Technical Overview

Back to AAS Basics: Tips and Tricks for Instrument Maintenance and Analysis

Atomic absorption spectroscopy is a robust instrumental technique for elemental analysis that can provide consistent and accurate results long term with a few key maintenance and system verification protocols.

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Introduction

Various iterations of atomic absorption spectroscopy (AAS) have long been known as workhorse instruments for elemental analysis. Whether based upon flame or graphite furnace atomization, AAS offers straightforward operation while yielding reproducibly sensitive and accurate results in a timely manner. As with all types of spectroscopy instrumentation, however, some degree of upkeep is necessary to ensure that AAS systems maintain their analytical performance. A few fundamental aspects of AAS maintenance provide high-yield benefits in terms of system operation and minimizing downtime, which specifically include care of the sample nebulizer, cleanliness of sample introduction components, preparation of accurate analytical standards, optimization of the incident light source, and verification of analytical sensitivity. Given the greater prevalence of flame atomization relative to graphite furnace systems, the primary focus of this summary will be on maintaining flame AAS platforms, with recommendations that are applicable across all AAS instruments.

Methods to Sustain Nebulizer Performance

Proper function of sample nebulizers is essential for AAS operation—blocked nebulizers can be a prevalent issue. Residual sample solution, if left within the sample capillary of the nebulizer, may crystallize and thereby clog the nebulizer. Additionally, blockages may also be caused by undissolved particulate matter in sample solutions, regardless of origin, including sediment, precipitates, dust, or even lint from wipes used in the laboratory. From a maintenance efficiency standpoint, the easiest approach is to prevent nebulizer blockages, rather than spending more time clearing blockages as they occur. Ensuring that sample introduction lines are rinsed with a blank solution before the flame is extinguished is a simple approach that can help to prevent blockages. For samples that have suspended particulates in solution, it may be necessary to filter, centrifuge, or allow the suspended particles to settle prior to aspiration. In the event that a nebulizer does become blocked, however, it is possible to clear the blockage. This requires complete disassembly of the nebulizer, followed by sonication of the components in a detergent solution, a rinse with deionized water, and reassembly before verifying clog removal.

Along with these approaches to sample handling, certain AAS system and method parameters can minimize blockages while balancing sensitivity and selectivity as needed for each application. A general recommendation for optimal performance involves fitting mixing paddles in the spray chamber, positioning the impact bead for best sensitivity, and using a narrow bore sample introduction capillary line. However, these method components should be altered to increase sensitivity when aspirating low-concentration samples requiring enhanced sensitivity, or in the case of solutions with a high total dissolved solids content, the impact bead should be adjusted closer to the nebulizer to minimize the impact of the suspended particulates aspirated through the sample introduction capillary line. Furthermore, at the end of each day, the system should be rinsed thoroughly via aspiration of an acid rinse solution with the flame still operating, followed by a flush of the spray chamber assembly with water.

Cleaning the Sample Introduction System

To further minimize downtime and improve instrument longevity, specific attention should be directed toward maintaining cleanliness of the sample introduction and atomization system, including the spray chamber and the burner components. Cleaning the spray chamber involves disassembling the system and washing the components in a detergent solution—then rinsing and drying. When reassembling the spray chamber, the physical condition of each component should be examined. The working parts of the spray chamber are critical for obtaining optimal sensitivity and functioning, so any sign of damage or wear—such as pitting on the surface of the glass impact bead or knicks or other damage to the O-rings—would indicate that this component is damaged and should be replaced. For the burner used with flame AAS, the primary concern pertains to cleanliness of the burner slot. Use of fuel rich flames or measuring samples with high levels of dissolved solids may create buildup of deposits on the burner, which can reduce the efficiency of atomization and decrease sensitivity. This type of residue can be cleared from the burner's surface by polishing the inside and outside of the burner slot using a metal polish recommended for cleaning brass. There are special non-metallic burner cleaning strips that can be used to introduce the polish into the burner slot. After polishing the burner slot, thoroughly flush with water and allow to dry before refitting to the instrument.

