

Atomic Absorption Spectroscopy

Introduction

Atomic absorption spectroscopy (AA or AAS) is one of the commonest instrumental methods for analyzing for metals and some metalloids.

Metalloids like antimony, arsenic, selenium, and tellurium are now routinely analyzed by hydride generation AAS (HGAAS; see www.shsu.edu/~chm_tgc/sounds/sound.html and www.shsu.edu/~chemistry/primers for animations and primers on that method). Inductively coupled plasma (ICP) is also a powerful analytical, instrumental method for these elements but at this point its much higher cost limits its widespread use as compared to AAS.

As the animation on AAS here shows, the main parts of the AAS system are a hollow cathode lamp, nebulizer, air/acetylene flame, and optical system. Alternate sample introduction systems such as graphite furnaces are also available but will not be discussed here. The job of each are detailed below:

Atomic Absorption Spectroscopy

Job of the hollow cathode lamp

*Provide the analytical light line for the element of interest
Provide a constant yet intense beam of that analytical line*

Job of the nebulizer

*Suck up liquid sample at a controlled rate
Create a fine aerosol for introduction into the flame
Mix the aerosol and fuel and oxidant thoroughly for introduction into the flame*

Job of the flame

*Destroy any analyte ions and breakdown complexes
Create atoms (the elemental form) of the element of interest
FeO, CuO, ZnO, etc.*

Job of the monochromator

*Isolate analytical lines' photons passing through the flame
Remove scattered light of other wavelengths from the flame
In doing this, only a narrow spectral line impinges on the PMT.*

Job of the photomultiplier tube (PMT)

As the detector the PMT determines the intensity of photons of the analytical line exiting the monochromator.

The Hollow Cathode Lamp

The hollow cathode lamp (HCL) uses a cathode made of the element of interest with a low internal pressure of an inert gas. A low electrical current (~ 10 mA) is imposed in such a way that the metal is excited and emits a few spectral lines characteristic of that element (for instance, Cu 324.7 nm and a couple of other lines; Se 196 nm and other lines, etc.). The light is emitted directionally through the

lamp's window, a window made of a glass transparent in the UV and visible wavelengths.

Nebulizer, Different Oxidants, and Burner Heads, and Waste

The nebulizer chamber thoroughly mixes acetylene (the fuel) and oxidant (air or nitrous oxide), and by doing so, creates a negative pressure at the end of the small diameter, plastic nebulizer tube (not shown in adjacent figure; see figure below). This negative pressure acts to suck ("uptake") liquid sample up the tube and into the nebulizer chamber, a process called aspiration. A small glass impact bead and/or a fixed impeller inside the chamber creates a heterogeneous mixture of gases (fuel + oxidant) and suspended aerosol (finely dispersed sample). This mixture flows immediately into the burner head where it burns as a smooth, laminar flame evenly distributed along a narrow slot in the well-machined metal burner head.

Liquid sample not flowing into the flame collects on the bottom of the nebulizer chamber and flows by gravity through a waste tube to a glass waste container (remember, this is still highly acidic). For some elements that form refractory oxides (molecules hard to break down in the flame) nitrous oxide (N₂O) needs to be used instead of air (78% N₂ + 21% O₂) for the oxidant. In that case, a slightly different burner head with a shorter burner slot length is used.

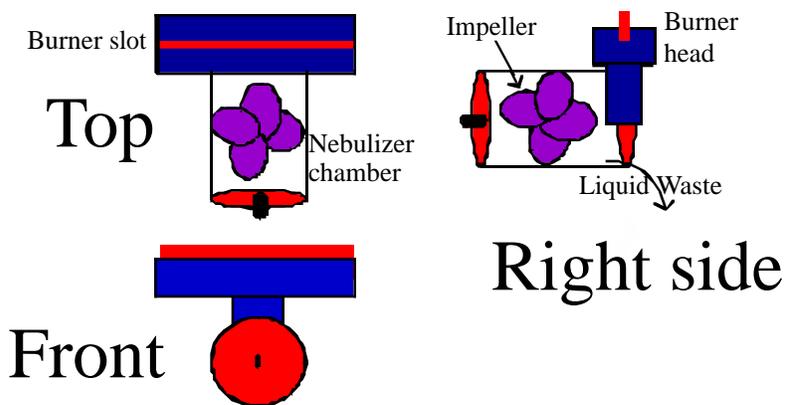
The Monochromator and PMT

Tuned to a specific wavelength and with a specified slit width chosen, the monochromator isolates the hollow cathode lamp's analytical line. Since the basis for the AAS process is atomic ABSORPTION, the monochromator seeks to only allow the light not absorbed by the analyte atoms in the flame to reach the PMT. That is, before an analyte is aspirated, a measured signal is generated by the PMT as light from the HCL passes through the flame. When analyte atoms are present in the flame--while the sample is aspirated--some of that light is absorbed by those atoms (remember it is not the ionic but elemental form that absorbs). This causes a decrease in PMT signal that is proportional to the amount of analyte. This last is true inside the linear range for that element using that slit and that analytical line. The signal is therefore a decrease in measure light: atomic **absorption** spectroscopy.

