Features and Operation of Hollow Cathode Lamps and Deuterium Lamps

Application Note

Atomic Absorption

Authors

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Abstract

This paper discusses the parameters which influence the operation of hollow cathode and deuterium lamps. Examples are given of how parameters can be selected in order to improve the quality of analytical results. Aspects of deuterium lamp operation for background correction are also covered.

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The Hollow Cathode Lamp

The primary requirement of a hollow cathode lamp is to generate a narrow emission line of the element which is being measured. This line should be of sufficient spectral purity and intensity to achieve a linear calibration graph with low noise level from the AA spectrometer.

A typical hollow cathode lamp construction appears in Figure 1.

When a discharge occurs between two electrodes via a gas at low pressure, the cathode is bombarded by the energetic, positively-charged gas ions (for example, ionized filler gas atoms) which are accelerated towards its surface by the potential existing in the discharge. 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 which are present. These collisions result in a transfer of energy causing the metal atoms to become excited. Since this excited state is not stable, the atoms relax back to their ground state, emitting radiation at the characteristic wavelength of that element. For most elements, more than one analytically useful spectral line is generated.

In order to obtain optimum performance from the lamp, there are a number of design parameters which must be carefully selected.

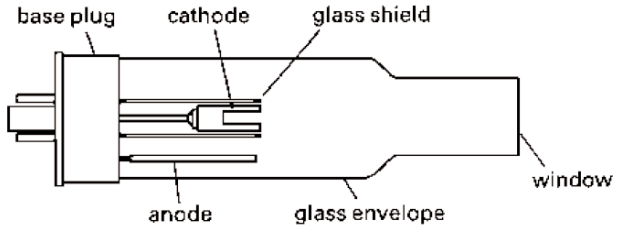

Figure 1. Hollow cathode lamp construction.

Design Characteristics of the Hollow Cathode Lamp

Cathode

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). If it is brittle, a sinter of pressed metal powder is used (for example, Mn, W). If however it is reactive in air, or has a relatively high vapor pressure, then the metal oxide or halide is typically used (for example, Cd, Na). The powder technique is also used for producing multielement lamps where two or more metals are present.

The bore diameter of the cathode is also important since the intensity of the lamp output depends on the current density.

Gas Fill

The filler gas must be monatomic in order to avoid molecular continuum spectra and thus it must be an inert, noble gas. The filler gas is usually argon or neon, with neon being the preferred choice. This is due to its higher ionization potential which produces a greater signal intensity. Argon is only used when a neon spectral line occurs in close proximity to a resonance line of the metal.

Helium is not used due to its low mass number making it not only an inefficient sputterer but also giving a short lifetime due to rapid "clean-up".

Clean-up is the lowering of filler gas pressure due to adsorption of gas atoms onto surfaces within the lamp. This eventually results in a gas pressure which is too low to sustain the discharge. At this stage the lamp has reached the end of its lifetime. Although the lamp will glow, no measurable atomic spectral line will be detected.

Anode

The anode is simply the electrode which provides the potential required for striking the discharge. Zirconium is employed for the anode due to its ability to act as a "getter". This property is explained below in Processing.

Envelope

The electrodes are enclosed within a glass envelope which has a quartz or a special borosilicate end window attached to it. Selection of the window material is based on its transmittance of the spectral lines of interest. For elements that emit at wavelengths of less than about 300 nm, quartz must be used. For higher wavelengths borosilicate is typically used.

Processing

Processing is an important step towards obtaining a functional lamp. This process is a means of purging the lamp of contaminants.

The processing steps include evacuation and out-gassing of the lamp at suitably high temperatures under high vacuum.

The processing operation includes reversal of the polarities so that the zirconium anode now becomes the cathode. Zirconium is a very active "getter" for impurity gases such as oxygen and hydrogen, and this discharge serves to purge the lamp of these impurity gases. During this discharge a sputtered film of zirconium is deposited on the envelope.

This is the dark film visible on the glass envelope near the anode. This activated film of zirconium will act to absorb impurity gases (hence "getter") that may have escaped the previous purification stage. Finally the lamp is then filled with spectroscopically pure gas and sealed. Processed lamps are then operated for several hours prior to testing.

