Background

Atomic absorption (AA) spectroscopy is an important technique in analytical chemistry that determines the concentration of a specific element within a sample by vaporizing and atomizing the sample, then passing a light that the target element can absorb through the atomized sample. Atomic absorption uses the unique energy absorption spectra of different types of atoms to probe the presence of specific elements in two main steps:

1) Produce free atoms from the sample, usually using a flame.
2) Irradiate atomized sample with light, and monitor the absorbance of light by the target element.

The absorbance of light corresponds to electronic transitions within the atoms; the strongest absorption results from the electronic transition from the ground state to the first excited state. This is known as the first resonance line, and is typically the line monitored in AA spectroscopy.

In flame atomic absorption spectroscopy (the method discussed below), vaporization and atomization are both accomplished using a flame. The sample is dissolved in a solvent, nebulized to an aerosol (a fine spray of droplets), and then converted into free atoms by combustion. An AA spectrometer usually includes an aerosol modifier that prevents droplets too large to be atomized from entering the flame. The flame converts the aerosol into free metallic atoms in three steps:

1) The solvent is evaporated, leaving a solid metallic salt;
2) The salt is vaporized;
3) The salt molecules are dissociated, resulting in neutral metal atoms.

The thin, controlled flame with the atomized molecule becomes the sample cell, or the location of irradiation of and absorption by the target atoms.

The light source is usually a hollow cathode lamp specific to the element to be detected. The cathode in the center of the lamp is made of, or lined with, the element and is surrounded by the anode. The lamp is filled with an inert gas (typically argon or neon) that is partially ionized by the charge separation between the two electrodes. The gaseous ions collide with the element in the cathode and release atoms of the element to the center of the lamp. These atoms then hit fast-moving gas molecules, are excited from their electronic ground states to higher-energy states (usually the first excited state), and subsequently return to the ground state by releasing the energy characteristic of their
first resonance line. Since the element in the cathode corresponds to the target element, the energy released in the lamp exactly matches the energy needed to excite the target molecules from the ground state to the first excited state.

The absorbance by the target molecule is monitored by detecting the difference between the absorbance of the flame without sample and the absorbance of the flame incorporating the atomized sample. The detector system has three components: a monochromator, a detector, and a data processor. The monochromator isolates the single wavelength of light being monitored from other wavelengths of light present (background light). A photomultiplier tube (PMT)—a very sensitive method of detecting light in the ultraviolet, visible, or infrared regions—detects the single wavelength of light that passes through the monochromator. The light that passes through the monochromator strikes an electrode coated with a photosensitive material, causing it to eject photoelectrons. The photomultiplier directs these ejected electrons at an electron multiplier that amplifies the signal. When the signal has been sufficiently amplified, the electrons reach an anode and generate a current pulse proportional to the signal. The current pulse is detected by the data processor, which produces a reading of the intensity of absorption of a specific wavelength by the sample.

Figure 1: Diagram of an atomic absorption spectrometer

The concentration of a sample in solution (and then potentially the molecular weight of a sample) can be determined from the concentration of a specific element in the sample. The Beer-Lambert law (Equation 1)—an empirical relationship that allows us to relate the concentrations of absorbing chemical species to the intensity of absorption—is frequently used to relate absorption of light to concentration.

---

1 http://www.chemistry.nmsu.edu/Instrumentation/AAS1.html
\[ A = -\log\left(\frac{I}{I_0}\right) = \varepsilon \cdot c \cdot L \]  

\( A \) is the absorbance, \( I \) is the intensity of the light transmitted, \( I_0 \) is the intensity of the light shone at the sample, \( \varepsilon \) is the molar absorptivity or extinction coefficient, \( c \) is the concentration of the absorbing species, and \( L \) is the path length. However, the Beer-Lambert law is difficult to apply to AA spectroscopy because the path length of the flame and the concentration of the sample within the flame are generally non-uniform. Instead, a curve of absorbance versus concentration is created using standards of known concentration of the element in question. The concentration of the sample is then determined using the calibration curve.

Atomic absorption detects individual elements very accurately but does have drawbacks: AA spectroscopy requires a hollow cathode lamp specific to each element to be detected. Also, AA works primarily on metals, though some nonmetals that absorb in the ultraviolet region can also be detected by AA. Finally, since the sample has been atomized before the optical analysis occurs, AA does not give any information about oxidation states or chemical environments.

**Procedure**

*Preparing samples for calibration curve and unknown*

You need to know the identity of the metals in your unknown before you can use AA spectroscopy on your unknown. Once you think you know what metal you’re looking for, you need to make the samples you will use for your calibration curve.

Different metals have linear absorption ranges at different concentrations of sample. To find the optimum concentration range for the element(s) you will be analyzing at [https://buck-scientific-norwalk.myshopify.com/collections/single-element-hollow-cathode-lamps](https://buck-scientific-norwalk.myshopify.com/collections/single-element-hollow-cathode-lamps). Find the correct element's lamp, and then open the documentation for direct aspiration (not furnace) at the bottom of the page.

Begin from a commercial standard solution of your metal to make five 25 mL solutions with different concentrations that cover the optimum concentration range for detection of the ion. Use volumetric flasks to make your solutions. Make sure your glassware and pipettes have been thoroughly cleaned and rinsed with deionized water only before using. If you use a cleaning solution, make sure to thoroughly rinse your glassware.

