Hollow Cathode Lamps – Yesterday, Today and Tomorrow

Application Note

Atomic Absorption

Authors

Douglas Shrader
Jonathan Moffett
Graeme Plant
Barry Sturman
J. V. Sullivan

Introduction

Hollow cathode lamps are an essential component of an atomic absorption (AA) analysis system. Current indications suggest that they will continue to be an essential component for several years, at least. The analytical performance of an AA system can be limited by the performance of the hollow cathode lamp. This presentation reviews some of the relevant characteristics of hollow cathode lamps, and shows some of the improvements that have been made. Particular attention is given to multi-element hollow cathode lamps and to boosted discharge lamps.

Agilent Technologies

How do Hollow Cathode Lamps Work?

Construction

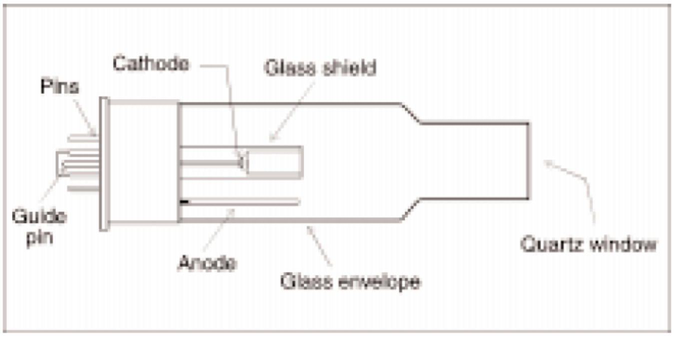

Figure 1. *A typical hollow cathode lamp.*

Hollow cathode lamps are essentially two electrodes enclosed in a low-pressure fill-gas. The cathode is made from the material that is to be determined. The fill-gas is either neon or argon. There is a two-step process to have light emitted.

Sputtering

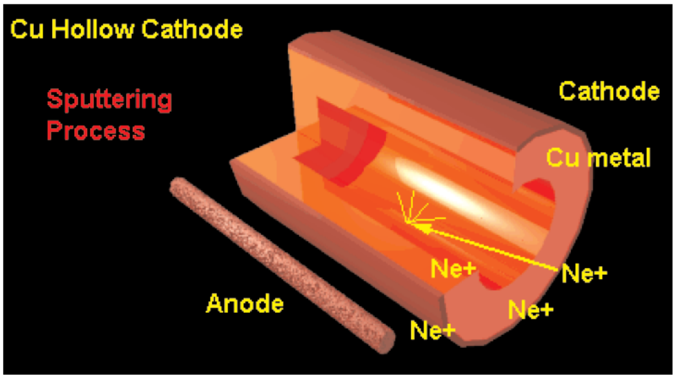

Figure 2. *A high voltage is applied across the electrodes. This ionizes the fill-gas. The ions are attracted to the cathode.*

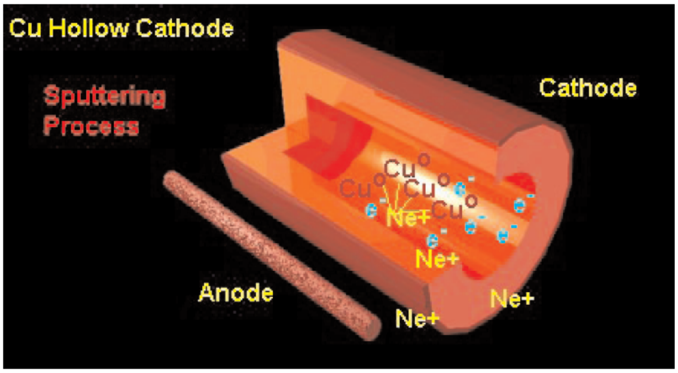

Figure 3. *The ions impact on the cathode surface and knock out metal atoms forming an atom plume.*

Excitation

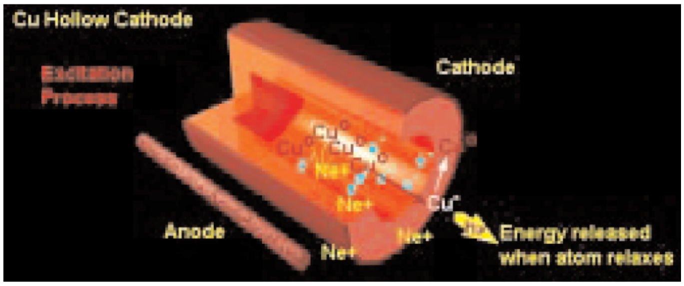

Figure 4. *The atoms in the plume are excited predominantly by interaction with metastable fill-gas atoms. The excited atoms subsequently relax emitting photons. The lamp construction ensures that sharp spectral lines are produced.*

Impact of Lamp Characteristics on Analytical Performance

If the intensity of the spectral line is too low, the noise performance of the instrument will be compromised by excessive photon shot noise. This arises from the random generation of electrons in the light detector.