Hollow Cathode Lamp Operation

There are two parameters of major importance which affect the analytical results. These are:

1. The hollow cathode lamp current, which affects the intensity of the source, and
2. The spectral band width (or slit width) of the instrument which affects the isolation of the spectral line.

In order to simplify the selection of these two parameters, Agilent supplies information on the recommended operating conditions for each lamp. However in special cases improved results improved results may be achieved by minor deviations from the recommended conditions. The choice of operating conditions depends greatly on whether the operator is searching for maximum precision at concentrations near the detection limit or whether samples are being measured over a wide concentration range.

Lamp Current

The principle effect of an increase in the lamp current is an increase in the intensity of the lamp emission. This is demonstrated in Figure 2.

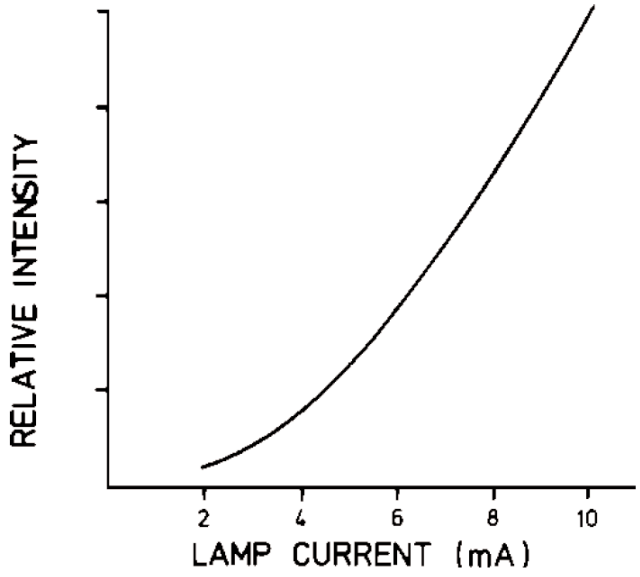

Figure 2. Intensity as a function of lamp current for Cd at 228.8 nm.

The intensity of the lamp affects the baseline (absorbance) noise level upon which the analytical signal is measured. This baseline noise level significantly affects the analytical performance in terms of precision and detection limits.

This noise level is inversely related to intensity of the light source and therefore the more intense the source, the lower the baseline noise will be (Figure 3).

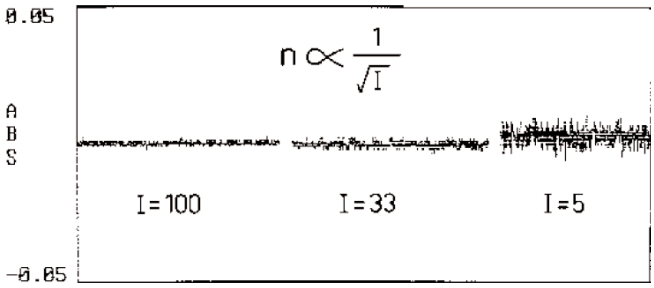

Figure 3. Relationship between light intensity (I) and absorbance noise level (n) for Ca at 422.7 nm.

If this were the only consideration then the lamp would be run at the maximum allowable current. However in practice it is not as simple as this.

As the operating current increases above the recommended value, increased broadening of the emission lines occurs until at very high currents the phenomenon of self-absorption is observed. This appears as an inversion of the peak top of the emission line due to a cloud of atoms in front of the cathode absorbing the cathodic emission within the lamp itself.

The resultant distortion of the lamp emission peak leads to reduced sensitivity (Figure 4).

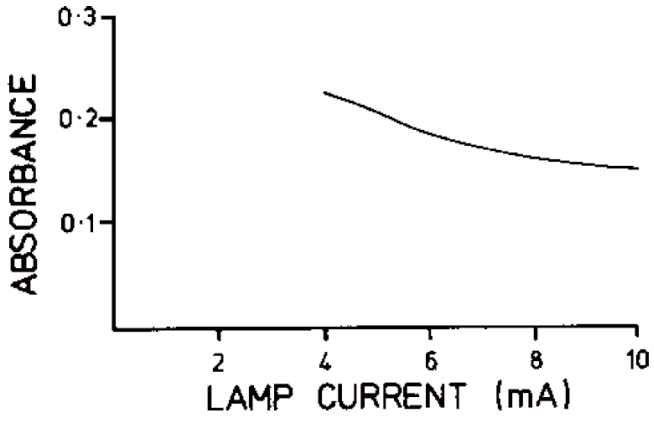

Figure 4. Sensitivity as a function of current for Cd at 228.8 nm.