**For all samples:** Record the exact concentration of each of the calibration samples. Make sure to mix all solutions well before filling the flask up to the line because solutions can have smaller volumes than pure solvent.
To prepare your unknown, dissolve 0.01 g of solid in 20 mL of a 1:1 mixture of concentrated (70%) nitric acid and water. To prepare the nitric acid solution, slowly add 10 mL of nitric acid to 10 mL of deionized water. The dissolution is exothermic, and if done too quickly, may cause NO₂ gas to form and turn your solution brown. Then, add your solid and stir until the solution is completely clear. Record the exact mass you have added to solution. Dissolution of your solid may take some time (even overnight).

From your dissolved sample solution, prepare two different 50 - 250 mL dilute solutions of your unknown in a volumetric flask. You should dilute to within the optimum concentration ranges for the metal ion concentrations you will be testing. You will need to make assumptions about what compounds are present in your sample and at what concentrations your monovalent ions have been substituted after your ion exchanges. For our purposes, HSOD groups can assume their samples are exclusively HSOD for this calculation, and ISOD groups can assume their samples are exclusively ISOD. From this you can calculate the number of moles of Na, K, Cu, or Ag that you would expect in 0.01 g of your sample. Use this value to prepare one dilute sample, and then dilute that sample 10-fold for your second unknown dilute sample. You may have to prepare and test additional dilute unknown solutions (that may be of higher or lower solid concentrations) depending on whether you find your measured concentrations to fall within the optimum range.

Using the AA spectrometer

Though the instructions below include the basic steps for getting AA data, you should get your professor or TA to show you how to use the AA spectrometer the first time you work with it.

1. Turn on the computer and the lamp with the red button on the side of the instrument. Make sure you are using the lamp designed for the element you want to detect and that this lamp is in the top position and connected to the input labeled #1; allow the lamp to warm up for at least twenty minutes.

   NOTE: If you have to switch lamps, you must remove the lamp in the top position and replace it with the desired lamp. You can only switch lamps with the instrument and flame off. If you switch lamps, the instrument must be re-aligned according to the procedure below. If you will be running more than one elemental analysis, can warm up lamps in the other two slots before you switch between lamps.

2. Make sure the vent valve is open the vent and the metal vent tube is unblocked.

3. Make sure the acetylene burner (the burner with the longer outlet) is attached. If it is not, ask for assistance.
4. Align the burner with the beam from the lamp. Use the card left on top of the AA or a sheet of paper to find the beam. Then shift the burner until the outlet is directly under the beam.

5. Make sure that you have selected the correct lamp on the AA screen (at the top). If not, you may select your lamp from the library. Press the “LIB” key. Make sure you are selecting for LAMP 1. Use the arrows to scroll until you find the correct element and lamp code. Check the lamp’s label for its code before selecting. Press “2” to select.

6. Set the wavelength of the monochromator to maximum wavelength specified in the name of the lamp, using the manual knob on the right side of the instrument. Set the wavelength to the first decimal. Then, optimize the wavelength by pressing the “ALIGN” key, and then turning the knob until you reach a maximum value of the detected energy displayed on the screen. Once you have done this, press “ALIGN” again.

7. Zero the absorption before igniting the flame by pressing “A/Z” and then “ENTER.”

8. For Cu, Ag, Na, and K analyses, you will use an air/acetylene flame. Open the valve on top of the acetylene tank (not the N₂O tank). The pressure on the acetylene tank, when open, should be 13 psi; the house air should be 60 psi.

9. Before you ignite the flame, you need to check that you have a significant flow of both air and acetylene. Hold down the “Air” button on the front of the instrument. If the flow of air or acetylene is under 5, adjust the fuel using the valve on the front of the instrument, so that the acetylene flow is between 5 and 6.

10. To ignite the flame, hold the “On” button on the front of the instrument until you get a flame using the lighter stored in the drawer below the AAS. (It will be very obvious if you ignite the flame.) Be careful when igniting the flame. If you touch the burner while igniting, turn off the flame and realign the burner.

11. Now you need to adjust the fuel so that you get an even, clear, blue flame. (A flickering, uneven, or orange flame gives poor sample distribution and inaccurate data.) A fuel level of around 3.5 usually gives a good flame, but you should play with the fuel level until you get the best flame you can. There should be no orange flame and the brightest blue cone at the bottom of the flame should at an even height.

12. Allow the flame to run for about 5 minutes before you begin collecting data.

13. Now turn to the computer screen on the front of the instrument.

14. Zero the instrument using deionized water. Insert the instrument tube into a blank sample (deionized water), and wait for the reading at the bottom of the screen to stabilize. Also, check that a small amount of liquid flows through the outlet tube. Then, press the “A/Z” button to
zero the reading. Then, press “ENTER.” Check that the zeroed reading is within +/-0.002 (it will oscillate a bit). If not, zero again.

15. Insert the tube into one of your samples. Allow the absorption to stabilize (or wait at least five seconds), and record the reading. Continue with your other samples, zeroing with your blank in between each sample.

16. When done, press “Off” to turn off the flame. Close the acetylene tank valve, and clear out the fuel by holding “Air” until both air and acetylene levels drop to zero. Turn off the instrument.

17. Make a calibration curve using a linear fit to the results from your standard samples, and then use this curve to determine the concentration of the element you’re detecting in your unknown solution. If your standard data does not appear to be perfectly linear, you may have falling outside of the optimum range, in which case you may use a second order polynomial to fit your standard data.

Troubleshooting:

If no liquid flows through the outlet tube and/or you don’t hear a difference in the noise from the instrument when you insert the capillary tube into your sample, you may need to change the tube. To do this, consult with Stephen.

References and Further Reading:

Willard, H. H.; Merritt, L. L.; Dean, J. A.; Settle, F. A. Instrumental Methods of Analysis. 7th Ed.