Experiment AA2: Quantitative determination of zinc in brass by flame atomic absorption

Learning Goals:
- to apply the instrument optimization procedures learned last week
- to complete the analysis of samples and standards using GLP
- to correctly calculate analyte concentrations in original solid sample

Pre-Lab Assignment:
1. Prepare a flow chart in your lab notebook which indicates the steps you will take when performing the experiment. Indicate the order and sequence of the steps.
2. Also in your notebook, calculate the dilutions required to make your standard curve, using your stock solution containing 100.0 mg/L of Zn, and based on the concentration range indicated in the procedure.
3. On looseleaf:
   Discuss the relationships between: concentration; absorbance; %transmission; and intensity of light from the hollow cathode lamp that is detected by the PMT. Use equations and proportionality statements to quantify your discussion.

Introduction

Since the first use of Flame Atomic Absorption Spectrometry (FAAS, or AAS) in the 1950's, the analytical scope of the technique has extended to cover many elements. FAAS has many advantages over traditional volumetric, colorimetric and gravimetric methods for metal analysis, including:
- specificity
- low detection limits (part-per-billion range for some analytes)
- minimal sample preparation
- very few chemicals or reagents required
- speed
- availability of automation

As a result, FAAS has largely replaced many traditional, time-consuming techniques. One disadvantage of FAAS is the cost of instrumentation (>-$30K) compared to ‘wet’ methods, which only require a few thousand dollars for glassware and chemicals. However, the many advantages of FAAS usually outweigh this aspect, especially for labs analyzing large numbers of samples. See Harris, D.C. “Quantitative Analytical Chemistry” 5th ed., pp 511-530 and 615-632.

Detection Limits

Detection limits for zinc, using the 213.9 nm line, are about 0.009 ppm; recommended range is from 0.4 to 1.6 mg/L.
Interferences

When analyzing any sample, the effect of direct and indirect chemical/spectroscopic interferences must be known, to avoid inaccurate assays. For example, brass is a common and widely used copper alloy which typically contains from 1 to 10% each of lead, tin and zinc, with the remainder as copper. The brass is dissolved in a mixture of nitric and hydrochloric acids. Although all the elements of interest are soluble in nitric acid, tin reacts slowly to form the slightly soluble hydrous oxide SnO\(_2\)·4H\(_2\)O, which precipitates out of solution. Hydrochloric acid prevents the formation of SnO\(_2\)·4H\(_2\)O, which would interfere with the determination of all the elements as they tend to be co-precipitated along with the tin.

Applications

Flame atomic absorption spectroscopy is an important analytical technique for metals, both in research and industry. It has wide application in the analysis of alloys in metal processing and in clinical and biological testing. Harris gives an example of a smokestack metal emission monitor that uses FAA as the analysis method.

Instrumentation

The technique is very specific because it is based on the absorption of energy by valence electrons of ground state atoms. Despite the simplicity of the principles involved, the instrumentation developed for this technique can be quite complex. Samples are introduced into the flame using a nebulizer. The flame is aligned in the light path between the source (cathode lamp) and detector (PMT).

Most flame absorption spectrometers use a nebulizer to introduce a solution into the mixer-burner. The nebulizer creates an aerosol of fine droplets, most of which (99%) are too large to remain suspended in the gas flow. The smallest droplets are swept from the nebulizer chamber into the flame. The heat from the flame evaporates the solution, and produces individual ground state metal atoms. These atoms can then absorb energy from the cathode lamp output, changing the amount of light received by the photomultiplier tube (PMT) and producing a signal.

Many factors will change the magnitude of the signal. Concentration of the analyte will, of course, change the signal size; however, so will flame temperature, nebulizer conditions, spectral interference, ionization, and other chemical interferences.

To relate absorbance values to concentration, one must obtain a ‘calibration curve’ by analyzing solutions of known concentration (standards). The signal obtained from the sample is then compared with the calibration curve, to obtain a concentration value.

