

Atomic Absorption (AA) and Emission (AE) Spectrometry

Introduction

In this laboratory you will measure the emission and absorption of electromagnetic radiation of free atoms and ions in the gas phase, i.e. apply *atomic spectroscopy* techniques. The Skoog book (*see below*) provides detail about these techniques. The key to atomic spectroscopy is atomization of the sample. We will use a standard pneumatic aspiration-nebulizer unit connected to a flame atomization/excitation source. The burner will use acetylene-air and should reach a flame temperature of ~ 2200 °K. This temperature is sufficient to induce collisional-energy gains of the gas phase atoms and ions to excited electronic energy levels. From there, they will spontaneously decay to lower electronic energy levels, emitting photons at discrete energies (wavelengths) corresponding to the energy difference between the upper-excited and lower-ground energy levels through atomic *emission*.

In atomic *absorption* spectrometry, atoms in the electronic ground-state (and ions to a much lesser degree) can absorb photons at energies (wavelengths) corresponding to the energy transition from the ground to the excited state. Because atomic absorption occurs over a very narrow band of energy, a conventional monochromator cannot be used to provide the light for absorption. Instead a hollow-cathode lamp specific for the element to be measured provides the narrow-band of light (wavelength < 0.001 nm) needed to measure absorption.

Skoog points out that only the small fraction of atoms & ions are actually excited by the flame emission process and that simultaneously a number of concurrent processes related to the sample matrix can cause interferences with the emission process. Although generally lesser in number and amount, matrix effects also occur for atomic absorption spectrometry. One of the goals of this laboratory is to address these sample matrix effects so that they have a minimal effect on both the accuracy and precision of your measurements.

In this experiment, you will use both atomic emission and absorption to measure calcium and sodium in water samples. Before beginning this experiment, you should familiarize yourself with AA and AE methods and the IL-457 instruction manual.

There are many ions present in water that are suitable analytes for either AA or AE methods. For example, many water sources are referred to as being “hard”, i.e. the water has a high concentration of calcium. The calcium in “hard water” will form deposits (“scale”) over time, especially in heated water, in water pipes, causes spots on glasses, bathtubs, teakettles, and insidiously inside water heaters. Another common effect is the decreased efficiency of soaps in dissolving hydrophobic materials like grease. “Hard water” is treated by installing a water softener in the water system. The water softener is generally nothing more than a sophisticated, rechargeable ion exchange resin system. It removes calcium ions and substitutes sodium ions. The resultant sodium-containing water is termed “softened”.

AA & AE can measure calcium and sodium in water and be used to determine both the degree of hardness and softness of water, as well as the efficiency of a water softener system. Calcium is an excellent analyte for AA, while sodium is a good analyte for AE. Hard untreated water should be high in calcium and low in sodium. Water that has been through an ion exchange resin should be low in calcium and higher in sodium by comparison. In this

experiment you will test this hypothesis. However, other hypothesis may be tested. For example, does a Brita or other type of filter affect the concentration of calcium and metals in water? What about bottled water? Are waters that claim to be sodium free, really sodium free?

There are different directions that this experiment can take. The instrument can be used to test for Li, Na, K, Mg, Ca, Sr, or Fe by AE and Ca or Fe (those are the lamps we have) by AA. The default experiment is measuring Ca & Na in a home water system before/after "softening. If you wish to perform a different experiment, you may, but you must discuss the experiment with your the instructor & TA, define the hypothesis you and your lab partner wish to test along and obtain the samples you wish to test. You also need to give the TA a 1-week warning before your designated lab period if you want to do something different from the default experiment. It is also your responsibility to do some research on the elements you want to study and have some idea about what needs to be done, what wavelengths you wish to follow, possible interferences and other effects that may need to be considered.

Ground rules for the lab:

- The lab consumes two lab periods. AE will be used the 1st week, and AA will be used the 2nd week.
- You must measure calcium content in your samples by both AE & AA.
- You must measure at least a 2nd ion by AE, typically sodium.
- You must measure your samples using both a simple standard curve calibration and by the method of standard addition.

