Hollow Cathode Lamps

Competitive Comparison

Figure 1. Agilent cadmium (Cd) hollow cathode lamp.

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.

Agilent Technologies

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.

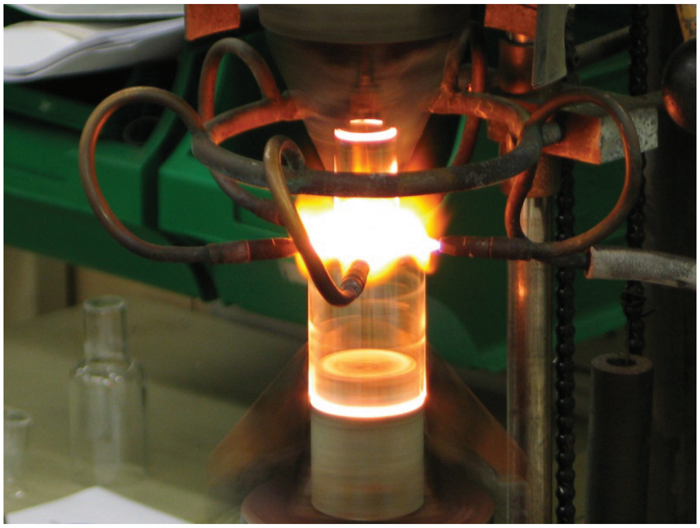


Figure 2. Agilent lamps are hand made in an ISO 9001 facility to guarantee performance and reliability. Here the graded seal is welded to the lamp base.

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.

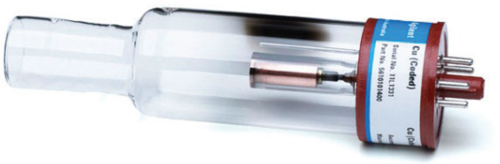


Figure 3. The black spot visible in the Agilent lamp is the active "getter" spot created deliberately to prolong lamp life and ensure continued spectral purity.

After purification, the lamp is filled with pure spectroscopic-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 use of spectroscopically pure materials ensure dependable performance and long life from Agilent hollow cathode lamps.

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. 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: selenium (Se) and lead (Pb). Selenium was selected because it has relatively low intensity, due to its difficulty in being sputtered from the cathode material and excited, and because the primary emission line is in the low UV region at 196.0 nm.

Lead was selected because it is one of the more volatile elements and is very easy to excite. While it is easy to achieve good intensity from a lead lamp, it can be difficult to achieve good lifetime because the 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 lead wavelengths.

Lamps from the following manufacturers were tested for performance in this comparison:

Photron Pty. Ltd, Australia
Part number P828 Pb hollow cathode lamp – Serial no. HKH0258
Part number P849 Se hollow cathode lamp – Serial no. HKC0996

Heraeus Noblelight GmbH, Germany
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
Hollow cathode lamp for Pb (no part number listed – Serial no. 17282)
Hollow cathode lamp for Se (no part number listed – Serial no. 2973)

General Research Institute for Non-Ferrous Metals (GRINM), China
Hollow cathode lamp Type As-1 for Pb
Hollow cathode lamp Type As-1 for Se

Varsal Instruments, USA
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 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 width, 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 (Table 1).

Table 1. Relative lamp intensity for lead (Pb) and selenium (Se) hollow cathode lamps. The gain for the Agilent lamp is comparable to many of the competitive lamps for both lead (Pb) and selenium (Se).

Lamp manufacturer	**% Gain for Pb lamp**	**% Gain for Se lamp**
Agilent	37	63
Heraeus	29	63
Photron	26	52
SGM	34	62
GRINM	34	50
Varsal	26	63

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 4 and 5).

Instrument detection limits were also calculated from the standard deviation of 10 consecutive blank readings (Table 2).

Table 2. Instrument detection limits calculated from the standard deviation on consecutive blank readings for lead (Pb) and selenium (Se) hollow cathode lamps. The Agilent lamp provided the lowest (best) detection limit for lead (Pb) and the second lowest (best) detection limit for selenium (Se).

