# Selection of Operating Parameters for a New Boosted-Discharge Bismuth Lamp

## Application Note

Atomic Absorption


## Author

Barry T Sturman


## Introduction

Agilent has developed a boosted-discharge bismuth hollow-cathode lamp that provides greater intensity and less curved calibration graphs than does the conventional bismuth hollow cathode lamp. This lamp is one of several new additions to Agilent's UltrAA range of boosted discharge lamps.

These lamps, based on the work of CSIRO scientists J. V. Sullivan and A. 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, the boosted discharge lamps employ a second discharge, electrically isolated from the sputtering discharge, to excite the sputtered atoms. The excitation process is thus largely independent of the sputtering process. In the conventional hollow-cathode lamp radiation from excited atoms in the cathode can interact with unexcited atoms on its way out of the cathode, and resonance lines undergo self-absorption. This can lead to curvature of atomic absorption calibration graphs. In the boosted discharge lamps the radiation from the boosted discharge has much less opportunity to interact with unexcited atoms, and consequently there is less self-absorption and the calibration graphs are less curved. Furthermore, the excitation conditions in the boosting discharge evidently favors the excitation of atomic resonance lines. Consequently these lines are relatively more intense compared with ion lines and non-absorbable atomic lines. This is another factor that reduces the curvature of calibration graphs when boosted lamps are used.

Results of experiments conducted to determine the optimum operating conditions for the new lamp are presented in this report.


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# Experimental

## Instrumentation

The performance of the new lamp in flame AAS was evaluated with an Agilent SpectrAA 50 spectrometer, using a Mark 7 burner for the air-acetylene flame. A conventional Agilent bismuth hollow-cathode lamp was used for comparison. The new lamp was operated with the standard boosting current supplied by the Agilent UltrAA lamp power supply.

Relative lamp intensities were calculated as the inverse of the photomultiplier gain. This was calculated from the displayed "% Gain" figures using proprietary conversion algorithms.

Photon shot noise was calculated by using the photomultiplier gain to estimate the current at the photocathode, given the anode current (obtained from the electronic designers). The photocathode current was expressed as electrons per second, and the shot noise calculated as the square root of this, assuming Poisson statistics. The noise on the photocathode current was then converted to noise on a zero absorbance signal at one second integration time, using the transfer functions involved in converting the photocathode current to an absorbance signal.

Detection limits for a 1-second integration period were calculated using the formula

$$DL\ (mgL^{-1}) = 3\sigma_p/S$$

where $\sigma p$ is the photon shot noise on a zero absorbance signal at one second integration time and S is the sensitivity in absorbance/mg $L^{-1}$. The sensitivity was obtained by dividing the absorbance signal for a low concentration solution (5 mg $L^{-1}$) by the concentration.

The detection limits so calculated are those that would be found if the photon shot noise were the only contributor to the noise on a blank signal. Experimental detection limits would be worse than the calculated ones, because they would include contributions from noise sources unrelated to the lamp, such as flame noise.

## Reagents and Solutions

All acids used were AR grade supplied by BDH (Poole, England).

Bismuth solutions were prepared from a 1000 mgL$^{-1}$ stock solution made by dissolving 1.000g bismuth metal in hot hydrochloric acid (with addition of a few drops of nitric acid) and diluting to 1 liter. All solutions were 1M in hydrochloric acid to prevent hydrolysis. The bismuth was coarse powder, made by crushing material milled from a portion of a commercial bismuth ingot.

# Results and Discussion

The conditions giving the lowest calculated detection limit were first determined. The calculated detection limit is the figure of merit that best indicates the performance of the lamp, because it includes both the sensitivity of the measurement and the noise associated with the detection of the light, which in turn is related to the intensity of the light at the wavelength of interest.

Figure 1 shows the calculated detection limit for Bi at the 223.1 nm line as a function of slit width and lamp current for the new lamp and for the conventional hollow cathode lamp. For either lamp, the lowest detection limit was obtained with the widest slit (1.0 nm) and the highest lamp current. (16 mA). The improvement in detection limit for lamp currents above 10 mA was rather small. The useful life of a lamp is greater at lower currents; consequently, 10 mA was selected as the recommended operating current for the new lamp. The conventional lamp has a recommended operating current of 10 mA.

As shown in Figure 1, the detection limit was always better with the widest slit. This means that any loss of sensitivity that may have resulted from the use of the wider slit was more than offset by the increased light throughput and the consequent reduction in photon shot noise.