Equipment

Instrumentation Laboratory Model 457 Atomic Absorption/Emission Spectrophotometer

- We will use it with a slot burner and an air/acetylene flame.
- A hollow-cathode lamp will be used for AA.

Experimental

Preparing your solutions

1. Determine what element(s) besides calcium you will be studying by AE and whether or not interference will be a problem. By default you will be measuring Ca and Na in home well water before and after the water has passed through a water softener. You can reduce the number of solutions by combining the two analytes in the same stock solution. See your TA about this point.
2. Prepare a large volume solution of 0.1% KCl (*the ionization suppressor*) in deionized water.
3. Prepare 1000-ppm stock solutions of the analytes using standard compounds provided by your TA. If you follow the lab as suggested, the standards will be CaCO₃ & NaCl. Prepare your solutions in deionized water in a volumetric flask. Note: you may need to add a small amount of concentrated HCl before diluting to the mark with water to get the salt to completely dissolve.
4. Prepare dilution solutions from your stock solutions in logarithmic intervals downward: 500, 100, 50, 10, 5, & 1 ppm.
 - a. Use volumetric flasks and pipettes.
 - b. Use the 0.1% KCl solution as the solvent for making these solutions.
 - c. Your TA can give you some guidance about which flasks and pipettes to use.

5. Make up a blank solution, which contains everything from your calibration solutions except for the analyte. Be sure to use only deionized water for all solution preparation.
6. Realize that your sample either (i) may be above the linear dynamic range of the detector and require dilution, or (ii) may be below the detection limit and be undeterminable. If it is the former you will need to prepare a dilution of your sample by pipetting the sample into a volumetric flask and adding deionized water.
7. Measure your standard curve & blank
8. Measure your samples & blank (diluting and remeasuring your samples if required).
9. Once you have made these measurements you will define whether the sample matrix is producing any interferences using the method of standard addition. What you will do is pipette a new set of samples containing the original (or diluted if required from your initial measurements) and standard added in addition to the sample:
 - a. Pipette an amount of sample into a series of volumetric flasks/beakers. Beakers or other containers can be used if you are defining the dilutions based upon the measured weight of solutions added.
 - b. One aliquot of sample receives no added standard (called the +0 sample).
 - c. Pipette an amount equal amount of the standard solution that is in a concentration one step greater than your sample's analyte concentration (called the +1 sample).
 - d. Pipette an equal amount of the standard solution that is the next concentration one step greater than the previous standard (called the +2).
 - e. These samples should be prepared in duplicate.
 - f. Add 0.1% KCl solution to each volumetric flask/beaker to bring each sample up to an equal volume.
 - g. Measure these samples.

Lab 1: Atomic Emission Spectrometry

At the instrument:

- 1) Start up
 - a) Be sure that no hollow-cathode lamp is attached to the instrument.
 - b) Turn on the instrument at least a half hour ahead of use.
 - c) Attach the waste receptacle to the drain hose.
 - d) Turn on the air tank to 40 psi.
 - e) Turn on the acetylene fuel tank to ~8 psi.
- 2) Flame
 - a) Press the *A.E.* button to set the instrument in AE mode.
 - b) Have a flask of deionized water ready and be prepared to do the following steps in quick succession.
 - i) Turn far left knob to *air*.
 - ii) When noise stops, turn to *air and fuel*.
 - iii) Push the pilot button.
 - iv) When the flame starts, put the capillary into the deionized water.