Preparing Analytical Standards Accurately

Because any correlation between AAS signals and analyte concentration depends on the accuracy of calibration data, quantitative results can be only as accurate as the calibration standard solutions that you've prepared. Errors in analyte quantitation can occur in a numerous ways, such as from preparation, contamination, or sample source issues. Along with the potential to yield inaccurate results, the use of inadequate reference standards can cause a loss of time from troubleshooting, excessive instrument downtime, and the need to prepare new standards and reanalyze samples. Furthermore, errors in standard preparation may even contribute to untimely deterioration of instrument components, failure of quality control audits, and possible loss of ISO accreditation.

However, these difficulties can be overcome by deliberate selection of high-quality certified reference materials, such as those manufactured by Agilent as outlined in Figure 1. Agilent's certified reference materials are produced in an ISO 9001, ISO Guide 34 facility using high-purity raw components in purified solvents with the maximal purity available, typically >99.999%. These pristine manufacturing conditions are backed up by quality assurance testing using the high-performance spectroscopy protocol developed by the National Institute of Standards and Technology (NIST). Agilent certified reference materials have ISO/IEC 17025 certification with certificates of analysis reporting concentrations for as many as 68 trace impurities. Correspondingly, any concentration and uncertainty values for Agilent certified reference materials are traceable directly to NIST SRM 3100 reference standards to ensure the highest accuracy and traceability. Furthermore, all Agilent certified reference materials are packaged within pre-cleaned PTFE or HDPE containers. The meticulous care used by Agilent in producing certified reference materials translates into an extended shelf life, most of which are 18 months or longer.

> Furthermore, inefficiency of analyte preparation methods in the context of complex matrices can yield samples with analyte only partially captured within solution.

Along with selection of optimal certified reference materials, proper sample handling methods and protocols for calibration standard usage are vital for maintaining the accuracy and precision of certified materials through to end use. Any reference materials used should be within the stated expiration date, after which the compound stability and purity cannot be guaranteed within the manufacturer's certified limits. Errors due to the actual sample handling can be minimized by regularly calibrating pipettes and using class

Highest ISO Accreditation	Manufactured in an ISO 9001, ISO Guide 34 facility and certified in an ISO 17025 testing laboratory
High purity	Manufactured from high purity raw materials and solvents which are tested for impurities
NIST traceable	Certified using NIST high performance ICP-OES test protocols Directly traceable to the NIST 3100 Series of SRMs
Contamination free	Packaged in pre-cleaned, high purity HDPE bottles Shipped in poly sealed bags
Long shelf life	Most offer a shelf life of 18 months Supported by short and long term stability studies
Thorough confirmation	Trace impurities assayed using Agilent ICP-MS Actual concentration reported on CoA for up to 68 trace impurities

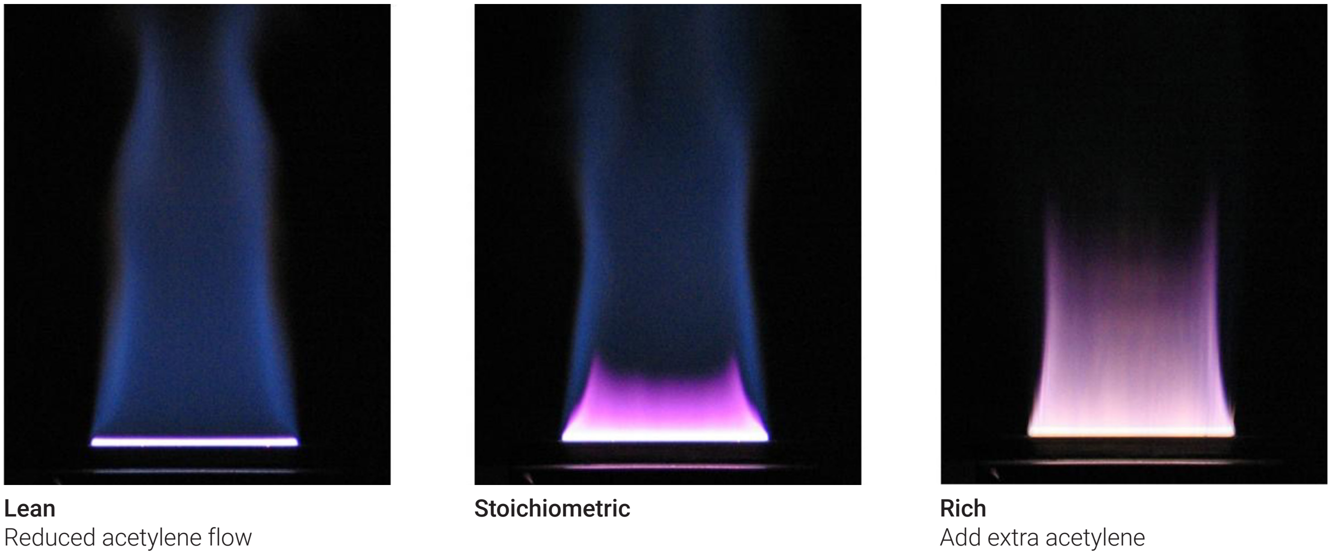
Figure 1. Value of Agilent's certified reference materials.

