

Experiment 3: Atomic Absorption Determination of Lead in Soil Samples

Inspired by Mielke, H. *American Scientist* 1999, 87, 62-73.

Experimental Work on March 3 and March 10-18 (in Olin-Rice 387)

Notebook and Formal Report Due on April 4 by 5 p.m. (20% per day penalty if late)

Introduction

- (1) Read the article by former Macalester professor Howard Mielke on the prevalence and danger of lead in urban soil
- (2) **Before lab on March 3, your team should collect three soil samples for analysis.** Think about interesting places to investigate, such as along Snelling Ave. or in the gardens of old homes. Do not use indoor samples (such as the potting soil inside Olin-Rice) that are expected not to contain any lead! Note the approximate distances between the samples—remember that the goal is to probe trends in Pb concentration. You need only ~2 g per sample. Confine your sampling to the soil surface.
- (3) It may be helpful to dry your samples before you digest them in lab on March 3. Contact me or your TA if you wish to use the oven in Olin-Rice 380.

Lab Work on March 3 (remember to construct a flowchart for Parts A and B before lab)

Part A: Sample Digestion (adapted from an Environmental Protection Agency procedure)

- (1) Transfer each of your ~2 g soil samples to a beaker. Weigh each sample to the nearest 0.001 g on an analytical balance.

In the next three steps, wear gloves and handle glassware with tongs to avoid getting concentrated HNO₃ on your skin!

- (2) **In a hood**, add to each beaker a mixture of 5 mL concentrated HNO₃ and 5 mL water. Mix each slurry and cover each beaker with a watch glass. Heat all samples to ~95°C on one hot plate and reflux for 10-15 min. **Do not allow your sample to boil.**
- (3) Allow each sample to cool, add another 5 mL of concentrated HNO₃, replace the watch glass, and reflux for another 25 min.
- (4) Repeat step (3) to ensure complete oxidation.
- (5) When the samples have cooled for the second time, add approximately 60 drops (*i.e.* ~3 mL) of 30% H₂O₂ to each beaker. Add the H₂O₂ **slowly** to minimize effervescence. Cover each beaker with a watch glass and return it to the hot plate. Heat (again, **do not boil**) your sample to start a reaction with the H₂O₂. (With all this effervescence happening, you need to be careful to minimize sample loss.) When the mixture stops effervescing, let it cool. Then add up to 50 additional drops of 30% H₂O₂ (*i.e.* ~2.5 mL) until additional effervescence is minimal.
- (6) Add 5 mL of concentrated HCl and **slowly** add 10 mL of water, replace the watch glass cover, and reflux for 15 minutes. (Yes, you should still avoid **boiling**.) After cooling, dilute to ~40 mL total volume with water.

- (7) Finally, filter each solution through qualitative filter paper into a 50-mL volumetric flask. Dilute to the mark and then commence obsessive-compulsive behavior (*i.e.* invert each of your three flasks at least 20 times to mix).

Part B: Standards Preparation

Your TA will have prepared a stock solution of lead (II) nitrate containing ~100 ppm Pb^{2+} . (Remember that this is a mass/mass ratio). The exact concentration will be reported that morning. Use this to make standards containing 20.0, 10.0, and 5.0 ppm Pb^{2+} . Prepare 100 mL of each standard. Stopper for use next week.

WASTE DISPOSAL: All washings from the soil digestion glassware can go down the drain. Any $\text{Pb}(\text{NO}_3)_2$ solution left over after you prepare your standards must go into a waste container.

Lab Work on March 10-18 (you do not have to include this in your pre-lab flowchart)

Part C: Analysis by Atomic Absorption Spectroscopy

At the start of the lab time slot on March 10, I will demonstrate how to use the Buck Atomic Absorption Spectrometer. Your team will sign up for a 90-minute time slot sometime between then and the day before Spring Break (March 18) to make measurements on your three standards and your three analyte solutions. Please come find me, your TA, or Rob Rossi if you need help using the instrument.