- v) Press the *integration* button.
 - vi) Set to 3 seconds, and press enter.
 - vii) Set voltage so that the scale reads around 1.
- 3) Zero signal
- a) Have a clean receptacle of deionized water ready.
 - b) Put the capillary into the water.
 - c) Press the gray *zero* button.
 - d) Press the blue *read* button.
 - e) Return the capillary to the water used for flushing the system. *Keep the capillary in the water when not taking measurements.*
- 4) Set the gain of the instrument
- a) Turn knob from *stand-by* to *operate*.
 - b) Push the gray *integration* button.
 - c) Set to 0.1 sec, and press *enter*.
 - d) Put the capillary into your highest concentration solution.
 - e) Push *auto*, then *read*.
 - f) Slowly turn the wavelength knob while watching the readout for an increase in signal. You should know what wavelength you are looking for because you have already looked up your wavelength of interest in the binders near the recorder.
 - g) Set the wavelength at the maximum value on the readout.
 - h) Turn up the voltage knob to maximize the signal. A reading of all t's means it is too high. Go down one notch.
 - i) Return the capillary to the deionized water to flush the system.
- 5) Measurement of standards and samples
- a) Have your standard and blank solutions ready.
 - b) Have your sample solutions ready.
 - c) Push the gray *integration* button.
 - d) Set to 3.0 sec, and press *enter*.
 - e) Put capillary into a standard sample.
 - f) Press blue *read* button.
 - g) RECORD VALUE MANUALLY!
 - h) Be sure to record several measurements for each solution.
 - i) When you have finished recording values, press *read* again to stop.
 - j) Put the capillary in deionized water to flush the system.
 - k) Be sure to record a value for the blank. When you work up your data, you will need to subtract the value for the blank from all other measurements.
 - l) Repeat with all standards and samples.
- 6) Shut down
- a) Push *read* to stop reading.
 - b) Turn voltage down all the way.
 - c) Turn lamp down all the way.

- d) Put capillary in deionized water to flush the system for a few minutes, then remove the capillary.
- e) Turn knob to *air*; allow flame to blow out, then turn knob to off;
- f) Turn fuel tank off.
- g) Drain the fuel line by turning the knob to *air*, then *air/fuel* and watch the fuel gauge until it reads zero. You will hear a thump.
- h) Turn air tank off.
- i) Drain the air line by turning the knob to air, watching the gauge, and listening for the thump.
- j) Turn other gauges off at the regulator.
- k) Turn the instrument to stand-by.
- l) Turn the power button off.
- m) Empty the waste receptacle.

Lab 2: Atomic Absorption Spectrometry Using a Hollow-Cathode Lamp

Obtain an emission spectrum of the hollow-cathode lamp of calcium and any other element(s) you want to measure. Do this step with the flame off and use the instrument's scanning mode. Assign major emission lines (i) to the atomic or ionic forms of the lamp element or (ii) to the lamp filler-gas.

Explore the effects of spectral bandpass and scan rate on line shape, line width, and line intensity using an intense emission line. Select an emission line for the analyte determination.

Prepare a 1000-ppm analyte stock solution by dissolving the appropriate amount of an appropriate salt in a minimum amount of concentrated HCl and deionized water in a volumetric flask. Dilute to the mark with deionized water. Using this stock solution, prepare (via serial dilution as described above for AE) a series of standard solutions varying in concentration from 1 ppm to 100 ppm. Note that, depending on the nature of your sample, you may want to include an *ionization suppresser* in your standards.

Prepare a series of samples in duplicate or triplicate with standard addition of the standard analyte to the samples, as described above for AE.

At the instrument:

- 1) Start up
 - a) Be sure that the appropriate hollow-cathode lamp is attached to the instrument.
 - b) Turn on the power at least a half hour ahead of time.
 - c) Attach the waste receptacle to the drain hose.
 - d) Turn on the air tank to 40 psi.
 - e) Turn on the acetylene fuel tank to ~8 psi.

- 2) Lamp
 - a) Turn knob from *stand-by* to *operate*.
 - b) Push the white *A.E.* button.
 - c) Push the gray *integration* button.
 - d) Set to 0.1 and press *enter*.
 - e) Push *read*.
 - f) Turn up the lamp current to ~10 mA with knob A.