Lamp manufacturer	**Measured detection limit for Pb (3 sigma) (mg/L)**	**Measured detection limit for Se (3 sigma) (mg/L)**
Agilent	0.05	0.97
Heraeus	0.08	0.97
Photron	0.31	1.06
SGM	0.13	1.41
GRINM	0.08	1.00
Varsal	0.08	0.57

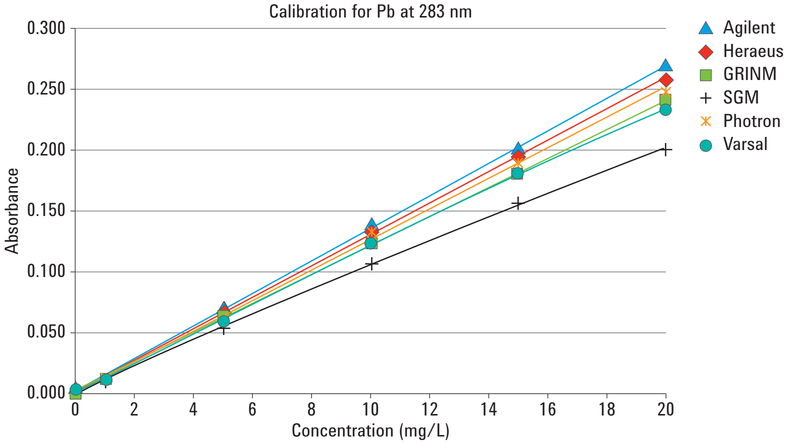


Figure 4. Comparison of calibration curves for lead (Pb) at 283.3 nm. The Agilent lamp provides the best sensitivity and linearity.

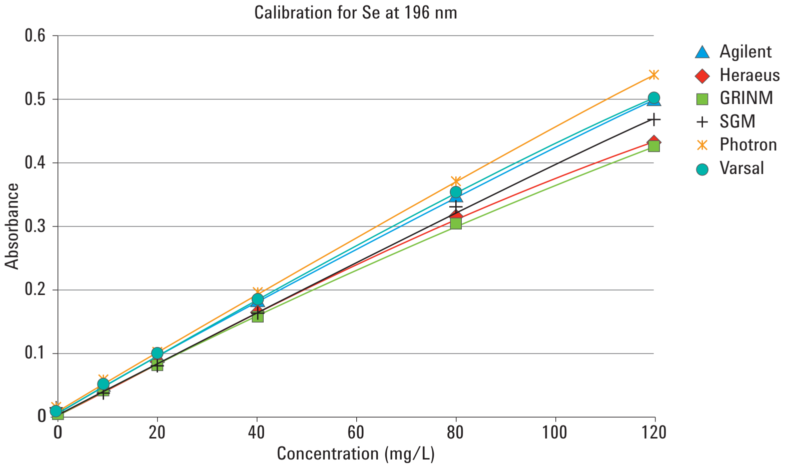


Figure 5. Comparison of calibration curves for selenium (Se) at 196.0 nm. The Agilent lamp ranks second in terms of sensitivity, comparable with the performance of the Varsal lamp. Only the Photron lamp provides better sensitivity, with similar detection limits.

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 6 and 7).

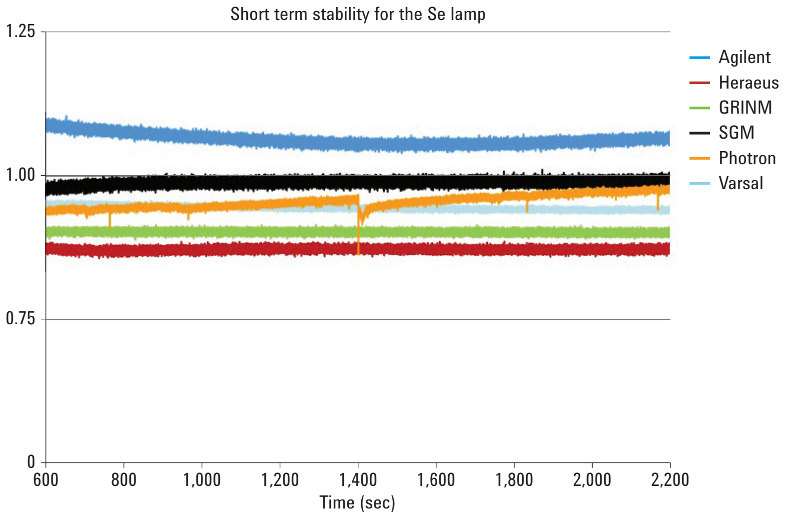


Figure 6. Short-term stability for selenium (Se) lamps, after a 10-minute warm up. While most lamps were suitably stable, the signal for the Photron lamp showed large spikes and never appeared to stabilize.