The FAAS used for Chem 361 is manufactured by the Varian company, and is a manual, standard instrument.

Note: Read all of the following instructions and attempt to follow them exactly. DO NOT call
the Instructor until you have been through all of the instructions at least once, unless otherwise indicated.

**Lamp Installation**

The most common lamp used for AAS is called the Hollow Cathode Lamp. The zinc lamp will be used for this experiment; check that the lamp in the top position of the turret is the one you need.

To change lamps:
1. Remove the lamp quadrant by pulling it horizontally away from the lamp turret.
2. See figure 1 below; press the white button and plug the lamp into the socket. Release the white button to lock the lamp in place.
3. Push the lamp quadrant back into the lamp turret.
4. You must align the lamp beam so it is focused on the detector. The lamp can be adjusted horizontally and vertically with the two, black, ‘knurled’ knobs (see figure 2).

![Image of lamp quadrant installation](image)

Figure AA2-1: Cathode lamp installation for Varian AA spectrometer.

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1 Definition of ‘knurled’: From Webster's Revised Unabridged Dictionary (1913): Knurl \Knurl\, v. t. To provide with ridges, to assist the grasp, as in the edge of a flat knob, or coin; to mill.
Spectrometer Setup

To set up the spectrometer, you must follow all the steps, in order.

General operation notes:
The ‘Cal Zero’ or ‘Read’ keys function as the ‘enter’ key. Whenever you change a numeric parameter, press the ‘Read’ key to enter the value and return to the display readout.

The ‘Time/Sec’ key is used to set the integration time.

Lamp and Monochromator Alignment

Before adjusting any settings in the optical circuit, you must ensure that the lamp is on. Use the Lamp x button set the lamp current for the correct lamp number (x = 1 or 2) and to the correct current (60% of the maximum indicated on the lamp).

Monochromator settings:
The monochromator is located on the top right side of the spectrometer, at the very back.
1. Select the nominal wavelength. For zinc, the wavelength is 213.9 nm. All monochromators use gears to change the position of the diffraction grating, thereby changing the wavelength of radiation passed to the detector (PMT). Therefore, the final wavelength setting must be determined experimentally (see below) and the number on the monochromator will often not be identical to the stated wavelength.
2. Set the slit to 1 nm (this sets the spectral bandwidth of the monochromator).
   • Locate the ‘peak meter’ on the top right of the spectrometer, at the back. Press the ‘SB Autogain’ key; the meter needle should stabilize at about 70% of full scale.

Monochromator adjustment:
   • Using the ‘Fine’ control of the monochromator, adjust the wavelength to maximize the needle reading.
   • If the needle goes off-scale to the right, press the autogain button again.
   • Repeat these two steps until the needle reading is maximized.

Lamp alignment:
   • Using the two ‘knurled knobs’ on the lamp holder, adjust the lamp position (by turning the knobs) while watching the peak meter.
   • Again, try to maximize the needle reading.
   • Press the autogain button if the reading goes off-scale (i.e., is buried on the right side).

Now repeat the monochromator adjustment to make sure that the monochromator is still aligned.

Analytical/Keyboard Settings

Start-up Default Conditions:
When you press the POWER switch, the following conditions are automatically selected; check all of the settings on the keypad (indicated by small red lights) and confirm that the instrument
is set for:

- The \textit{Cal Zero} light will be flashing; the digital readout may display a row of decimals with or without digits. The '\textit{SB auto gain}' light may be flashing.
- \textit{Single-beam} (auto gain)
- \textit{Lamp current} (both lamps): 3mA (to see this, press the lamp current button; the current will be displayed in the output window. Press the CalZero button to restore output display.)
- \textit{Abs} operating mode (i.e., \textit{Abs}orption rather than \textit{Emiss}ion)
- \textit{Abs} expansion 1 X (seldom requires any other setting)
- Readout Mode: \textit{Int repeat}
- Integration period: 1 second (set by the \textit{Time-Sec} button)

Change the following keyboard settings (you will have to push the keyboard buttons hard!):

- \textit{Lamp x}: set the lamp current for the correct lamp number (x = 1 or 2) to 60\% of maximum current for Zn. \textit{(already done above)}
- Set the integration time to 3 s by pressing the \textit{Time} button, entering the correct value from the number keypad, and pressing the \textit{Read} button. The spectrometer will now average each measurement for three seconds before displaying it in the readout window. You will hear a beep each time the measurement is displayed.
- \textit{BG Setup}: set up the background measurement parameters as directed in the instrument manual.

