Chemistry 151L Quantitative Analytical Chemistry

Determination of Copper and Zinc in Old and New American Pennies Using Atomic Absorption Spectroscopy (AAS)

I. Required Reading

In addition to reading this project description and answering questions in the prelab, you should read Chapter 24 (introduction to absorption spectroscopy) and Chapter 28 (atomic absorption spectroscopy) in order to understand the instrument operation and sample preparation. Review Chapter 8C, which discusses standard calibration. Read Chapter 36C on microwave digestion.

II. Introduction

Flame atomic absorption spectroscopy (AAS) remains the most widely used of all atomic spectral methods. This is largely due to its relatively low cost and simplicity of instrument operation and maintenance. In AAS, monochromatic light with precisely the wavelength to be absorbed by atoms of a specific element is sent through a flame, plasma, or furnace environment. Such high-temperature sources are used in order to break the analyte molecules down to individual atoms and their ions. Errors (matrix effects) occur when such as stable oxides or other refractory complexes persist, even at high temperatures.

Two types of atomizers are used for AAS - flame and electrothermal (graphite furnace). The flame atomizer used in the instrument for this experiment consists of a nebulizer that converts the sample solution into a fine mist of aerosol particles that is fed into the burner. The aerosol particles are then vaporized and broken down to the level of individual atoms.

The most effective lamps are those that emit radiation that is an exact match to the analyte atom. This can be accomplished by using a hollow cathode lamp (see textbook’s Figure 28-17, and the accompanying discussion) containing a small amount of the element to be determined. The light emission from these lamps is caused by electrons dropping from high energy states to ground states in the same atoms; hence the energy is a precise match to the absorption lines. Since the bandwidth of light emitted from a hollow cathode lamp is extremely narrow, AAS offers less interelement interference relative to AES (atomic emission spectroscopy) wherein the resolution between interfering wavelengths is determined by the optics of the system. In general, this corresponds to a resolution of 0.01 nm for absorption lines and 0.5 nm for emission lines. The lamp used for this experiment contains several elements, including Ca, Cu and Fe, that emit non-interfering lines. Background interference is further reduced by use of a diffraction grating monochromator between the flame and the photon detector so that only radiation of the desired energy reaches the detector. Double beam techniques with synchronized alternation are used to reduce effects of instrument drift and to minimize other effects on background signals.

If the concentration of atoms in the flame is too high, all the light will be absorbed and portions of the flame will not be sampled. Thus, saturation absorption is reached and a linear calibration curve for the elemental concentration does not apply. Therefore, samples must be kept reasonably dilute, frequently in the range $10^{-3}$ to $10^{-5}$ M. Since only a small volume of solution (a few mL) is aspirated, the method uses only small amounts of reagents, sample, or standards.

Several problems are inherent in the method and must be kept in mind whenever AAS is
employed; the most prevalent of these are from spectral and chemical sources. Spectral interference occurs when the absorption/emission of interfering species overlaps the desired elemental transition. However, as previously described, interferences due to overlapping lines are rare for AAS relative to AES. Hence, spectral interference sources in AAS take the form of combustion products which absorb or scatter radiation, effectively diminishing the power of the transmitted beam. A deuterium lamp is most often used in tandem with the hollow cathode lamp to effectively provide a background correction. In this method, the UV radiation from the deuterium lamp is not absorbed by the analyte, so any decrease in the intensity from the deuterium lamp is a direct consequence of absorption or scattering effects by matrix components in the sample.

Chemical interference is more problematic than spectral interference for AAS. The most common type of interference is from anions which form non-volatile compounds with the analyte. An example of this phenomenon is the decrease in calcium absorption when sulfate or phosphate is present in the sample matrix. Releasing agents are typically used in such samples whereby a source of cations is added to react preferentially with the anions to free up the analyte atoms. Common releasing agents are small amounts (e.g. < 1%) of lanthanum or strontium ions.

Another method that may be used to circumvent chemical interference problems is the use of higher-temperature flames such as oxygen/acetylene or nitrous oxide/acetylene. However, in these flames, ionization becomes a significant factor that governs line intensities. An atomic absorption spectrum consists of resonance lines resulting from transitions from the ground state to higher excited states. However, if a large fraction of atoms are ionized in the flame, there will be fewer atoms available to absorb the characteristic lines from the hollow cathode lamp, and a decrease in line intensity will be observed. For example, in a flame, ground state potassium atoms are capable of absorbing radiation of the appropriate energy for electronic transitions from a 4s level to higher excited orbitals (e.g., 4p or 5p levels). However, if a large number of K atoms are converted into $K^+$ ions, these atomic transitions will be suppressed. A method used to prevent excessive ionization is the addition of alkali metals such as strontium which provides a high concentration of electrons to the flame and effectively suppresses the ionization of the analyte.