If there is non-absorbable radiation within the spectral bandpass of the monochromator, the calibration curve will bend towards the concentration axis. This causes a loss of sensitivity at high absorbances.

Such non-absorbable radiation can result from:

- Presence of another spectral line within the spectral bandpass of the monochromator
- Presence of continuum background radiation
- "Self absorption" of the analytical line, whereby the central portion of the emission line is absorbed by ground-state atoms in the lamp.

If there were an absorbable line of another element within the spectral bandpass of the monochromator, that element would, if present in the flame or furnace, contribute to the total absorbance signal. The selectivity of the atomic absorption measurement would be compromised.

History

Development and manufacture of hollow cathode lamps in Australia began in the 1950s when the late Sir Alan Walsh and his colleagues at the Australian Government's Commonwealth Scientific and Industrial Research Organisation (CSIRO) developed atomic absorption spectrometry (AAS) for elemental analysis. The first commercial hollow cathode lamps to be made in Australia were produced in conjunction with CSIRO by the scientific glassware company Ransley Glass in Collingwood, near Melbourne, in 1963/64. The demand was so great that a separate company, Atomic Spectral Lamps, was formed to manufacture hollow cathode lamps. Both companies operated from the same factory in Collingwood. In 1965 Ransley Glass and Atomic Spectral Lamps merged with Techtron Pty Ltd, the Australian electronics company that had worked with CSIRO on the commercial development of AAS in Australia. Production of hollow cathode lamps continued in the Collingwood factory until 1967, when the operations were transferred to the Techtron factory in Springvale Road. In October, 1967 Techtron merged with Varian Associates (Agilent Technologies, 2010) of Palo Alto, California. Manufacture and development of hollow cathode lamps has been an important part of Agilent's atomic absorption instrument business ever since.

Boosted Discharge Lamps

These lamps, based on the work of CSIRO scientists J. V. Sullivan and the late Sir Alan Walsh in the mid 1960s [1], are similar to conventional hollow-cathode lamps in that an atomic vapor is produced in a hollow cathode by cathodic sputtering. Unlike conventional hollow-cathode lamps, these boosted discharge lamps employ a second discharge, electrically isolated from the sputtering discharge, to excite the sputtered atoms. The excitation process is thus independent of the sputtering process. In the conventional hollow-cathode lamp the only way to increase the intensity of the emitted light is to increase the lamp current. This causes more atoms to be sputtered. Radiation from excited atoms in the cathode can interact with unexcited atoms on its way out of the cathode, and resonance lines undergo selfabsorption. This can lead to curvature of atomic absorption calibration graphs. In the boosted discharge lamps the sputtered atoms are excited by the second discharge, independently of the sputtering process. This often leads to preferential excitation of the lines of analytical interest. Additionally, the radiation does not have to pass through a cloud of ground-state atoms on its way out of the lamp. Consequently there is less self-absorption and the calibration graphs are less curved.

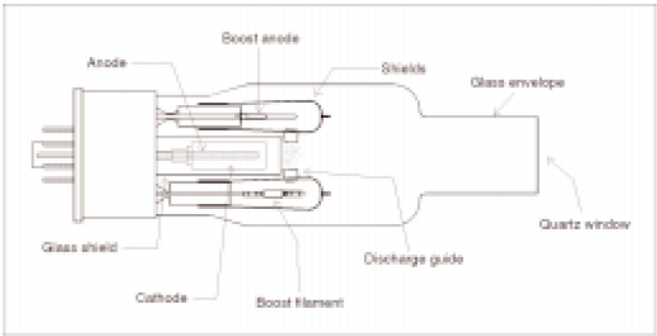

Figure 5. A diagram of a boosted lamp showing the additional circuit electrodes to boost the intensity.

Figure 6. The additional boosting circuit requires its own power supply.