Acidic Content and Oxidation State of Samples and Standards

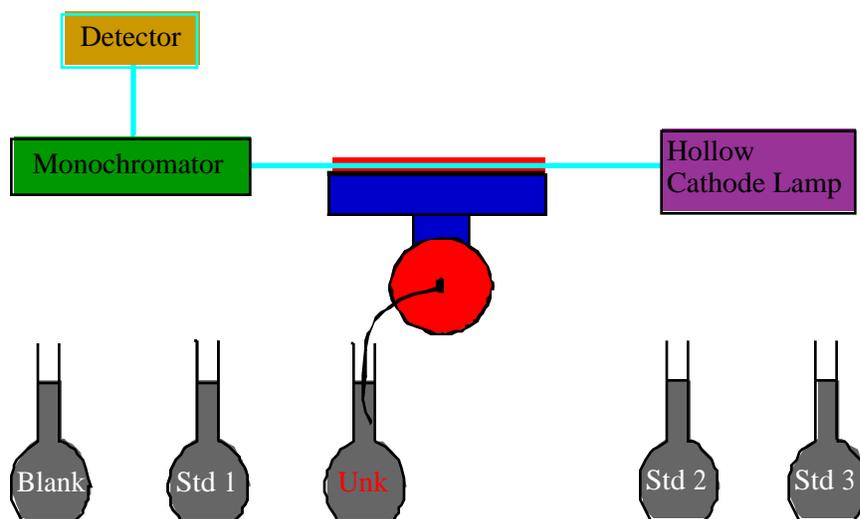
The samples and standards are often prepared with duplicate acid concentrations to replicate the analyte's chemical matrix as closely as possible. Acid contents of 1% to 10% are common. In addition, high acid concentrations help keep all dissolved ions in solution.

The oxidation state of the analyte metal or metalloid is important in AAS. For instance, AAS analysis of selenium requires the Se(IV) oxidation state (selenite). Se(VI), the more highly oxidized state of the element (selenate), responds erratically and non reproducibly in the system. Therefore, all selenium in Se calibration standards and Se containing samples must be in the Se(IV) form for analysis. This can be accomplished by oxidizing all Se in the sample to selenate using a strong



Nebulizer and Flame

oxidizer such as nitric acid or hydrogen peroxide and then reducing the contained selenate to selenite with boiling HCl.



Double Beam Instruments

The light from the HCL is split into two paths using a rotating mirror: one pathway passes through the flame and another around. Both beams are recombined in space so they both hit the PMT but separated in time. The beams

alternate quickly back and forth along the two paths: one instant the PMT beam is split by the rotating mirror and the sample beam passes through the flame and hits the PMT. The next instance, the HCL beam passes through a hole in the mirror and passes directly to the PMT without passing through the flame. The difference between these beams is the amount of light absorbed by atoms in the flame.

The purpose of a double beam instrument is to help compensate for drift of the output of the hollow cathode lamp or PMT. If the HCL output drifts slowly the subtraction process described immediately above will correct for this because both beams will drift equally on the time scale of the analysis. Likewise if the PMT response changes the double beam arrangement take this into account.

Ignition, Flame conditions, and Shut Down

The process of lighting the AAS flame involves turning on first the fuel then the oxidant and then lighting the flame with the instrument's auto ignition system (a small flame or red-hot glow plug). After only a few minutes the flame is stable. Deionized water or a dilute acid solution can be aspirated between samples. An aqueous solution with the correct amount of acid and no analyte is often used as the blank.

Careful control of the fuel/air mixture is important because each element's response depends on that mix in the burning flame. Remember that the flame must breakdown the analyte's matrix and reproducibly create the elemental form of the analyte atom. Optimization is accomplished by aspirating a solution containing the element (with analyte content about that of the middle of the linear response range) and then adjusting the fuel/oxidant mix until the maximum light absorbance is achieved. Also the position of the burned head and nebulizer uptake rate are similarly "tuned." Most computer controlled systems can save variable settings so that methods for different elements can be easily saved and reloaded.

Shut down involves aspirating deionized water for a short period and then closing the fuel off first. Most modern instruments control the ignition and shutdown procedures automatically.

These notes were written by Dr. Thomas G. Chasteen; Department of Chemistry, Sam Houston State University, Huntsville, Texas 77341. Copyright 2000.