A volumetric glassware, while contamination from solvents can be minimized by using deionized 18 MΩ-cm water or high-purity organic solvents. During the dilution process, large drops in concentration when crafting calibrants from concentrated stock should instead be replaced by serial dilution stages until the target concentration is reached. Once diluted, lower concentration (µg/L) calibration standards must be remade regularly to ensure the concentration is known and stored in plastic PFA or FEP vessels with added acid for stabilization of analyte.

Other possible routes of sample contamination and inaccuracy can even lie outside of the sample materials and containers. Plastic components such as disposable pipette tips and centrifuge tubes with any added coloration should be avoided. The coloring agents in plastic goods may leach into solution during sample preparation or storage, with this route as a common culprit for introducing Cu, Fe, Zn, and Cd impurities. Similarly, pipette tips should never be inserted into stock solutions and especially so with acids. Particulate contamination can result from powdered gloves and airborne dust, as well. Analyte loss may even be observed in the case of highly volatile compounds. Furthermore, inefficiency of analyte preparation methods in the context of complex matrices can yield samples with analyte only partially captured within solution. The use of reagent and method blanks within sample batches combined with spiking of samples (pre- and post-digest) and taking a standard reference material of a similar matrix through your sample preparation process are all valuable ways to note issues introduced by your preparation methods, but also potential contamination from the reagents and vessels you're working with.

AAS System Operating Conditions and Sensitivity

After accounting for common confounding factors, an AAS system's operation as a whole should be verified to be sure that it is in the maximal operating condition. Each working component of the instrument should be considered when ensuring the overall system will function optimally, but particular attention must be given to the burner, nebulizer, and impact bead positions as well as the flame composition. The burner alignment should be such that the maximum analyte population from the flame atomizer will be exposed to the incident light beam. Burner alignment cards included with Agilent AAS systems have a target region to facilitate optimum positioning of the burner. With the burner in position and a standard being nebulized at the appropriate rate of ~5 mL/min, optimize the burner location by adjusting the height, rotation and lateral position while monitoring for maximum output signal. In a similar manner, the impact bead position can be adjusted closer to, or away from the nebulizer in order to maximize sensitivity, based upon the resulting signal while a standard solution is aspirated. For AAS systems utilizing a nitrous oxide-acetylene gas mixture for the flame atomizer, the flow of acetylene may need to be increased to as high as 8 L/min for ideal signal strength. This higher ratio of acetylene is necessary for achieving the "rich" flame (Figure 2) that is desirable for the more refractory elements, which are requiring the nitrous oxide-acetylene flame, such as Al, Mo and Si.



Lean
Reduced acetylene flow

Stoichiometric

Rich
Add extra acetylene

Figure 2. Optimization of the nitrous-oxide/acetylene flame.