Boosted Discharge Lamps Not Equally Effective for all Lines

Some analytical lines (for example, the 217.0 nm Pb line) are greatly enhanced in intensity in a welldesigned boosted discharge lamp. Other lines, such as the 422.7 nm Ca line and the 357.9 nm Cr line, show little or no increase in intensity. The 553.6 nm Ba line is actually reduced in intensity in a boosted discharge lamp. The reason for this is presumably that the excitation conditions in the boosted discharge promote the excitation of other lines of these elements at the expense of the lines of analytical interest.

Examples of Boosted Discharge Lamps

Multi-element

Ag/Cd/Pb/Zn	Silver/Cadmium/Lead/Zinc
Al/Ca/Mg	Aluminium/Calcium/Magnesium

Single element

As	Arsenic	Mn	Manganese
Au	Gold	Pb	Lead
Bi	Bismuth	Se	Selenium
Co	Cobalt	Si	Silicon
Cu	Copper	Sn	Tin
Fe	Iron	Te	Tellurium
Ge	Germanium	Tl	Thallium

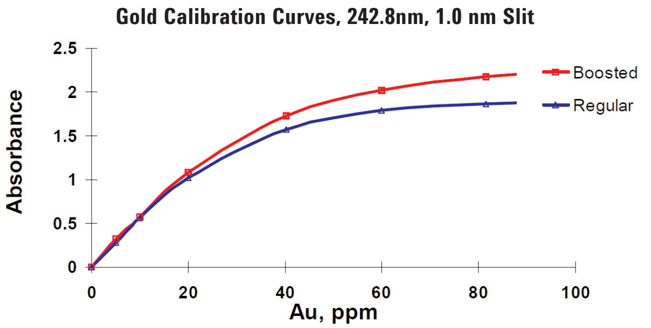
Gold Calibration Curves, 242.8nm, 1.0 nm Slit

Figure 7. The calibration curves for the determination of gold by flame AAS with an air-acetylene flame. The curve obtained with the boosted discharge lamp is much less "flattened" at high absorbance values. At low absorbances the curves are very similar. Both lamps were operated at 4 mA; the boosted discharge lamp was 4.7 times as bright as the regular hollow cathode lamp at the 242.8 nm gold line.

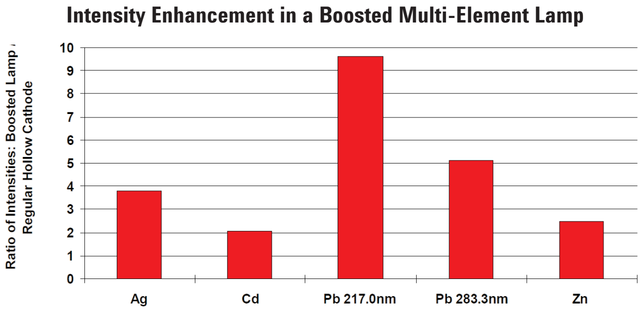
Intensity Enhancement in a Boosted Multi-Element Lamp

Figure 8. The increase in spectral line intensity achieved with a boosted discharge lamp, compared to a conventional hollow cathode lamp having a cathode made of the same material. Analytical lines were: Ag 328.1 nm, Cd 228.8 nm, Pb 217.0 nm and 283.3 nm, and Zn 213.8 nm. Note the great enhancement for the Pb lines.

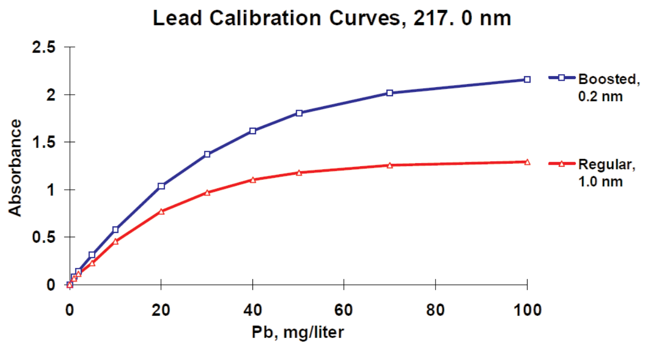
Lead Calibration Curves, 217. 0 nm

Figure 9. The improvement in sensitivity that can be achieved with a boosted discharge lamp, compared to a conventional hollow cathode lamp having a cathode made of the same material. Both lamps were operated at 5 mA. A spectral bandpass of 0.2 nm was used for the boosted lamp, while a spectral bandpass of 1.0 nm had to be used for the regular hollow cathode lamp to obtain the same detected light intensity.