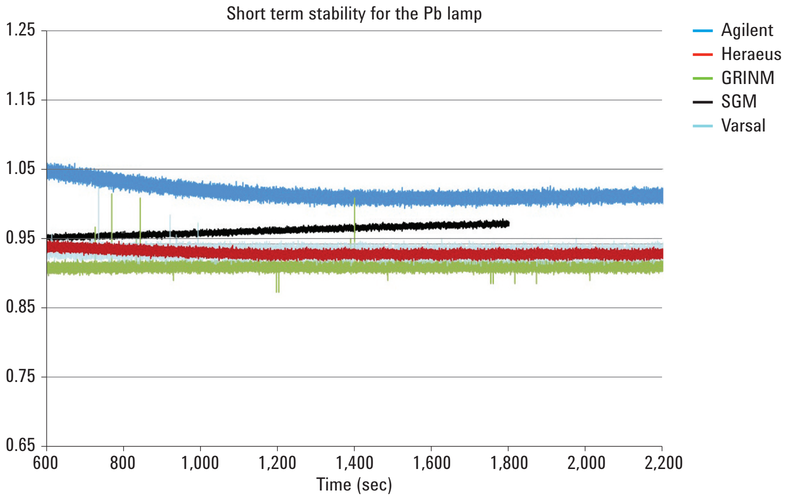


Figure 7. Short-term stability for lead (Pb) lamps, after a 10-minute warm up. While the Agilent and Heraeus lamps were suitably stable, the signals for both the Varsal and the GRINM lamps showed large spikes. The SGM lamp never appeared to stabilize.

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 8 and 9).

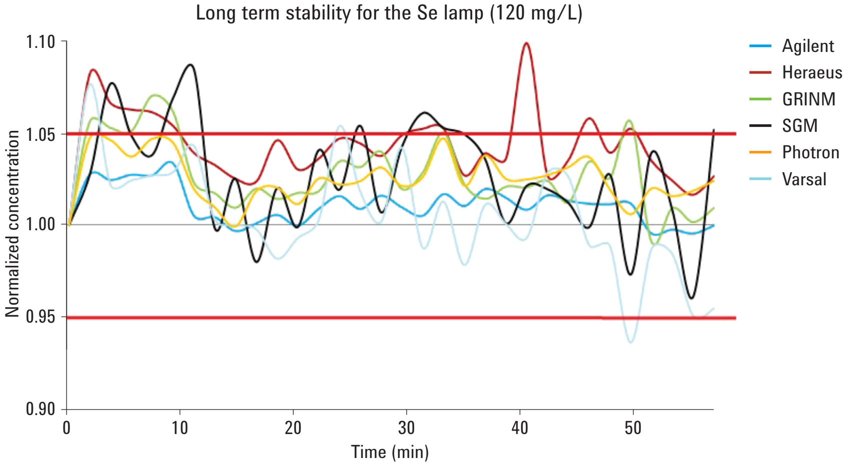


Figure 8. Long-term stability for selenium (Se) lamps based on measured absorbance for a 120 mg/L calibration standard. The solid red lines show ± 5% variation from the expected result. The Agilent lamp shows the best stability. The average precision for the Agilent lamp was < 1% RSD for all measurements over this 1 hour period, compared with the worst result of < 3% RSD for the Varsal lamp.

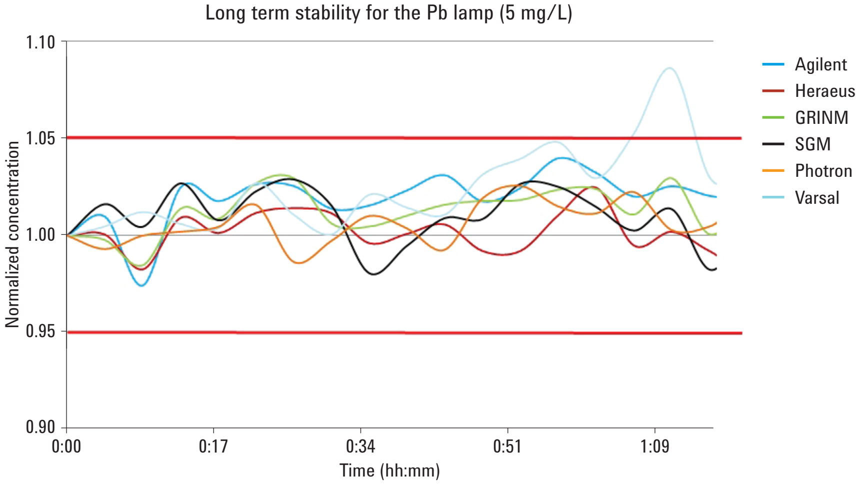


Figure 9. Long-term stability for lead (Pb) lamps based on measured absorbance for a 5 mg/L calibration standard. The solid red lines show ± 5% variation from the expected result. The Agilent lamp shows good long-term stability with an average precision of < 1.6% RSD for all measurements over this 1 hour period, compared with the worst result of > 2% RSD for the Varsal lamp.

