Hollow Cathode Lamps

Competitive Comparison

The hollow cathode lamp is a discharge lamp designed for use as a spectral line source with atomic absorption (AA) spectrometers. A single or multi-element hollow cathode lamp is required for each element to be determined using the AA technique. The key requirement for the hollow cathode lamp is to generate a narrow emission line for the element being determined. The emission line should be of sufficient spectral purity and intensity to achieve a good calibration (preferably linear) with low noise.

While many users assume the performance of lamps from different manufacturers is the same, there are often significant differences in performance, which can affect the accuracy and reliability of AA results. Typical performance issues can include:

- Low sensitivity, which degrades detection capabilities
- Poor stability or high noise, which degrades precision and accuracy
- Excess calibration curvature, which reduces the linear dynamic range
- Poor lamp stability, which can waste time with troubleshooting and re-analysis of samples, reducing productivity
- Short lamp lifetime, which increases routine operating costs as more replacements are required.

This article compares the performance of hollow cathode lamps from different suppliers, focusing on aspects that are critical to performance.
History of Agilent Lamps

Agilent's experience with hollow cathode lamps started in the early 1960s when, as Ransley Glass, we worked with staff in the Spectroscopy section and Instrument Laboratory at the Division of Chemical Physics of CSIRO (Australia) to develop and manufacture a range of reliable lamps while the AA technique was still in its infancy. As the demand for lamps grew with the rapid evolution of the AA technique, Ransley Glass supplied lamps for use with Techtron, PerkinElmer, and other instrument manufacturers. Ransley Glass grew to become Atomic Spectral Lamps, which later merged with Techtron Pty. Ltd. Techtron merged with Varian Associates in 1967 to become Varian Techtron Pty. Ltd. Varian Associates in turn was subsequently acquired by Agilent Technologies, Inc. in May 2010. As outlined in this short history, Agilent has continuous experience in the development, production and improvement of lamps right from the very beginning of the AA technique.

Production of Agilent Lamps

Production of hollow cathode lamps is an intricate process that requires expertise in many diverse disciplines including glass blowing, quartz/glass welding techniques, inter-metallic species and metal alloy fabrication, and lamp purification/stabilization techniques.

In the first stage of production of Agilent hollow cathode lamps, the lamp structure is assembled from prefabricated components in the lamp base. This includes the cathode support and anode assembly. The cathode is prepared in a separate production area, which is isolated to ensure purity and where necessary, to protect the cathode materials from degradation. The cathode is fitted to the support assembly, and the lamp is then sealed by welding the graded seal (with the quartz end window for most lamps) to the body of the lamp (Figure 2). The fully assembled and sealed lamp is then subject to a unique purification and stabilization process.

Lamp purification is the most critical step as this aims to remove impurities from the cathode. This is achieved by out-gassing the lamp at a suitably high temperature under high vacuum. During this purification stage, a layer of the cathode material is deposited inside the glass envelope of the lamp. The amount of material deposited varies, depending on the volatility of the cathode.

The purification operation also uses ion bombardment of the zirconium anode. This vaporizes and deposits a small amount of the zirconium anode material inside the lamp envelope. This creates the black "getter" patch characteristic of the Agilent lamp (Figure 3). This zirconium film is highly reactive and acts as a very efficient scavenger of impurity gases such as oxygen and hydrogen. After the final gas fill, this active "getter" patch absorbs any remaining impurity gases, ensuring extended lamp life and spectral purity throughout the life of the lamp.

After purification, the lamp is filled with pure spectroscopy-grade gas (neon for most lamps) and sealed. The lamps are then operated under controlled conditions for several hours to condition and stabilize the lamp prior to final performance testing. The extended processing and the use of spectroscopically pure materials ensure dependable performance and long life from Agilent hollow cathode lamps.

Figure 2. Agilent lamps are hand made in an ISO 9001 facility to guarantee performance and reliability. Here the graded seal is welded to the lamp base.