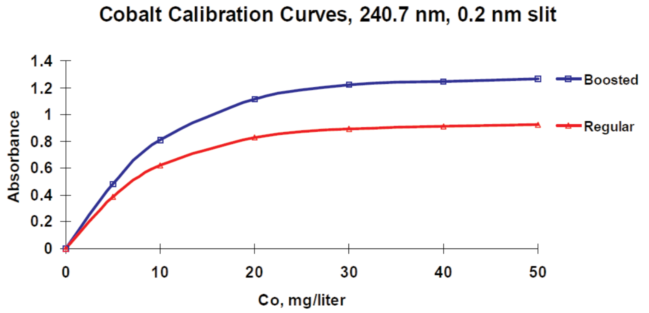
Cobalt Calibration Curves, 240.7 nm, 0.2 nm slit

Figure 10. Another example of the improvement in sensitivity that can be achieved with a boosted discharge lamp, compared to a conventional hollow cathode lamp having a cathode made of the same material. Both lamps were operated at 7 mA and with a spectral bandpass of 0.2 nm. The boosted lamp was 2.3 times as intense as the regular lamp.

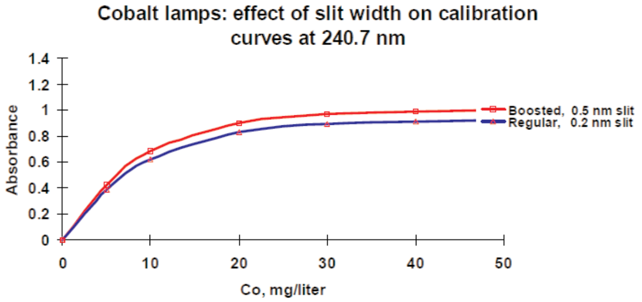
Cobalt lamps: effect of slit width on calibration curves at 240.7 nm

Figure 11. This Figure shows how a wider slit can be used with the boosted lamp to obtain an increase in intensity of detected light (and hence a reduction in photon shot noise), Both lamps were operated at 7 mA. The spectral bandpass was 0.2 nm for the regular lamp and 0.5 nm for the boosted lamp. The detected light with the boosted lamp was over 6.8 times as intense as that with the regular lamp. The calculated photon shot noise was only 40% of that with the regular lamp.

Fast Sequential (by Element) Atomic Absorption

Figure 12. Award-winning SpectrAA 220FS, a commercial fast sequential (by element) AA spectrometer.

Modern AA spectrometers can determine large number of elements rapidly and automatically. Only a limited number of lamps can be installed; the number of elements that can be determined automatically is limited by the number of elemental spectra provided by these lamps. There is consequently an increased need for hollow cathode lamps that emit the spectra of more than one chemical element. Additionally, the spectra should be as intense as possible and they should provide sensitive atomic absorption measurements of the elements of interest.

Fast Sequential (by element) AA highlights the need for multi-element lamps that can deliver analytical performances comparable to those of single-element lamps. Development of such lamps presents a number of challenges. The lamp developer must consider the following:

- Is the desired combination of elements spectroscopically feasible?
- Can the cathode material contain the elements of interest in proportions needed to ensuring optimum intensity of the required spectral lines?
- Will the material be manufacturable, consistent in properties, and provide a lamp having a long useful life and a short stabilization time?

Examples of Multi-Element Lamps

The following combinations have been found to give satisfactory emission with minimal or no spectral interferences.

Ag/Cd/Pb/Zn

Al/Ca/Mg

Co/Cu/Cr/Fe/Mn/Ni

Cu/Fe/Mn/Zn

Cu/Zn

Ba/Cr

Summary

Hollow cathode lamps are still the most cost-effective method for generating the atomic spectral lines required by the atomic absorption technique. It is possible to enhance the output of several elements by boosting the lamp. This provides more intense, spectrally sharp emission lines. Such lamps are most suitable for furnace or hydride elements work although benefits can also be seen in flame work.

The SpectrAA 220 Fast Sequential instrument requires all its lamps to be powered simultaneously. A number of multi-element lamps are now available to complement this technique. The lamps can also be used for normal AA measurements.

Frequently Asked Lamp Questions

Why Does a New Agilent Lamp Look "Used"?

One of the many processes applied to the lamp during manufacture is to heat-treat the cathode under vacuum to ensure that all absorbed gases are removed. This process results in some of the cathode material being deposited on the inside of the glass envelope of the lamp. The amount of material deposited varies, depending on the volatility of the element.

What is the Black Spot?