\textbf{WARNING}

The following safety practices should be strictly observed:

a) Always operate your spectrophotometer with the sample compartment front panel in place and flame shield closed.

b) Always wear approved safety glasses designed to screen out hazardous radiation and afford mechanical protection for the eyes.

c) The instrument chimney becomes very hot. Do NOT touch the chimney until you have turned the flame off and allowed the chimney to cool.

\textbf{Lighting Instructions - Manual Gas Control for Air-acetylene Flame}

- Ensure that the trap is full of water
- Ensure that both the fuel and oxidant flow controls are fully clockwise (front left panel); turn the oxidant selector to OFF.
- \textbf{With the Instructor supervising}, go to the gas tanks at the back of 336, slowly open the tank valves for the Acetylene and the Air tanks. Use the regulator valve to set the output pressures as outlined in Table 1.
Table 1: Compressed Gas Settings

<table>
<thead>
<tr>
<th>Gas Type</th>
<th>Minimum Tank Pressure</th>
<th>Output Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>100 psi</td>
<td>60 psi</td>
</tr>
<tr>
<td>Acetylene</td>
<td>100 psi</td>
<td>10 psi</td>
</tr>
</tbody>
</table>

**WARNING**

If the flame does not ignite, unburnt acetylene and air will accumulate in the burner chamber. This can result in an explosion.

- Go back to the instrument and turn the oxidant selector to 'air'; note that the flow meter registers at least 5.5 units. *Make sure that the oxidant control is turned fully counterclockwise; the ‘bar’ on the control must be exactly horizontal.* Turn the ‘Oxidant’ flow adjuster to give a flow reading of 7².
- **With the Instructor supervising**, you adjust the fuel control to give a flow between 3 and 4 units on the flow meter. Push and hold the 'ignite' button until the flame lights.

**NOTE:** If the flame does not ignite within 30 seconds, turn off the fuel flow at the instrument; ask the Instructor for advice.

- You will notice that the flame is glowing with a creamy color. This is caused by excess fuel in the flame (the unburned carbon absorbs thermal energy and emits it as white light). For good analysis, the flame should be an "oxidizing flame" with a **non-luminous** hazy blue inner core of unburnt gas. How will you adjust the fuel control to create an oxidizing flame?
- Do not adjust the height of the burner unless you are instructed to do so.

*If the instrument has not been used for some time, or has been moved or otherwise disrupted:*

Ensure that all gas supply hoses are correctly fitted and that supply regulators are set as follows:  
- **Air** 414 KPa (60 p.s.i.g.)
- **Acetylene** 83 KPa (12 p.s.i.g.)

Check all gas connections carefully for leaks using a suitable leak-detecting solution ('Snoop' for example).

**Experimental Procedure**

**Note:** the term ‘aspirate’ is used to describe the following procedure:

- remove the nebulizer tube from the rinse beaker
- wipe off the outside of the tube with a ‘kimwipe’
- place the tube into the sample

²If the flame will not ignite, make sure that the liquid trap was filled; once the trap is full and begins to overflow, you should see liquid draining through the tygon tubing at the bottom of the trap. If the trap is full, then check that the oxidant selector is turned completely counter-clockwise, so that it is perfectly lined up with the Air marker, and can’t be turned any further (don’t strong-arm the control, just make sure it won’t turn any further CCW).
wait at least 10 seconds for the nebulizer and burner to rinse, or use the time
determined by you in the tutorial last week
press the read button and note the absorbance
repeat the last step until the absorbance has stabilized (i.e., is not consistently
rising or falling); then begin writing down the absorbance values.
place the nebulizer tube back in the rinse beaker. Wait until the reading has
returned to zero before analyzing the next sample. If the reading stabilizes at an
average other than zero, use the CalZero key to reset the absorbance to zero.