Lamp Selection for Optimal Performance

Rounding out the ways to enhance AAS performance is the appropriate selection and optimization of hollow cathode lamps. The hollow cathode lamps produced by Agilent include both coded and uncoded varieties, with the coded variants featuring additional pins on the base for automated identification by Agilent systems of the element. While uncoded Agilent hollow cathode lamps cannot provide automatic element recognition, such lamps offer the best overall value and are compatible with AAS systems from most other AAS manufacturers (except PerkinElmer – Agilent also offers a range of lamps specifically for PerkinElmer AAS instruments). Higher intensity lamps—such as the Agilent UltrAA lamp series—are beneficial for trace analysis due to greater analyte sensitivity and a reduction in detection limits resulting from the greater source emission and lower baseline noise. The notable longevity advantage of Agilent lamps, which are of the order of >5000 mAh for conventional hollow cathode and >8000 mAh for UltrAA lamps, comes from a proprietary processing approach to maximize gas fill and maintain high material purity. Correspondingly, AAS systems fitted with Agilent hollow cathode lamps benefit from stable light sources and low-noise spectra yielding consistent and accurate measurements. Short- and long-term stability of Agilent hollow cathode lamps provide confidence in the predictable behavior of Agilent lamps relative to competitors (Figure 3). Similarly, compared to less expensive lamps produced by other manufacturers, Agilent hollow cathode lamps offer highly competitive dynamic ranges and lower limits of detection as shown for two example elements, lead, and cadmium (Figure 4).

Another misunderstood aspect of the hollow cathode lamp is the choice between single- and multi-element lamps. Single-element lamps are often selected based on the perception that multi-element lamps yield poorer lifetimes and reduced analytical performance, but actual usage data contradict these myths. The large range of multi-element lamps offered by Agilent—such as the Co/Mo/Pb/Zn, Cu/Zn, Na/K, Ag/Cd/Pb/Zn, and Cr/Co/Cu/Fe/Mn/Ni combinations—all have lifespans in excess of 7500 mAh, or a 1.5x increase in life versus conventional single-element hollow cathode lamps. Likewise, multi-element lamps provide comparable analytical sensitivity and measurement precision when operated using the recommended operating conditions as conveyed in Figure 5.

Figure 3. Performance of Agilent HC lamps. Short term stability measured after a 10 minute warm-up, and long term stability determined by reading a standard that gave good S/N repeatedly over an hour. Lamp lifetime was determined by operating the lamp continuously until failure.

Figure 4. Performance of Agilent HC lamps. Comparison of calibration curves for Pb and Cd. Instrument detection limits (3 sigma) are also shown.