Directions for Using the Buck 200A Atomic Absorption Spectrometer

Lamp adjustment:

1. Put your safety goggles and a pair of disposable gloves on! Then hit the red power switch (lower right) on the AA. You may assume that the Pb hollow cathode lamp has already been installed and properly aligned.
2. Turn the main function switch (the second knob from the left) to the L1 (lamp 1) position. Adjust the lamp current (the current is displayed in mA on the digital display) using the LAMP1 control knob to the recommended current of 10 mA. Be sure not to exceed this current, as this will significantly shorten the lamp's life.
3. Make sure that the AUTO ZERO button is out. Then, turn the function switch to the PMT VOLTS position and use the ABSORBANCE ZERO knob to adjust the photomultiplier tube (PMT) voltage until the energy level dial (in the upper right) is at ~80% of full-scale deflection.

Do these three steps before you retrieve your standards and analyte solutions—you want to maximize the warm-up time for the instrument.

4. Tune the grating angle to the desired wavelength using the control knob on the right side of the instrument. (For Pb, this is ~283 nm.) Note that the knob controls the angle of the

grating. Our goal is to “aim” the 283-nm light directly into the PMT. The slit width, which is set using the lever mounted on the back of the instrument, should already be set at 7 Å.

5. Once the wavelength is close to the nominal λ_{\max} , make slight adjustments to the wavelength control knob to maximize the light intensity hitting the PMT. The light intensity hitting the PMT is measured by the needle on the ENERGY LEVEL meter. It is likely that as you optimize grating angle, you will cause the needle to deflect full scale. When this happens, decrease the magnitude of the detector voltage (by rotating the ABSORBANCE ZERO knob) to return the needle deflection to ~80% of full scale. Do not be surprised if the optimal position is a few nm different from the nominal λ_{\max} —the wavelength dial is only approximate. Write down in your notebook your final settings for wavelength and detector voltage.

Burner alignment and adjustment:

6. Have the thin Teflon aspirator tube immersed in a 250-mL Erlenmeyer flask of distilled water.
7. Open the air jet on the north wall, which is connected to a filter system. Confirm that the pressure in the air line is ~30 psi.
8. Open the main valve of the acetylene cylinder completely. **The cylinder should not be used if the cylinder pressure has dropped below 50 psi (lb/in²),** as too much acetone will be extracted (acetylene is dissolved in acetone to prevent explosions). The line pressure should be about 8–10 psi (and no more than 14 psi). Unscrewing the black knob (that's CCW) on the regulator will lower the line pressure.
9. Be sure the drain line is entering the waste bucket. The line should drop away from the burner assembly so as to prevent water from backing up into the nebulizer.
10. Having the igniter in place, flip up the FUEL ON/OFF toggle valve, turn the oxidant selector knob (left side of AA) to AIR and light the flame. **(If you ever need to extinguish the flame quickly, flip the FUEL ON/OFF toggle valve back down.)** Water should begin to be aspirated.
11. Check that the flow rates of both AIR and FUEL are close to 5 (as measured by the flow tube bobs). If not, tweak the AUX AIR and FUEL knobs.

General measurement procedure:

12. Turn the main function switch to ABSORBANCE ZERO.
13. Make sure that the INTEG/NORMAL switch is out (i.e. in the “normal” position).
14. While aspirating your blank (in this case, keep aspirating pure deionized water), depress the AUTO ZERO button to enter auto zero mode. Depress the ZERO button. The button will light for about 7 seconds while the spectrometer sets the absorbance to 0.000. If the reading is more than ± 0.003 away from zero after the ZERO button light turns off, depress the ZERO button again. (However, don't depress the ZERO button more than five times. Excessive use of the ZERO button will burn out a chip in the spectrometer's circuit.)
15. Make sure you are always aspirating some liquid whenever the flame is on. Else, you risk overheating and damaging the burner. Re-fill the 250-mL flask with water as needed.
16. Leave the AUTO ZERO button in for the rest of your measurements.