When running the instrument, the nebulizer tube should always be left in solution. If it is not in
the sample solution, place it in the rinse beaker!

1. Using the samples and stock standards prepared last week, calculate the dilutions needed
to make standards containing from 0.1 to 1.5 mg/L of zinc. Also prepare a method spike
sample. Calculate your dilutions so they can be easily made up using your volumetric
glassware (i.e., volumetric pipets and flasks).

2. Filter any samples which contain particulates (i.e., are visibly cloudy) using the syringe
and filters in the drawer below the AA; follow the procedure as given below.

   ▶ Rinse the plastic syringe with deionized water, three times.
   ▶ Rinse the syringe with the sample three times.
   ▶ Draw 10 mL of sample solution into the syringe. Attach a filter to the end of the
   syringe, and dispense the solution into a 20 mL disposable beaker. Remove the
   filter; draw up another aliquot of sample; replace the same filter, and dispense.
   ▶ Repeat the above three steps for each sample to be filtered. Use a fresh filter for
each sample.

3. Aspirate deionized water and touch the ‘cal zero’ button to obtain zero absorbance.
Aspirate the standard with the highest concentration.

4. The absorbance should now read between 0.1 and 0.6. If the ‘over range’ light comes on
(top left corner of the LED display), your calculations for the standard are likely incorrect.
Try diluting your highest standard by 10, and run it again.

5. Once the instrument is set up as above, and you are ready to start running your solutions,
press the int. hold button. Rather than continuously reading the detector signal, using the
‘Int Hold’ mode means the spectrometer only reads the signal when the ‘Read’ button is
pressed.

6. Proceed with the sample sequence outlined in the GPL appendix. With the nebulizer tube
in the same sample, write down at least five separate readings for the solution. After each
sample, you must aspirate deionized water to clean the burner. Check the baseline at
this point - if it has changed, reset it by pressing the ‘Cal Zero’ button. Wipe the
nebulizer tubing with a clean Kimwipe before and after each analysis. Be sure to identify
the standards and samples on your chart recorder output.

7. You may find that your unknown or spike samples, as prepared, give an ‘over range’
response. The instrument may display 1.5, or a blank screen, and the ‘Overrange’ light in the top left corner will be lit. If this occurs, you will need to dilute your sample and run it again.

Shut Down Procedures

1. When finished the sample sequence, turn off the acetylene at the cylinder (have the lab instructor to supervise as you follow the instrument shut down procedure). Continue to aspirate with deionized water for at least five minutes to clean the burner; this is especially important for solutions containing Cu and Ag as these elements form extremely unstable and explosive acetylides if allowed to accumulate.

• To turn the flame off, shut off the acetylene valve at the cylinder, allow the flame to go out and wait a further ten seconds to allow adequate purging. Now turn the regulator valve off (i.e., turn the valve CCW for 5 or 6 turns).
• Likewise, shut off the air valve at the cylinder; then turn the air regulator valve off.
• Now close the fuel and oxidant controls on the spectrometer gas panel, and switch the Oxidant lever to OFF.
• Dispose of all concentrated samples and standards in the waste beaker for metals; dilute solutions (<50 mg/L) can be neutralized and washed down the sink.

Treatment of Data

Write a full experiment report for AA2.

1. Construct an analytical calibration curve by plotting the absorbance of each standard against its concentration. Evaluate your standard data for curvature using the criteria/examples given in the graphing appendix.

2. Determine the concentration of Zn in your samples. Report the results as \( \frac{\mu g \, Zn}{g \, \text{sample}} \), and also as \%Zn.

3. Calculate your spike recoveries.

4. Address all issues required by the ‘discussion’ as per the introduction.