This will also be passed on as more pronounced curvature in the calibration plot as shown for cadmium (Figure 5). It should be noted that this example is one of the most current-sensitive of elements. Other elements may show little or no effect from current variation (Figure 6).

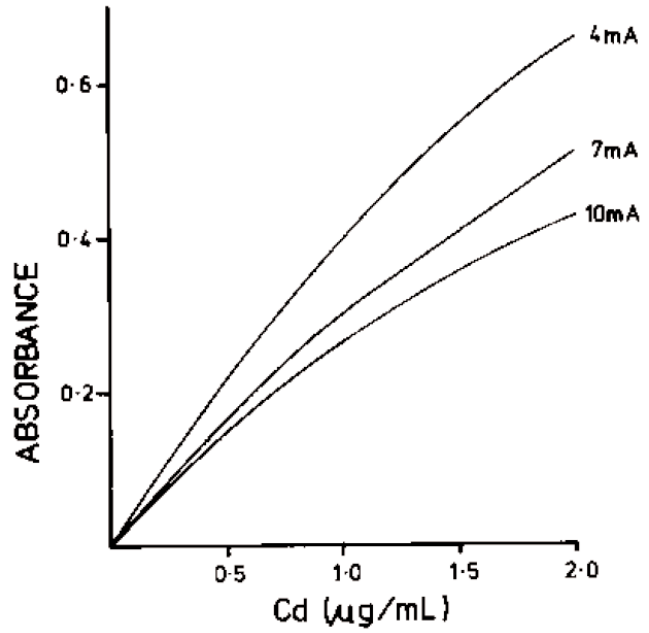

Figure 5. Calibration graphs for a Cd hollow cathode lamp operated at various currents.

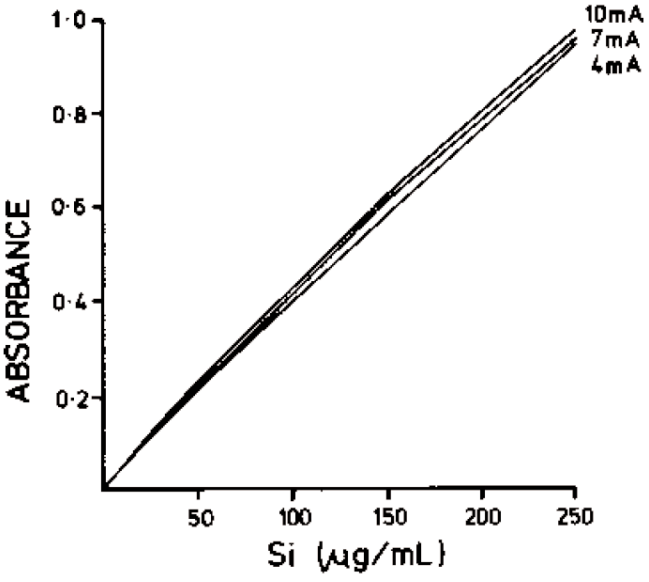

Figure 6. Calibration graphs for a Si hollow cathode lamp operated at various currents.

Excessive lamp currents applied to the lamp will accelerate the sputtering process and will shorten the lifetime of the lamp. This is especially true for the more volatile elements.

For measurements near the detection limit (where baseline noise is important) there may be advantages in using a higher lamp current than is recommended. This is especially true for those elements which show little loss in absorbance with increased lamp current.

On the other hand, a lower lamp current may yield a more linear calibration for an extended range but at the expense of extra noise level.

It becomes apparent that a compromise may be required to obtain the best sensitivity coupled with a high signal-to-noise ratio and a long lamp life. Agilent Technologies provides a set of recommended operating conditions with each lamp.

Lamp Intensity

Each analytical line from each hollow cathode lamp has a characteristic intensity which relates to the observable signal-to-noise level of the atomic absorption instrument. The greater the intensity of the analytical line, the lower the noise level. Such differences in the measured noise level between different lamps are quite normal. For example the silver line at 328.1 nm has a greater intensity than the iron line at 248.3 nm and the resultant baseline noise levels illustrate this in the signal graphics traces in Figure 7.

