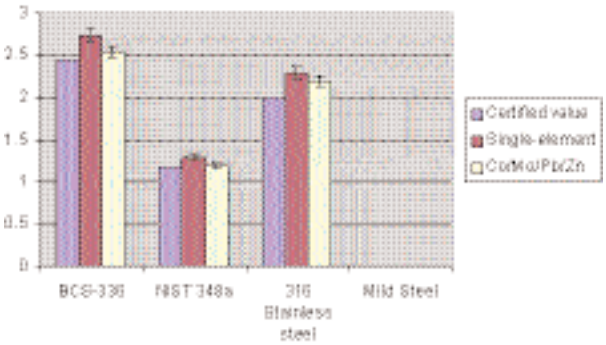

Figure 7: Concentration of Mo determined in samples of steel, all values are percent by mass.

The Mo results are slightly biased, irrespective of the lamp type.

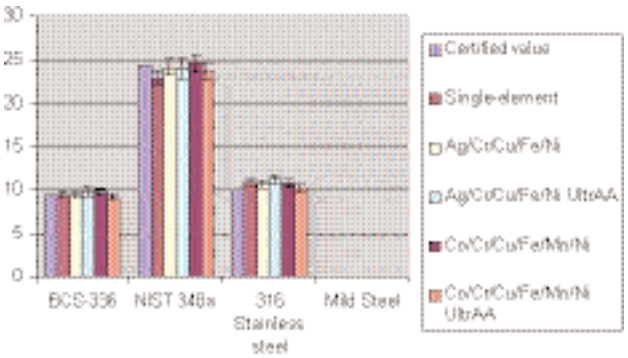

Figure 8: Concentration of Ni determined in samples of steel, all values are percent by mass; 316 specifies 10.0–14.0%.

The results for Ni in the reference materials agree within experimental error. The specifications for mild steel do not have a Ni value. The values for 316 stainless steel lie in the specified range of 10.0–14.0%.

This study has shown that results obtained using single-element and multi-element lamps are all very similar. The reference material results also demonstrate that either single-element or multi-element lamps can be used with good results.

Conclusion

Multi-element lamps can deliver performance similar to that of single-element lamps. There is some trade-off in calibration graph curvature and intensity of emission. In many instances, using the boosted discharge lamp can minimize the last two effects.

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