ATOMIC ABSORPTION

Required Reading

D.A. Skoog, Principles of Instrumental Analysis, Fourth Edition, Ch.10.

Related Reading

Rubinson and Rubinson, Contemporary Instrumental Analysis, Prentice Hall, p. 373-391


Bauer, Christian and O’Reilley, Chapter 10


INTRODUCTION

Atomic absorption (AA) spectroscopy is based on the absorption of ultraviolet or visible radiation by free atoms in the gas phase. These free atoms are produced by nebulizing a solution in a flame (acetylene/oxygen) and are detected when they absorb light from a hollow cathode discharge lamp. The lamp emits discrete wavelengths (lines) which are specifically absorbed by a particular atom; thus, one needs a different hollow cathode lamp for each species to be monitored. This gives the AA process a great deal of specificity, but at the expense of acquiring many lamps and changing them when a different atom is to be studied.

The amount of radiation absorbed by the atoms in the flame is dependent on the number of atoms in the ground electronic state, the effective path length of the flame and the absorptivity of the ground state atoms. These considerations are analogous to those used in formulating Beer’s Law for molecular solution species, and we might reasonably expect that there is a similar absorption/concentration relationship in AA. One can indeed easily derive such a proportionality, but care must be taken in AA because “Beer’s Law” plots usually have a limited linear range. Analytical determinations may still be made in a non-linear region, provided sufficient care is taken to construct non-linear calibration curves.

This experiment is designed to acquaint the student with the atomic absorption apparatus, the optimization of the various instrumental parameters, the sensitivity of the AA experiment and possible chemical interferences (matrix effects). The solubility products (K_{sp}) of some sparingly soluble copper salts will be determined using AA to measure the copper concentrations in saturated solutions. Also, the copper composition of two pennies will be determined from the calibration curve. Running other tests, such as lead or iron, are done just like it is for copper, except a different hollow cathode lamp and detection wavelength are used.
APPARATUS AND REAGENTS

Perkin-Elmer 3110 Atomic Absorption Spectrometer
Computer with monitor and printer
Copper hollow cathode lamp
Cu(NO₃)₂, CuBr₂, CuCl₂ and CuSO₄ stock solutions (250 ppm)
Saturated copper salts for Ksp: Cupric Iodate, Cupric Carbonate & Cupric Oxalate

START-UP

Power ON computer, monitor and printer, then turn on the AA.
Insert the Copper Lamp through opening on right side of AA near top, if necessary.

Click “Flame”, then double-click the dimmed “3110” button on the bottom-left of screen. This button **must** be illuminated before communication between the computer and AA can be established.

Double-click “Manual”, then click “Defaults”, then click on the appropriate element (Cu).

WINDOWS → Element Parameters, then set the following parameters:

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
<th>AA Slit Width</th>
<th>Read Time (sec)</th>
<th>Replicate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>324.8</td>
<td>0.7</td>
<td>5</td>
<td>4</td>
</tr>
</tbody>
</table>

For calibrations, click on “Calib” box → Enter ID and Concentrations of Standards (Calib. Units = mg/L = ppm). Use the ppm numbers as the ID’s.

Calibration standards will be 1, 3, 5, 7 & 9 ppm Copper Nitrate solutions.

“Options” → Check the boxes on both of these: Calibr. Curves & Element Parameters

Lamp Alignment

It is essential that the lamp is aligned towards the middle of the detector. The better the alignment, the more signal that the detector can see, resulting in lower detection limits.

WINDOWS → Align Lamp

Set Current = 15 mA & Element = Cu

During the lamp alignment, the blue bar on the computer screen is equal to the signal the detector receives from the lamp. **The longer the bar, the better.** If the bar goes off-scale (gets full length), press the F2 button, which will autoscale the bar back to the middle of the scale.

Set the slit width to the desired setting, and set the high-low lever (slit height) to **high.**
Adjust the wavelength using the large knob on the left side of the AA.
Adjust the focusing of the lamp by pushing/pulling the lamp in and out to obtain best signal, then adjust the lamp position with the two black knobs located above the lamp.
**Burner Alignment**

Adjust the horizontal and vertical position of the burner head so that the red beam from the hollow cathode lamp passes directly over the burner slit without being blocked. This is done with a white card with a line drawn on it to center over the burner slit, and aligning the red beam to hit the line. **NOTE:** The entire length of the slit should be aligned with the red beam, not just the middle. This is because you want the beam to travel through the entire length of the 10 cm. flame.

Adjust the front-back position of the burner so that the lamp beam is directly over the middle of the burner.

Rotate the Burner position such that the light travels the entire burner length. Use the white card to follow the path of the lamp. This is a very important step!

Click on “Close” (the top-left box with the black bow-tie in it). Close the Element Parameter window.

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**Notes for AA**

--- The flame should be lit only when measurements are to be made. Make solutions first, *then* measure. Do not have the flame burning while preparing solutions, as this wastes acetylene.