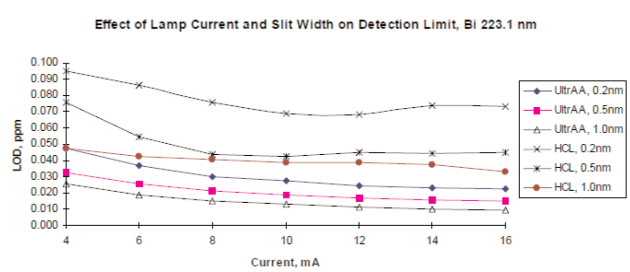


*Figure 1. Effect of lamp current and slit width on detection limit, Bi 223.1 nm line.*

The relationship between slit width and sensitivity is unusual. There is another bismuth line at 222.8 nm that is about 3.6 times less sensitive than the 223.1 nm line [2]. It is not possible to select this line with the SpectrAA 50, because the automatic wavelength peaking routine locks onto the nearby (and somewhat more intense) 223.1 nm line. When the 0.5 nm and 1.0 nm slits are used, both of these lines are detected. Figure 2 shows calibration curves at each slit width for each of the two lamps. It is clear from these curves, which extend to only moderate absorbances, that the best sensitivity is obtained with the narrowest slit (0.2 nm). There is little difference in sensitivity between the 0.5 nm and 1.0 nm slits. This is in accordance with expectations because the 222.8 nm line is detected in either case, along with the 223.1 nm line. Consideration of curves such as those in Figure 2 probably led to the recommendation to use the 0.2 nm slit with the conventional lamp.

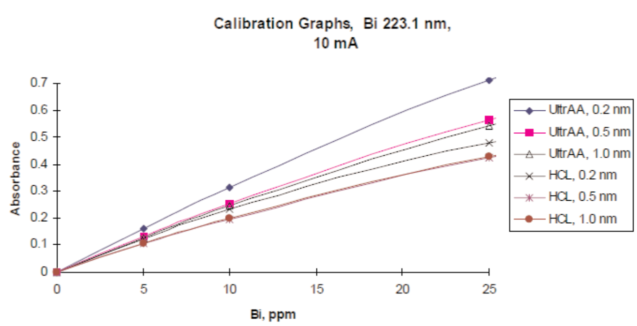


*Figure 2. Comparison of Bi 223.1 nm calibration graphs using different design lamps and conditions.*

It is noteworthy that the sensitivity with the new lamp at the widest slit is better than that with the conventional lamp at the narrowest slit.

Figure 3 shows the same calibration curves as Figure 2, but this time extended to much higher concentrations. The curve for the conventional lamp and the 0.2 nm slit "flattens out" at a much lower absorbance than do the curves obtained with wider slits. This means that calibration curves with the wider slits have a greater dynamic range. This provides a second reason for preferring a wider slit with the conventional lamp. With the new lamp, there was little difference in the calibration curves at the higher end of the absorbance range. The widest slit is preferred because it gave the best calculated detection limit.

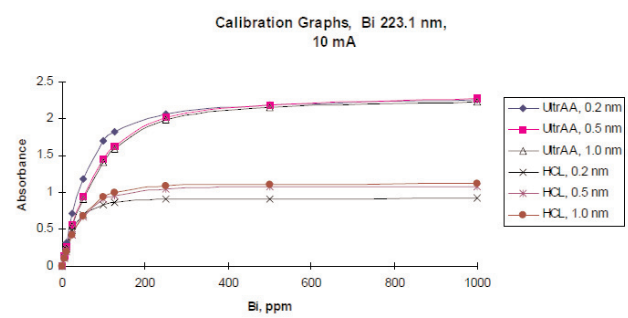


*Figure 3. Comparison of Bi 223.1 nm calibration graphs using different design lamps and conditions.*

## Conclusion

The recommended operating parameters for the new bismuth UltrAA lamp are to use a lamp current of 10 mA with a 1.0 nm slit at the Bi 223.1 nm line. Significant improvements in sensitivity and dynamic range over those obtained with the conventional unboosted lamp are achieved with the new lamp. The photon shot noise is considerably reduced, leading to an improvement in the (calculated photon noise) limited detection limit.

## References


1. J. V. Sullivan and A. Walsh, Spectrochimica Acta, 21, 721, **1965**
2. "Hollow Cathode Lamp Data", VarianTechtron Pty Ltd, Mulgrave, Victoria, Australia , 1972, page 3


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