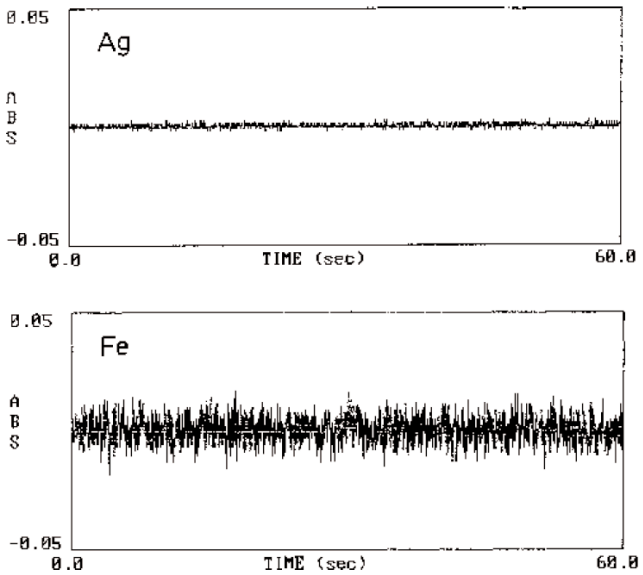

Figure 7. Inherent noise levels of Ag and Fe hollow cathode lamps operated under recommended conditions.

It should be noted that the photocathode response characteristics of the photomultiplier tube will affect the noise level observed. Agilent use a photomultiplier tube which has a high response over a wide wavelength range.

Spectral Band Width

The spectral band width (SBW) affects the spectral isolation of the analytical line. The spectral band width required is normally dictated by the nearest adjacent line in the spectrum (Figure 8).

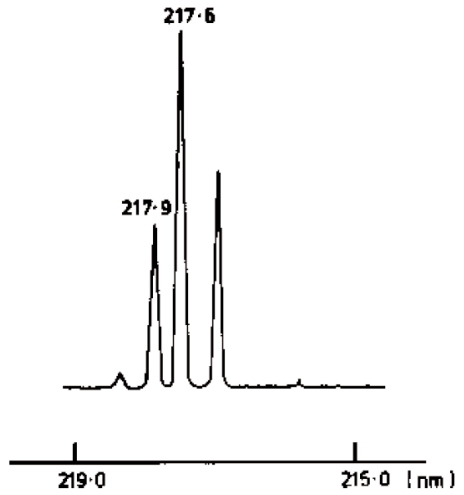

Figure 8. Spectral scan of Sb lamp in the vicinity of the 217.6 nm resonance line.

From the spectral scan of antimony shown in Figure 8 it can be seen that when using the most intense line at 217.6 nm, a SBW of less than 0.3 nm is required to avoid interference from the 217.9 nm line. By studying the effect of altering the SBW on the absorbance of an analyte solution the optimum SBW can be determined (Figure 9).

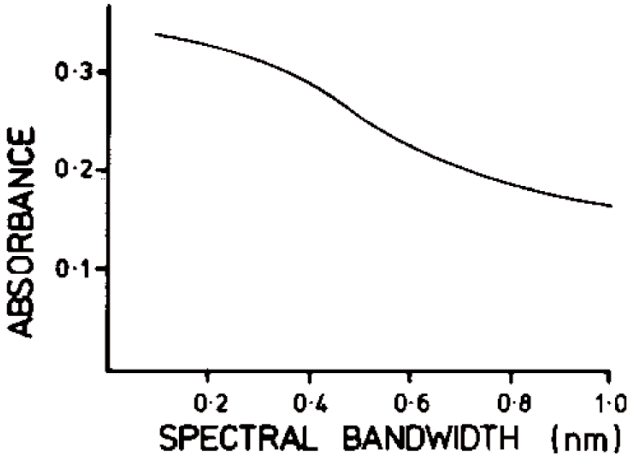

Figure 9. Sensitivity as a function of spectral bandwidth for Sb at 217.6 nm.

Warm-Up Time

Stability of the hollow cathode lamp signal is very important. Typically hollow cathode lamps require a warm-up period after switch on, during which time the lamp achieves an equilibrium state and the output stabilizes.