--- If the flame is sooty, then the mixture is too fuel rich; decrease the fuel or increase the supporting gas (compressed air).

--- Always aspirate something (usually DI water, or 5% Nitric acid to clean the inlet tube line) when the flame is on.

--- Keep flame door closed when making measurements (air drafts can bend flame over, affecting results).

--- Don’t use flow controllers for air and acetylene to shut off gases after flame is optimized -- use needle valve at tank for acetylene & use support select to OFF for compressed air (optimize with valve all the way open).

--- Make sure that the burner does not block optical path. This can happen if position of burner is too high.

--- Clean burner slot with card or small screwdriver to remove deposits, if needed.

--- Make sure sample is aspirated quickly (high flow rate). A slow flow rate often indicates that the aspirator tube may be obstructed.

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**Effect of Burner Vertical Position**

When a copper sample is passed through the flame, the color of the flame will change. It is important that the area of the flame with the most copper in it is properly aligned where the light beam from the hollow cathode lamp passes through. Prepare 100 mL of 5 ppm Cu(NO$_3$)$_2$ from the stock solution with deionized water (*see page 5*). Set up the instrument as in the operating
instructions. Use a slit width of 0.7 nm. and the most sensitive wavelength given in the instruction manual (called the primary wavelength).

With the flame OFF, we have already visually set the burner to the best horizontal position. The red beam should pass over the middle of the entire burner slit. Once this is achieved, do not adjust these settings! Now, light the flame and test the effect of the burner vertical position by obtaining absorbance vs. position readings.

The oxidant gas (compressed air) is always turned on first, then the acetylene gas. Safety reasons dictate this.

Turn on the Air cylinder to 50-60 psi, and the Acetylene cylinder to 12-14 psi. Open the main cylinder valves, then the small valve on the compressed air regulator. The gas controls on the AA are located at the front, at the bottom left. Gas flow meters are located there as well.

Turn the Oxidant knob to Air, set the flow level, then adjust the acetylene flowrate. With the Fuel = 2 and Oxidant = 4, then press “Ignite” button on AA. If the gases shut off and the ignite button lights up, turn Oxidant to Off, then back to Air and try again. You may need to place a match in the white holder and light the flame with the match.

WINDOWS ➔ Continuous Graphics. This will show the absorbance as a function of time. Place the blank into the feed tube and note the absorbance value. It should be zero. Press the auto-zero button (F3) to zero the blank. Then run the 5 ppm copper solution. Write the absorbance in your lab manual. We will then make changes the burner height by rotating the large black knob located under the burner just above the springs. Then once again run the blank, zero it, then run the copper sample. Repeat. Remember to re-zero between each measurement, as the initial signal will change as the burner position changes. Obtain a minimum of 5 data points.

➔ Set the burner position for a maximum absorbance before proceeding.

**Effect of Slit Width**

Again, using the 5 ppm Cu(NO\(_3\))\(_2\) solution and the blank, study absorbance vs. slit width. Record absorbance values at slit widths of 0.2 and 0.7 nm. with the slit height set to high. Set the slit for the maximum absorbance before proceeding. This should be the larger slit width, as it allows more signal to pass through and reach the detector. Again, remember to make sure the blank is showing no absorbance.

**Effect of fuel-air ratio**

Test the effect of fuel-air ratio by setting the support gas flow rate at ~3.0 to 4.5 and varying the fuel flow rate between 1.0 and 2.0. Again use the 5 ppm Cu(NO\(_3\))\(_2\) solution. Be sure to reset the zero absorbance for the blank after each change in the fuel-air ratio. Take a minimum of 4 data points. Set the ratio for maximum absorbance before proceeding.

**The Atomic Absorption Spectrometer is now ready for running the experiment.**

Remember to shut the flame OFF if the samples have not been made, so as to not deplete the gases.
EXPERIMENTS

Measurement of $K_{sp}$

We will need to prepare the standard solutions of 1, 3, 5, 7, 9, 25 and 50 ppm Cu(NO$_3$)$_2$ by dilution of the stock solution with deionized water. First, make a 10 ppm Cu(NO$_3$)$_2$ solution by pipetting 10 mL of the 250 ppm stock solution into the labeled 250 ml volumetric flask and dilute to the mark. This 10 ppm solution will be used to make 100 mL of the 1, 3, 5, 7 and 9 ppm standard solutions. To easily make these five standards, use may want to use the following flow chart:

![Flow Chart]

Finally, make 100 mL of the 25 & 50 ppm copper solutions from the original 250 ppm stock solution.

Matrix Effects

Prepare 5 ppm solutions of Cu(NO$_3$)$_2$, CuBr$_2$, CuCl$_2$ and CuSO$_4$. Aspirate the solutions and measure their absorbances. Then, after these samples have been run through the AA, add 0.05 g. of EDTA to each solution. Swirl and then measure the absorbances after the addition of EDTA. Are the values any different?