In this experiment, you will be analyzing American pennies from various years to determine the amounts of Cu and Zn. Although pennies from both America and Canada used to consist mostly of copper, in recent years, the national mints have reduced the amount of copper in these coins to reduce production costs. For example, in Canada, the switch from solid copper to copper-plated zinc has reduced this cost from over a penny/coin to 0.9 of a cent for each coin.

III. General Procedural Notes:
1. Read thoroughly all instructions provided with the instrument or presented by the lab TA before attempting to use the AAS instrument. The instructions on how to operate the instrument are printed on sheets of paper and can be found next to the computer.
2. You will be handling concentrated acids. Gloves must be worn, and you should make sure you know where the eye washes, showers and bicarbonate are located. Microwave digestion bomb can produce high temperature and pressure within the reaction vessel. Be sure to cool the bomb before slowly opening the cap, so as to prevent accidental acid splash.
3. The AAS instrument must have water aspirating through it whenever the burner is on and not being used for a measurement. Always clean off the dip tube before placing it in your analyte solution, and always aspirate nanopure water between different samples. The instrument is very sensitive and will detect the presence of contaminating residues.

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4. Your solutions must all be filtered well so they do not contain particles that could clog
the nebulizer. If the solutions are visibly clear, you don't have to perform an additional filtering
step.

5. The metal door in front of the burner should be in place during your measurements in
order to prevent fluctuations in the absorbance readings.

6. There are a large number of solutions to be made up in this experiment involving many
dilutions. The AAS instrument will report accurately on the contents of your samples. However,
your results will only be as good as your skill at making accurate, clean solutions. You will need
to be very organized to avoid mistakes. Work together carefully as a team to decide on the
division of procedure steps, labeling flasks, etc., to avoid errors. You will also need to work
quickly and efficiently to get everything finished in your appointed lab period.

7. The instrument reading is an average based on a number of samplings per minute. You
do not need to run any solution for more than one minute. You only need to get one good (mean)
absorbance for each solution you prepare.

IV. Procedure

(a) Preparation of Standard Solutions

Using the 1000 ppm stock solutions of Cu and Zn (that your TA will provide), prepare a
series of standards (4 standards per element) in the range 0 - 10 ppm, using 250 mL volumetric
flasks and the appropriate volumetric pipette(s). Good choice of standard solutions would be 2.0,
4.0, 8.0, and 10.0 ppm. You will need to share your volumetric flasks to make the solutions.

Before coming to the lab, calculate how much stock solution you will need to prepare
these standard calibration solutions (prelab question). Your TA will verify the correctness of
your calculations before you will be allowed to start.

(b) Preparation of Two Penny Samples (Old and New)

Repeat this procedure three times: (1) for new pennies; (2) for old pennies; (3) for
the blank sample. The masses / volumes which used in this procedure should not
be exceeded under any circumstances (see Chapter 36C for details).

1. Unscrew the screw cap from the bomb body. Inside will be the Teflon reactor, comprised
of the Teflon lid, Teflon o-ring, and Teflon cup. Using pressure through the bottom of
the assembly, push the reactor and bottom plate out of the bomb and remove the Teflon
lid from the reactor

2. Inspect the Teflon o-ring on the lid, ensuring that there are no cracks in the o-ring

3. Work within a fumehood to place approximately 0.05g of a penny (weighted to 0.0001g)
into the reactor. For **old penny**, which consists predominantly of copper, add 2 mL of
concentrated HNO₃. For **new penny**, which consists predominantly of zinc, and 1 mL
concentrated HNO₃ and 1 mL of nanopure water. Brown gas evolving during the reaction
is NO₂. The pennies have been cut into small pieces for you already. Because the weight
used is very small, it is likely that everything will dissolve completely without
microwaving the solution. If this is the case, proceed directly to step 12.

4. Steps 4-11 should only be undertaken if your penny bits have not dissolved completely.
Replace the lid of the reactor. Place the bottom plate into the bomb body ENSURING
THAT THE ROUNDED CORNERS ARE FACING DOWN. Fit the reactor into the bomb body WITH THE LID FACING UP.