Figure 3. The black spot visible in the Agilent lamp is the active "getter" spot created deliberately to prolong lamp life and ensure continued spectral purity.
Lamp Performance Factors

The performance of any hollow cathode lamp varies with many factors of the lamp design. Key parameters include cathode composition, gas fill pressure, bore diameter of the hollow cathode, and the operating current. For most lamps, the recommended operating parameters have been optimized so as to achieve the best overall performance. For example, using a higher current than the recommended lamp current can increase lamp intensity, but this reduces lamp lifetime as the rate of sputtering from the cathode increases and the gas fill is used up at a faster rate. The higher operating current can also distort the shape of the emission peak, reducing sensitivity. Lamps from different manufacturers will use different recommended operating parameters based on their specific lamp design. That means the user may observe significant changes in performance when comparing lamps from different manufacturers.

The operating lifetime of the lamp is largely dependent on the gas fill pressure inside the lamp. When the lamp is operating, atoms from the fill gas are gradually adsorbed onto surfaces within the lamp. This "consumes" the gas within the lamp, gradually reducing the gas pressure. When the gas pressure in the lamp is too low, the discharge is not effective. Although there still may be a glow in the lamp, there is no detectable atomic emission. This defines the operating lifetime for the lamp. However, the gas fill pressure also influences the emission intensity and sensitivity achieved. While a high gas fill is desirable for long lamp life, this can reduce the emission intensity and provide reduced sensitivity due to self-absorption within the lamp. Again, a compromise in the gas fill may be required to ensure adequate lamp life, while still achieving good emission intensity and signal-to-noise (S/N) performance.

Lamp Testing Methodology

Lamps for the following elements were selected for performance testing – arsenic (As), selenium (Se), cadmium (Cd), lead (Pb), gold (Au), copper (Cu) and sodium (Na). These elements were selected to cover the full range of wavelengths detectable by an Atomic Absorption Spectrometer (AAS). The results presented here are based on evaluation of lamps completed in 2014 and 2017.

Arsenic and Selenium were selected because both elements have relatively low intensity, due to difficulty in being sputtered from the cathode material and excited, and because the primary emission lines are in the low UV region at 193.7 nm and 196.0 nm respectively.

Cadmium and Lead were selected because they are both more volatile elements which are very easy to excite. The high volatility means that while it is easy to achieve good intensity, it can be difficult to achieve good lifetime because the cadmium and lead in the cathode can be sputtered completely, well before the fill gas inside the lamp has been used up. So while there may still be a visible glow from the cathode, the instrument cannot detect any usable emission lines at the selected analytical wavelength. The Agilent lead lamp was retested in 2017 as a new cathode formulation had been introduced in August 2015. This change was made to improve lamp lifetime, and retain or improve analytical performance.

Gold and Copper were selected, as the preferred analytical wavelengths are in the UV region at 242.8 nm and 324.8 nm respectively. Intensities achieved from both lamps are stable for long periods of time.

Sodium was selected for its primary wavelengths are in the visible region around 589 nm and the sputtered atoms are easily ionized. This can reduce the lamp emission, such that the lamp is not fit for analysis.
Lamps from the following manufacturers were tested for performance in this comparison:

**Photron Pty. Ltd, Australia**
(manufactured in Thailand) – tested in 2014
- Part number P828 Pb hollow cathode lamp – Serial no. HKH0258
- Part number P849 Se hollow cathode lamp – Serial no. HKC0996

**Heraeus Noblelight GmbH, Germany**
(manufactured in China) – Tested in 2014
- Part number 80079139 Pb hollow cathode lamp – Serial no. 13100447
- Part number 80079417 Se hollow cathode lamp – Serial no. 12350467