- g) Slowly turn the wavelength knob while watching the readout for an increase in signal. You should know what wavelength you are looking for because you have already looked up your wavelength of interest in the binders near the recorder.
 - h) Set the wavelength at the maximum value on the readout.
 - i) Turn up the voltage knob to maximize the signal. A reading of all t's means it is too high. Go down one notch.
- 3) Recorder
- a) Turn on recorder.
 - b) Turn off chart.
 - c) Set recorder to 0.1V. The max signal on the recorder will be 0.1V (the top of the scale).
 - d) Look up values for scan rate of instrument in the yellow binder (pp. 3-6).
 - e) Select a rate for the strip-chart recorder and determine a conversion factor for nm of wavelength /cm on the paper.
 - f) Put in pen. *Do not lose the cap!*
- 4) Taking the spectrum
- a) Reduce the wavelength by moving the knob to a convenient starting number, and RECORD this value.
 - b) Turn the bandwidth knob to the highest setting.
 - c) Turn on the chart on the recorder.
 - d) Push in the wavelength scan knob and turn to high.
 - e) Record the spectrum.
 - f) Repeat at all bandwidths.
 - g) Measure the full width at half maximum on spectrum to determine the effect of bandwidth on line width. (Do on your own, not your partner's.)
 - h) With the bandwidth at its lowest setting, change the scan rate to low, and record the spectrum again to define the effect of scan rate.
 - i) Turn off the strip chart recorder.
- 5) AA measurements of your standard and sample solutions
- a) Light the flame as per above for AE.
 - b) Be sure that you now have the instrument set in the **AA**, not **AE** mode.
 - c) Zero your absorbance with a blank solution. Periodically recheck the blank to make sure the absorbance is zeroed.
 - d) Measure the absorbance for each standard solution
 - i) Plot an analytical curve.
 - e) Using one of the more dilute standard solutions, determine the detection limit for the analyte.
 - f) Measure your samples. Report ppm analyte in the sample.
 - g) Make sure measurements are performed in replicate so that you may determine appropriate statistics for this experiment.
- 6) Shut down – *as per above for AE*

Questions

1. Why is a narrow line source used instead of a continuum source for atomic absorption?
2. How linear was your analytical calibration curve, especially at the low and high analyte concentrations? How large was the linear dynamic range? What was the uncertainty in the curve (computed via linear regression analysis)?
3. What was the detection limit for each analyte and mode (AA v. AE)? Report the absorbance sensitivity – how does this differ from the detection limit?

Lab Report Guidelines

Introduction:

- Explain the purpose of the experiments and the hypothesis you wish to test.

Methods:

- Discuss the Beer-Lambert Law and how it applies to this experiment. Are there expected limitations?
- How does the instrument work and why are you using it in this experiment?

Results:

- Include calibration curves and instrument spectra
- Report the actual concentrations of the analytes in your real samples
- Report the detection limits for the analytes as well as the linear dynamic range
- Be sure to do appropriate statistical analyses
- Discuss the information collected in section 2 - particularly how you selected your emission line

Discussion:

- Make some conclusions about the hypothesis you set out to test.
- Explain how the detection limit was computed.
- Discuss the method of standard addition and determine whether your results differ using the standard addition method. If so, what can you say about matrix effects for your samples?
- How good is this instrument at AA? AE?
- What would be a better instrument for either technique?

References

- *Analytical Methods for Atomic Absorption Spectrophotometry*; Perkin-Elmer Corporation: Norwalk, CT, 1982.
- D.A. Skoog, F.J. Holler & S.R. Crouch, *Principles of Instrumental Analysis*, 6th ed, 2007:
 - Chap 8: An introduction to optical atomic spectrometry
 - Chap 9: Atomic absorption and atomic fluorescence spectrometry
 - Chap 10: Atomic emission spectrometry
- D.C. Harris, *Quantitative Chemical Analysis*, 6th ed, 2003:
 - Chap 4: Statistics
 - Chap 5: Calibration methods
 - Chap 21: Atomic spectroscopy