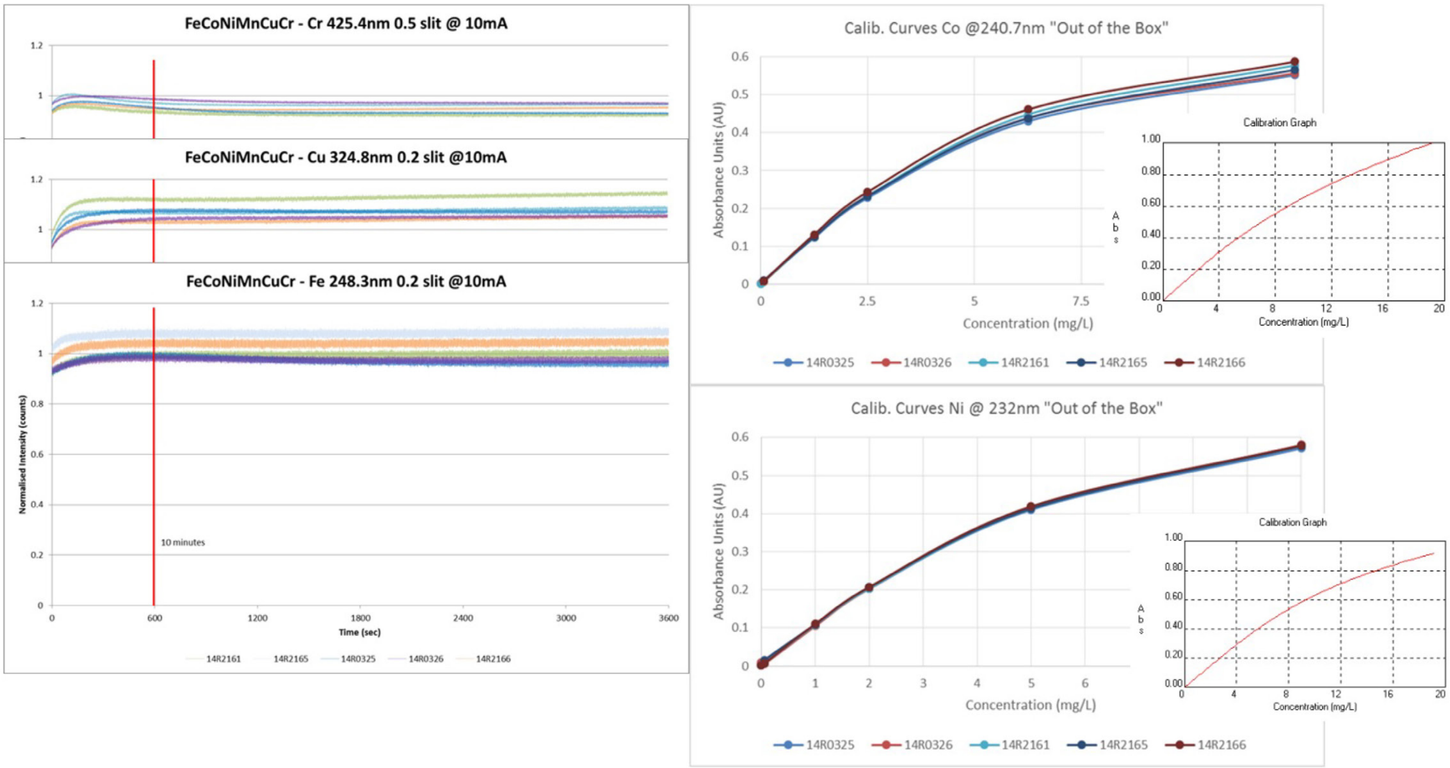


Figure 5. Multi-element HC lamps. Performance for Co/Cu/Cr/Fe/Mn/Ni shows good stability after a 10 minute warm-up and matches the expected performance for each element as listed in the flame AAS "cookbook".

Maximizing Performance of Graphite Furnace AAS Systems

Although flame atomization is most often encountered in AAS, another common atomization technique involves graphite furnace AAS which provides better sensitivity compared with flame AAS, and is the obvious choice for trace metal analysis applications using AAS. As with flame AAS, graphite furnace AAS systems benefit from preparation of accurate calibration standards made from certified reference materials as well as optimization of the hollow cathode lamp. However, some aspects of optimization must be tailored specifically to graphite furnace systems, including sample injection parameters, the furnace temperature programming, and other properties unique to graphite furnace AAS platforms. For sample injection into the graphite furnace, the position of the workhead must be verified as appropriate for passing the light source beam through the center of the graphite tube. This can be accomplished by aligning the lamp without the workhead, positioning the workhead, and rechecking overall alignment. The injection process itself should occur at a carefully adjusted depth into the furnace with the tip of the dispensing capillary cleaned externally beforehand with isopropanol. It is also recommended that the rinse solution used in the graphite furnace AAS autosampler is acidified with ten drops of nitric acid and five drops of a suitable surfactant (such as Triton X-100) to help clean the dispensing capillary between injections, and improve the dispensing characteristics. With respect to the furnace temperature program, optimization first requires an adjustment of the conditions for drying samples such that the deposited solution dries in a uniform and smooth manner without boiling. Matrix removal can be accomplished during the ashing stage, where the ashing temperature is dependent upon the matrix. The aim is to remove as much of the matrix as possible while retaining analyte in the graphite tube. Additionally, analyte atomization should occur with rapid heating to ensure a strong signal. The optimum ash and atomization temperatures can be determined automatically by the SRM Wizard, built into the software of the Agilent graphite furnace AAS instruments. The SRM wizard uses a mathematical model based on results from 12 experiments to determine the optimum ashing and atomization temperatures for the specific sample matrix. Before using these systems, the graphite tube should be conditioned to remove any possible surface contamination, prepare the tube for analysis while also improving atomization efficiency by coating the tube interior with the selected modifier (if selected in the method). This ensures it will work effectively from the start of the analysis.

Conclusion

Both flame and graphite furnace AAS are highly sensitive and accurate systems, but as with all instrumentation, following specific maintenance and optimization procedures is necessary to sustain peak performance. Sample introduction and nebulization, accurate preparation of analytical standards, optimizing the system operating parameters, and hollow cathode lamp selection are all critical areas to target for upkeep while minimizing downtime.

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DE44413.8783449074

Printed in the USA, September 2, 2021
5994-3979EN

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