**Beijing ShuGuang-Ming Electronic Lighting Instrument Co. Ltd. (SGM), China**
Tested in 2017
- Hollow cathode lamps for Pb – Qty 4 (no part number listed – Serial nos. 34000, 34003, 34008 & 33051)
- Hollow cathode lamps for Au – Qty 4 (no part number listed – Serial nos. 8431, 8429, 8443 & 8462)
- Hollow cathode lamps for Cu – Qty 4 (no part number listed – Serial nos. 31254, 32412, 32444 & 32445)
- Hollow cathode lamps for Na – Qty 4 (no part number listed – Serial nos. 7232, 10639, 10648 & 12716)
- Hollow cathode lamps for Cd – Qty 4 (no part number listed – Serial nos. 23376, 23412, 27004 & 27180)
- Hollow cathode lamps for As – Qty 4 (no part number listed – Serial nos. 13515, 13518, 13526 & 13531)

Tested in 2014
- Hollow cathode lamp for Pb (no part number listed – Serial no. 17282)
- Hollow cathode lamp for Se (no part number listed – S/N 2973)

**General Research Institute for Non-Ferrous Metals (GRINM), China**
Tested in 2017
- Hollow cathode lamp Type As-1 for Pb
- Hollow cathode lamp Type As-1 for Au
- Hollow cathode lamp Type As-1 for Cu
- Hollow cathode lamp Type As-1 for Cd
- Hollow cathode lamp Type As-1 for Na
- Hollow cathode lamp Type As-1 for As – Qty 2

Tested in 2014
- Hollow cathode lamp Type As-1 for Pb
- Hollow cathode lamp Type As-1 for Se

**Varsal Instruments, USA (manufactured in China)** – Tested in 2014
- Type 1.5” hollow cathode lamps for Pb (no part number listed – Serial no. Pb 17970)
- Type 1.5” hollow cathode lamps for Se (no part number listed – Serial no. Se 3036)

Lamps from these manufacturers were tested and compared using the following performance criteria:
- Emission intensity
- Analytical sensitivity (including detection limits)
- Calibration linearity
- Lamp lifetime
- Short- and long-term lamp stability
- Ease of use

All tests were performed using an Agilent AA instrument. The reasons for selecting these specific aspects of lamp performance and the testing methodology used are outlined below.
**Emission intensity**

Every analytical line from a hollow cathode lamp has a characteristic intensity that relates to the observable S/N performance. The greater the intensity, the lower the noise level. As noted earlier, use of a higher lamp current can increase lamp intensity and reduce lamp lifetime and sensitivity. As each lamp manufacturer recommends different operating parameters, variations in the emission intensity between lamps is quite normal.

To enable optimization of the lamp position in the Agilent AA instrument, the user selects the required operating parameters (wavelength, slit position, and operating current) and optimizes the lamp position to achieve maximum light throughput along the optical path. Once the lamp is correctly aligned, the relative emission intensity can be noted as the % gain displayed on the lamp optimization screen. The lamp current used for this test was the manufacturer’s recommended lamp current. A lower % gain indicates that the emission intensity of the lamp was higher (Figure 4).

**Calibration Linearity and Detection Limits**

The linearity of the calibration relies on the absence of neighboring interfering emission lines (influenced by the cathode composition) and the recommended operating current. Where there are neighboring interfering emission lines, the use of a higher operating current can increase the prominence of the main resonance line, reducing the effects of the interference. Alternatively, a narrow slit can be used to improve resolution and isolate the resonance line from the interfering line. However this reduces light throughput, increasing noise and the % gain figures. Use of a higher operating current can also distort the emission peak, reducing sensitivity and introducing pronounced curvature in the calibration.

Therefore, most lamps use optimized operating parameters, which balance the variables to obtain the best sensitivity coupled with high S/N performance and adequate lamp life.

Calibration linearity was assessed by overlaying the calibration curves obtained for each lamp. The same set of standards were used, and the lamps were operated at the manufacturer’s recommended operating current (Figures 5 to 11).

Instrument detection limits were also calculated from the standard deviation of 10 consecutive blank readings (Table 1).