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 × elapsed hours of use) until failure (Figures 10 and 11).

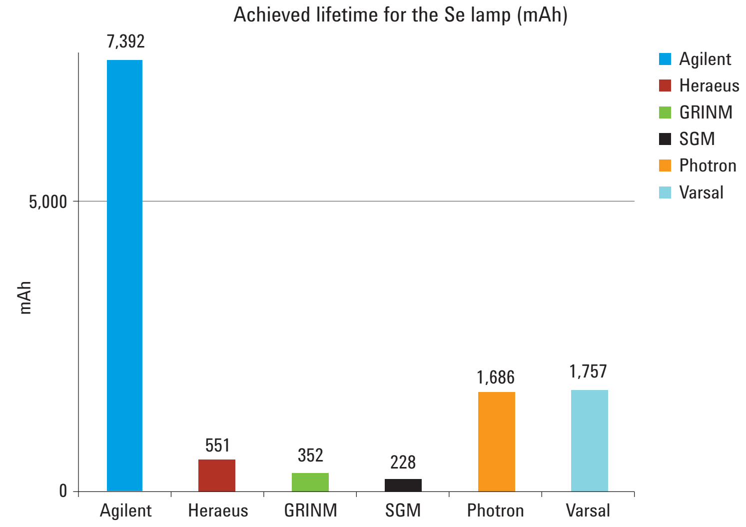


Figure 10. Lifetime of selenium (Se) lamps. The Agilent lamp gave the longest life, well over four times longer than the nearest competitor.

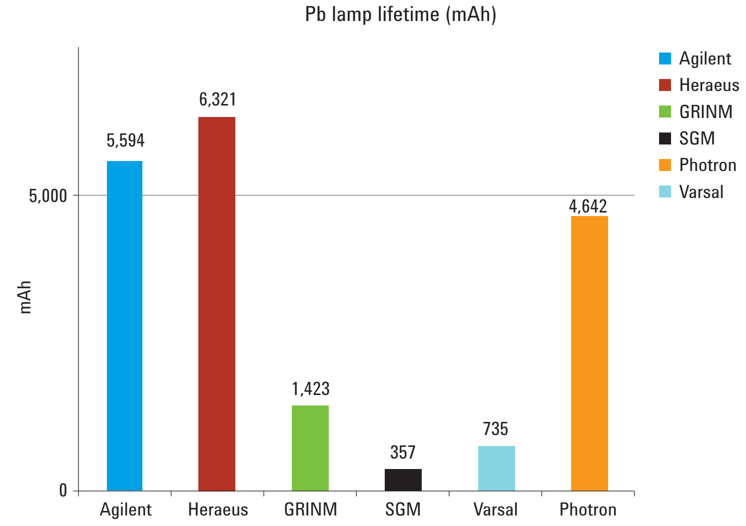


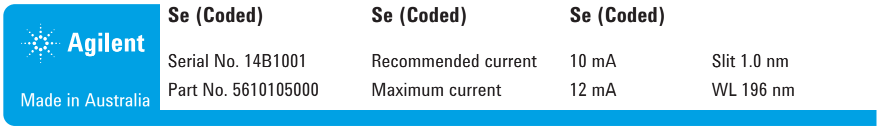
Figure 11. Lifetime for lead (Pb) lamps. The Agilent lamp gave the second longest life, even with this volatile element.

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 12).

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.



Agilent	**Se (Coded)**	**Se (Coded)**	**Se (Coded)**	
	Serial No. 14B1001	Recommended current	10 mA	Slit 1.0 nm
Made in Australia	Part No. 5610105000	Maximum current	12 mA	WL 196 nm

Figure 12. Close up of the label applied to every Agilent lamp, illustrating the recommended operating conditions provided to assist users.

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 PerkinElmer and Shimadzu instruments that have self-reversal correction). 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

The Agilent Periodic Table/AA Lamp Selection Poster, available at http://www.agilent.com/chem/AALampPoster

Agilent application note "Features and Operation of Hollow Cathode Lamps and Deuterium Lamps", available at http://www.chem.agilent.com/Library/applications/aa083.pdf

Agilent Lamp FAQs (including typical gain settings) at http://www.chem.agilent.com/en-US/Technical-Support/Instruments-Systems/Atomic-Spectroscopy/240FS-AA/Pages/default.aspx

Agilent Technical Overview for UltrAA lamps, available at http://www.chem.agilent.com/Library/technicaloverviews/Public/UltrAA-Lamp_Tech-Overview_5990-6711EN.pdf

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