5. Screw the screw cap onto the bomb body until a GENTLE pressure will not cause the cap to spin. Then, continue to tighten for 1/8 of a turn.

6. Place the bomb into the microwave and react for 30 seconds on high. ENSURE THAT THE HOOD SHIELD IS DOWN DURING THIS PROCESS

7. Let the bomb sit for 1 minute in the microwave, then react for another 30 seconds

8. Let the bomb sit for 1 minute in the microwave, then place in an ice bath for 10 minutes.

9. Slowly loosen the screw cap and remove the reactor.

10. If the penny pieces are not completely dissolved, repeat step 6-9.

11. If there is any residual carbon deposits in the reactor, add 0.5 mL HNO₃ to dissolve the residual carbon deposits. DO NOT MICROWAVE. Adding the HNO₃ to the reactor and letting it sit for 1 minute will be sufficient to dissolve the residuals.

12. Once the penny is completely dissolved, quantitatively transfer this mixture into a 500 mL volumetric flask and make up to the mark with nanopure water. This solution should be free of any suspended particles.

13. Even if you do not see any suspended particles, filter this solution so that you will not clog up the AAS sample inlet.

14. Ensure you record the visual appearance of your penny, prepared solutions, and label all flasks.

15. Important: Repeat the exact same steps to dissolve the second penny sample.

16. Important. Prepare a BLANK solution which contains all the steps above, without penny.

![Diagram of high-pressure microwave digestion](image)

**Figure 1:** Container for high-pressure microwave digestion

(c) **Analysis**

1. Set the hollow cathode lamp to a wavelength of 324.8 nm (for Cu analysis) - the desired program is chem151LCu (refer to the printed instructions next to the instrument)

2. Measure the absorbances for the 4 Cu standards. Plot the calibration curve. Is this linear? Make sure that you record the number of replicates that the software measures - *i.e.*, the value you use for a solution absorbance is the mean of a number of replicates.

3. Set the hollow cathode lamp to a wavelength of 213.9 nm (for Zn analysis) - the desired program is chem151LZn.

4. Measure the absorbances for the 4 Zn standards and plot the calibration curve. Is this linear? Again, record the number of replicates used for each absorbance measurement.

5. Analyze the blank solution you prepared above prepared in step b) above for Cu and Zn. The blank solution should give you very small signals unless you had contaminations.
6. Analyze each of the penny stock solutions you prepared in step b) above for Cu and Zn, ensuring that the absorbance values are in the range of your standards for each element. If they are off scale, you will need to calculate an approximate dilution factor to bring these within your standard range and carry out precise dilutions (using volumetric pipettes and volumetric flasks) on these samples. Once the absorbance values for all of your solutions are within the range of the standards, calculate the concentration of each element in each solution. Don't forget to take into account the dilution factors.

7. Turn off the AAS instrument following the printed instructions.

(d) Disposing of your solutions

In order for solutions containing Cu or Zn to be disposed of in the drains they must have an acceptable concentration. Solutions containing Cu need to be below 3 ppm and solutions containing Zn must be below 10 ppm. Estimate how much water you will need to dilute your most concentrated solutions; dilute them by this amount and dispose of them in the drain.

V. What to Submit in Your Report

1. As usual, turn in your prelab at the beginning, your duplicate copies of all the notebook pages at the end of the laboratory session. Remember: your lab will count for nothing if your lab notebook pages are not submitted or contain meaningless information. Be sure to include your name and student number, names of your group members, and the project title on the title page.

2. Include calibration plots for Zn and for Cu in your report (measured absorbance as a function of Zn/Cu mixing ratio in ppm). Add linear fits to your calibration graphs to show that Beer’s law is obeyed. Calculate the standard deviation in the slope and the intercept of your fit following the procedure described in Chapter 8C.

3. You will need to calculate standard deviations for the measured Cu and Zn concentrations of the unknowns. You should use formula 8-18 for this calculation. An Excel spreadsheet is provided to you on the course website to help you with this calculation.

4. Report the concentrations as %(w/w) of Cu and Zn in the old and new American pennies. Propagate uncertainties in weighting, solution preparation, fitting, etc, to obtain the standard deviations for your results.

5. Using literature search find out the probable year in which the penny composition was changed. Are your data consistent with this information?

VI. References