---

**Figure 4.** Relative lamp intensity for lead (Pb), selenium (Se), arsenic (As), cadmium (Cd), gold (Au), copper (Cu) and sodium (Na) hollow cathode lamps. The gain for the Agilent lamp is comparable to many of the competitive lamps.
Table 1. Instrument detection limits calculated from the standard deviation on consecutive blank readings for the selected hollow cathode lamps. The Agilent lamp provided the lowest (best) detection limit for arsenic (As), lead (Pb), cadmium (Cd), gold (Au), copper (Cu); the second lowest (best) detection limit for selenium (Se), with a comparable detection limit for sodium (Na).

<table>
<thead>
<tr>
<th>Lamp manufacturer</th>
<th>Pb (283.3nm)</th>
<th>Se</th>
<th>As</th>
<th>Pb (217.0nm)</th>
<th>Cd</th>
<th>Au</th>
<th>Cu</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agilent</td>
<td>0.05</td>
<td>0.97</td>
<td>0.21</td>
<td>0.010</td>
<td>0.0007</td>
<td>0.005</td>
<td>0.001</td>
<td>0.0008</td>
</tr>
<tr>
<td>Heraeus</td>
<td>0.08</td>
<td>0.97</td>
<td>NT</td>
<td>NT</td>
<td>NT</td>
<td>NT</td>
<td>NT</td>
<td>NT</td>
</tr>
<tr>
<td>Photron</td>
<td>0.31</td>
<td>1.06</td>
<td>NT</td>
<td>NT</td>
<td>NT</td>
<td>NT</td>
<td>NT</td>
<td>NT</td>
</tr>
<tr>
<td>SGM</td>
<td>0.13</td>
<td>1.41</td>
<td>0.41</td>
<td>0.025</td>
<td>0.0011</td>
<td>0.019</td>
<td>0.009</td>
<td>0.0008</td>
</tr>
<tr>
<td>GRINM</td>
<td>0.08</td>
<td>1.00</td>
<td>*</td>
<td>0.027</td>
<td>0.0039</td>
<td>0.008</td>
<td>0.091</td>
<td>0.0007</td>
</tr>
<tr>
<td>Varsal</td>
<td>0.08</td>
<td>0.57</td>
<td>NT</td>
<td>NT</td>
<td>NT</td>
<td>NT</td>
<td>NT</td>
<td>NT</td>
</tr>
</tbody>
</table>

* GRINM ‘As’ lamps were inoperable  
NT – not tested

Figure 5. Comparison of calibration curves for lead (Pb) at 283.3 nm, based on tests conducted in 2014 and 2017. In each case, the Agilent lamp provided better sensitivity, especially at lower concentrations. The Agilent lead lamp tested in 2017 has an improved cathode composition, which explains the change in sensitivity from the lamp tested in 2014.

Figure 6. Comparison of calibration curves for selenium (Se) at 196.0 nm. The Agilent lamp ranks second in terms of sensitivity, comparable with the performance of the Varsal lamp. Only the Photron lamp provides better sensitivity, with similar detection limits.
Figure 7. Comparison of calibration curves for arsenic (As) at 193.7 nm. The Agilent lamp shows slightly higher curvature when compared to SGM, however the Agilent lamp has better sensitivity at lower concentrations. GRINM lamps were also tested, but ceased operating before completion of the study.

Figure 8. Comparison of calibration curves for gold (Au) at 242.8 nm. The Agilent lamp provides the best sensitivity and linearity.

Figure 9. Comparison of calibration curves for copper (Cu) at 324.8 nm. The Agilent lamp provides the best sensitivity and linearity.

Figure 10. Comparison of calibration curves for cadmium (Cd) at 228.8 nm. The Agilent lamp provides the best sensitivity and linearity.

Figure 11. Comparison of calibration curves for sodium (Na) at 589.0 nm. The Agilent lamp provides the best sensitivity and linearity.
Lamp Stability

For best performance and stability, it is always recommended that hollow cathode lamps be given some time to warm up (after being switched on) before commencing analysis. Lamps that require excessive stabilization times or lamps that never reach equilibrium create problems for analysts. Once analysis begins, drift in lamp intensity will change the analytical signal, introducing significant errors. This is especially critical at trace levels where the drift can be more than the sample absorbance. The short-term stability of the lamps was determined by monitoring the emission signal from the lamp continuously for a period of 20 minutes (after a suitable warm-up time, typically 10 minutes) (Figures 12 and 13).