Sparingly Soluble Salts

The first step in the experimental procedure is the preparation of the sparingly soluble copper salts. The solutions used are Cupric Iodate, Cupric Carbonate & Cupric Oxalate. If the solutions have already been prepared, then just swirl them to insure a saturated solution. Allow the solutions to remain undisturbed until needed for measurement.

If the solutions have not been prepared, place a small amount of copper salt (~1 g.) in the appropriate plastic bottle. Add ~100 mL of deionized water and swirl or shake the bottle. Should any of the salts dissolve completely add more copper salt to the solution. *For meaningful results the solutions must be saturated.*

These solutions MUST be filtered through filter paper before they are run into the AA. If a small piece of solid got stuck in the small feed tube, it could clog the tube.
Copper Pennies from 1982

The year 1982 was an interesting year for our US Treasury. The cost of copper was getting so expensive that it was costing well over 1 cent to produce each penny. Naturally, this was not a good economical situation for the government. Late in that year, the composition of the penny was changed to predominantly zinc, with copper being used only to coat the surface. Both types of 1982 pennies will be analyzed.

Running Standards

Obtain absorbance readings for each standard copper solution, with the instrument set to optimum conditions as found earlier. Record the calibration curve absorbance values for each standard in your lab notebook. On the Manual Control window, click on both Save Data & Printer on/off buttons so that both are darkened.

CALIBRATION → Auto Zero with DI water running into AA. Zero reading if necessary.

Place STD 1 in inlet tube, then CALIB → S1
Place STD 2 in inlet tube, then CALIB → S2
Place STD 3 in inlet tube, then CALIB → S3
Place STD 4 in inlet tube, then CALIB → S4
Place STD 5 in inlet tube, then CALIB → S5

Click on the Display Calibration window.

Expand the graph from the top-right Full box block, then FILE → Print Image

Running Samples

Click on Display Data window. To run the samples, aspirate the sample into the AA, then press “F4” to read solution. REPEAT for the remaining samples.

Run the 25 and 50 ppm copper nitrate solutions through the AA. Do these samples show linearity to the 1→9 ppm standards?

Run the matrix effect samples, then run them again after the addition of EDTA.

Run the sparingly soluble salts. Remember to decant and filter the sparingly soluble salts, making sure no solid is in the sample. DO NOT RUN SATURATED SAMPLES IN THE AA!! Record the absorbance values for these salts. Do these absorbance values fall within your calibration values on your calibration curve? (If not, how can you make them fall within the linear portion?)

Finally, take one of each type of 1982 penny, and record the mass of each. Then, dissolve both pennies separately in around 40 mL of 6M Nitric acid in a 100 mL beaker in the hood. Once dissolved, dilute the solution in a 100 mL volumetric flask. Then, dilute 1 mL of this solution into a 100 mL volumetric flask. Determine the ppm of copper in each of these, and from this, determine the percentage of copper by weight for each penny.
**Secondary Wavelength**

Now consult the lamp manual and set the monochromator to a secondary analytical wavelength. Optimize the instrument for this wavelength. **NOTE: Only the wavelength optimization is required.** The lamp and burner positions will still be aligned from the earlier optimizations. **REPEAT** the standards, including the 25 and 50 ppm solutions, and run the two different penny samples.

**Shut-Down**

Run DI water through the AA to clean the inlet line.  
**FILE →** Exit to DOS. Close the acetylene valve, then the compressed air valve.  
Power OFF the AA, computer and printer.

**Treatment of Data**

1) Tabulate the data from the instrument optimization. Are these settings the same for all flames and elements? Why or why not? How are the atoms produced in the flame?

2) Tabulate the data from matrix effects. Why are the absorbances different before and after the addition of EDTA? Suggest reasons for any systematic effects in the data.

3) Plot the calibration curves. What is the linear range for each curve? Which curve has the most linear range? Why? At what concentration did each curve become non-linear? Why do the curves become non-linear? Over what concentration range is each curve analytically useful? Is it different for the secondary wavelength?

4) Determine the copper concentration in each of the three salts from the calibration curves. Calculate the “simple” solubility product constant from the copper concentration using:

   \[
   \text{CuA}_n (s) \rightarrow \text{Cu}^{2+} + n\text{A}^{2/n} \quad \text{K}_{\text{sp}} = [\text{Cu}^{2+}][\text{A}^{2/n}]^n
   \]

   You must use the stoichiometry of the compound to determine the anion concentration in terms of the copper concentration.

5) Compare your \( K_{\text{sp}} \) values to literature values. Check several sources (i.e. CRC Handbook, *Handbook of Analytical Chemistry*, etc.).

6) Determine the weight percent of copper in each of the two types of 1982 pennies from your data for both wavelengths. Compare your results with the actual weight percent of these pennies given by the US Treasury.