We put in the black spot quite deliberately. The presence of that spot contributes to the long shelflife of Agilent lamps. The anode of the hollow cathode lamp is made of zirconium. During processing, we subject the anode to ion bombardment that vaporizes a small amount of zirconium and deposits it on the lamp envelope near the anode. This film of zirconium is highly reactive and acts as a very efficient scavenger of traces of oxygen and other molecular gases that might otherwise reduce the lifetime of the lamp. It is called a "getter". Look for the dark smudge behind the anode. It is there to help prolong the useful life of the lamp.

What is the Purpose of Fill Gas?

The fill gas allows the sputtering of the cathode material. The gas is ionized when a high voltage is applied. These ions are accelerated towards the cathode. When they hit the cathode they knock metals atoms loose. The atom plume thus formed is excited during this process to emit the light required for the atomic absorption principle.

How Much Fill Gas is Added?

After the lamp has been processed, it is evacuated and backfilled with high-purity neon or argon. The fill gas pressure is carefully selected to give the optimum balance between lamp intensity and useful operating life.

Why Treat the Cathode?

The filled lamp is then subjected to an aging process, during which the lamp is operated under controlled conditions to ensure that when delivered the lamp it is ready for immediate use. All "settling in" of the lamp is done before it leaves the factory - before the warranty period begins. After aging, the lamp is subjected to thorough testing. No lamp leaves our factory without having met our standards of intensity and stability.

Does the Flickering Glow Around the Anode Mean the Lamp is Faulty?

No. This is a consequence of current flowing through low pressure gas. It has no effect on the atom plume. "Lamp flicker" applies only to emission from the cathode. Most element emission lines are in the invisible UV. Use the instrument's optimize page. Good lamps, properly aligned, should have a low value for % gain or EHT and a fairly steady emission signal. Danger signs are a high value and a wildly fluctuating emission signal.

Do the Other Elements in a Cathode Affect Lifetime?

No. Lamps should last at least 5000 mA-hours regardless of the element actually determined.

Is There a Compromise in Intensity with the Ag/Cd/Pb/Zn or Al/Ca/Mg Lamps?

Ca, Cd, Mg, Pb, Zn are present in the optimum solid concentration. The respective intensities are comparable with those of the single-element lamps. The relative intensities of Ag and Al are less compared with those of the single-element versions. These elements are so intense anyway that the reduction has no real practical disadvantage.

Is There Any Compromise with the Co/Cr/Cu/Fe/Mn/Ni Lamps?

The atom plume of this lamp contains all the elements so the intensity of each element will be less compared with the corresponding single-element lamp. This does raise the shotnoise level. In flame work, flame flicker is the dominant noise factor. This lamp is very popular because because it allows the practical determination of six elements with one lamp.

Can All Lines be Used in Multi-Element Lamps?

This is a valid question for multielement lamps. For Agilent multi-element lamps, all the usual primary lines may be used. The use of secondary lines is not supported by the factory.

Is There any Spectral Interference?

Ag/Cd/Pb/Zn: there is a weak silver ion line close to Pb 217.0 nm. The calibration graph is a little less linear at higher absorbances compared with that obtained from the single-element lamp. This effect is minimized with the UltrAA version.

Al/Ca/Mg: none known.

Co/Cr/Cu/Fe/Mn/Ni: there is a weak Mn line close to Cu 324.7 nm line. The calibration graph is flatter at high absorbances compared with that obtained from the single-element lamp.

Can Spectral Interferences be Overcome?

Yes. The use of UltrAA (boosted) lamps minimizes the effects.

Why Do Lamps Wear Out?

The most common cause of lamp failure is that which claims most pieces of scientific glassware: physical damage from rough handling or accidents.

Even the most carefully handled lamp will eventually fail to operate, however, as the fill gas is adsorbed into the internal surfaces of the lamp. In time, the pressure of fill gas will fall to a level that can no longer sustain the electrical discharge and the lamp will no longer "strike".

Operating the lamp at excessive lamp currents will accelerate this process.

Attempts to run a lamp at extreme currents can cause the cathode to overheat, and this can damage the cathode.

To get the most out of every lamp handle it with care and do not exceed the recommended operating current.

References

1. J. V. Sullivan and A. Walsh, Spectrochimica Acta, 26B, 721 (1965).
2. J. V. Sullivan, Progress in Analytical Atomic Spectroscopy, 4, 311 (1981).

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem www.agilent.com/chem

Printed in the USA
November 1, 2010
A-AA14

Agilent Technologies