The long-term stability of the lamps was determined by reading the absorbance for a standard that gave good S/N performance every 2 minutes for an hour (after a suitable warm-up time, typically 10 minutes) (Figures 14 and 15).
Lamp Lifetime

As noted earlier, lamp life is dependent on the gas fill inside the lamp, but a compromise in the gas fill can be required to also ensure good emission intensity and high S/N performance.

Lamp lifetime was determined by operating the lamp continuously (at the manufacturer's recommended operating current) until failure occurred. Failure in this context was taken to be either no detectable emission from the lamp, or an excessively unstable signal. The elapsed hours-of-operation were calculated and are displayed as the total number of milliamp hours (lamp operating current x elapsed hours of use) until failure (Figures 16 and 17.)
Ease-of-Use

The lamp manufacturer can assist regular and first time users of AA instruments with lamp operation by providing clear guidelines, including recommended operating conditions. While less critical for experienced users, it is still an important consideration for novice users or for any user when switching between lamps.

Agilent provides clear guidelines with each hollow cathode lamp. Recommended operating conditions are conveniently listed on the label on the lamp base. For more detailed analytical information, the analyst can consult the recommended operating conditions sheet supplied with every lamp. This details all usable wavelengths with relative intensities and sensitivities for each element plus the recommended slit widths to ensure best performance (Figure 18).

The lamps from other manufacturers evaluated in this comparison failed to provide the same guidance. The documentation supplied with the lamps from SGM and GRINM were less than satisfactory, with the recommended operating conditions extremely difficult to understand.

Figure 18. Close up of the label applied to every Agilent lamp, illustrating the recommended operating conditions provided to assist the user.

What Makes Agilent Lamps Different?

As shown by this comparison, Agilent lamps provide many advantages for AA users.

- **Optimum performance** – A combination of the proprietary cathode composition and unique lamp processing procedures ensures good intensity and sensitivity, low noise and long-term stable operation.

- **Longer service life** – Users can expect longer lifetime due to the proprietary cathode composition and optimum gas fill within the lamp. Typical lifetime for Agilent lamps exceeds 5,000 mA hours of operation.

- **Better stability** – The “getter” spot inside the Agilent lamp and proprietary processing ensures the lamp works right out of the box with good stability. All lamp conditioning is completed before shipment, so you can use the lamp immediately with great performance.

- **High sensitivity and the best performance** – The proprietary cathode composition and optimized operating parameters deliver the best S/N performance to extend detection capabilities and improve quantification at trace levels.

- **Agilent quality** – Agilent lamps are manufactured by hand in an ISO 9001 certified environment and use proven processing steps. Prior to shipment, every lamp is analytically tested to ensure that it meets Agilent’s demanding standards for intensity, noise and stability. Test equipment is regularly calibrated.

Agilent offers an extensive range of single element and multi-element lamps. Our uncoded hollow cathode lamps are suitable for use with most major brands of AA instruments (except Shimadzu instruments that have self-reversal correction and PerkinElmer; Agilent also offers a comprehensive range of coded 50 mm lamps for use with all PerkinElmer AA systems). We also offer a range of coded lamps, which provide the benefit of automatic lamp recognition to reduce operator errors when working with multiple lamps. For enhanced performance, Agilent also offers a comprehensive range of high intensity boosted discharge hollow cathode lamps that can replace conventional lamps for AA determinations. Agilent UltrAA lamps lower detection limits for the most demanding AA applications.
Additional Resources


Agilent Lamp FAQs (including typical gain settings) at https://www.agilent.com/search/?No=0&Nrpp=20&Ntt=lamp+FAQs&redirect=0

To order your AA hollow cathode lamps, visit
www.agilent.com/chem/aalamps
To find a local Agilent representative, go to
www.agilent.com/chem/contactus