Warm-up time is particularly important for single beam instrument operation. With single beam instruments (such as the SpectrAA–10) the change in intensity of the lamp is reflected in the baseline of the instrument, That is, the baseline drifts as the lamp drifts. Therefore it is important that the lamp be allowed sufficient time to warm-up prior to performing any analytical measurements. For the majority of elements 10 minutes is a suitable warm-up period to achieve a stable signal. Exceptions to this are As, P, Tl and the Cu/Zn multielement lamp where longer warm-up times are recommended.

With double beam optical configuration, the instrument is able to compensate for changes in the sample beam intensity by making continual comparison with the reference beam. This comparison is carried out at 50 or 60 Hz with the Agilent SpectrAA series, giving a sample and reference beam measurement every 20 or 16 milliseconds respectively.

With double beam instruments, the lamp warm-up time is not apparent. Nevertheless it is desirable to allow a short warm-up before attempting precise analytical measurements. This is because the profile of the emission line from the lamp can change during this period, and small changes in analytical signal may result. With double beam instruments, the zero absorbance level will always be maintained.

Note also that the SpectrAA Zeeman instrument offers true double beam operation when the analytical measurement occurs, although it is optically a single beam instrument.

Multielement lamps

Multielement lamps may consist of up to six different elements. The elements are combined in the cathode as metallurgical powders. Such lamps are convenient to the analyst, but there are some limitations to this approach.

Some combinations of elements cannot be used because their emission lines are so close together that they interfere with each other. The recommended conditions are often quite different from those for the single element lamp and should be strictly observed for best results.

Single element lamps yield superior quality results in terms of calibration linearity than for the same element in a multielement combination. Multielement lamps do, however, provide convenience of operation for less demanding analyses.

The Deuterium Lamp

The deuterium lamp is a continuum radiation source used to correct for non-atomic or background absorption. The source used is a deuterium filled discharge lamp which emits an intense continuum spectrum from 190 nm to about 400 nm. This is the region where most atomic absorption lines occur and where the effects of background absorption are most pronounced.

A polyatomic gas, D_2, is used in the lamp because a continuum is produced rather than a line spectrum.

The deuterium lamp is different from a hollow cathode lamp in construction and operation (Figure 10). The lamp incorporates a heated, electron-emitting cathode, a metal anode and a restrictive aperture between the two. A discharge current of several hundred milliamperes excites the deuterium gas. The discharge is forced to pass through the small aperture, forming a defined area of high excitation and hence high light emission. A suitable window transmits the light to the spectrometer's optical system.

To obtain successful background correction the deuterium lamp must be correctly aligned and its intensity must be matched to that of the hollow cathode lamp.

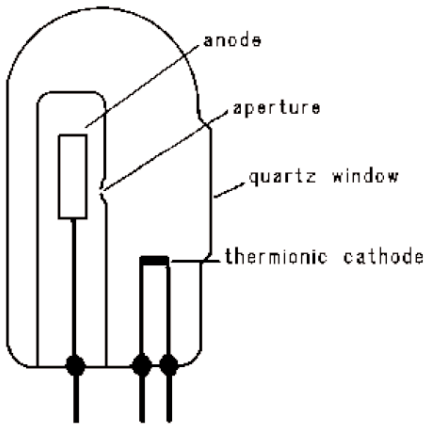

Figure 10. Deuterium lamp construction.

It is important that both the deuterium source and the hollow cathode source are aligned to follow the same optical path. If they are not, then the two measurements may not be made on the same atom population and significant errors may occur.

In order to balance the intensity of the deuterium lamp with the hollow cathode lamp, it may be necessary to change the hollow cathode lamp current to a higher or lower value depending on the relative intensities of the lamps.

In Agilent instruments an attenuator can be placed in front of the deuterium lamp (automatically in some models) in order to reduce its intensity and assist in achieving a balance.

If the continuum source is still too intense for the hollow cathode lamp then the spectral bandwidth should be reduced. This is because the energy from the continuum source increases with the square of the spectral bandwidth, whereas the energy of the atomic spectral line from the hollow cathode lamp increases linearly with the spectral bandwidth.

By the same argument the spectral bandwidth should be increased if the hollow cathode lamp intensity is too great for the deuterium lamp. By these means a suitable balance should be achieved.

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