17. Aspirate your 20.0-ppm Pb standard, reading the absorbance from the display. (I checked this mixing ratio in February, and got a reading of ~ 0.2 . Your reading should be close to this value.) Then aspirate water for a least a minute. Check that the reading returns to 0.000 ± 0.003 whenever you are aspirating water. If it doesn't, re-zero the instrument, and make a note of this issue in your notebooks.
18. Repeat this procedure for your other two standards, and your analyte solutions. You should cycle through all of the solutions at least three times. Re-zero the display with the blank solution at the start of each cycle.

Shutdown procedure:

19. Run distilled water through the aspirator for a minute to rinse the burner head.
20. Stop the acetylene flow by closing the FUEL ON/OFF valve and then turn the oxidant selector knob to off.
21. Close the valves on the acetylene cylinder and on the air supply at the wall.
22. Turn off the spectrometer, and clean up after yourself!

Write-Up

You should present a set of sample calculations in your notebook. The rest of your data analysis, including a copy of your spreadsheet and a plot of your calibration curve, should appear in your formal report (details below). As always, you can choose to turn in either one report for the entire team, or individual reports.

1. Use the Excel spreadsheet you constructed for Experiment 2 to determine the equation of your calibration curve. Your x-axis will be ppm Pb^{2+} (*i.e.* $\mu\text{g Pb}^{2+}/\text{g solution}$). Fit one line to all your calibration data. This will maximize the precision of your determination.
2. Use the curve to determine $[\text{Pb}^{2+}]$ in each of your three analyte solutions.
3. For each of your three analyte solutions, determine s_x , the standard error in $[\text{Pb}^{2+}]$, by evaluating Equation (5-14) on p. 87 of Harris. Remember that you should use the s_y value predicted from Equation (5-7) of Harris. (Taking the standard deviation of the three absorbance measurements on a sample would underestimate the true uncertainty in y .) You do not have to also determine s_x by propagation of s_m , s_b , and s_y .
4. For each of your three samples, convert the $[\text{Pb}^{2+}]$ and its standard error determined in Steps 2 and 3 (which are per 50.00 mL of solution) to $[\text{Pb}]$ and its standard error per gram of that soil sample. Then convert each standard error to a 95% confidence interval.
5. Present your results in a formal report. Your report should follow the style and formatting of lab reports most of you have written either for the Chemistry 112 first year course or for Chemistry 311. Assume your reader is a student taking analytical chemistry who is familiar with atomic absorption spectroscopy, but who has not done this particular experiment.

Your written report should contain each of the following sections, in the order given.

Title
Your Name(s)
Abstract
Introduction
Procedure
Results and Discussion
Conclusions
References

The **Title** should be specific and descriptive.

The **Abstract** should provide a less-than-150-word summary of the entire work: the purpose, procedure, key results, and their significance should all be **briefly** addressed in this essential part of your report. Note that today's web-based scientific databases typically allow one to search titles and abstracts, but often not the main bodies of papers. You should write your Title and Abstract accordingly. The Abstract is not the place to introduce the experiment or describe the underlying principles in any detail. Stated in another way, the paper really begins with the Introduction, not the Abstract. Most scientists write the Abstract after they have written the rest of the paper, since it *summarizes* the work described. Never present material in the Abstract that you have not also presented somewhere in the main body of the report.

The **Introduction** should describe the specific goals of your experiment. What have you analyzed, and why? Briefly discuss some of the key ideas from Mielke's paper. State the hypothesis you were testing with the soil samples you chose. You should also briefly discuss the theory underlying your analytical method.

The **Procedure** should provide a concise description of how the experiment was *actually* conducted. While it should not provide an exhaustive account of every step in the experiment, you should not simply write, "See the lab handout for details." Remember that your reader has not performed the experiment. She should, after reading your procedure section, have a clear understanding of what you did and how to repeat your work. Note important observations (especially events that likely introduced error) and highlight any deviations from the instructions in the handout. You do not need to draw (or reproduce drawings of) any apparatus used in the experiment unless you feel it will aid your discussion.

The **Results and Discussion** section presents the key numerical results—the concentration (in ppm) of lead in each of your soil samples, and their 95% confidence intervals. You should briefly describe how these values were obtained, making reference to your spreadsheet and calibration curve, which should appear physically in this section also. You should discuss potential sources of both random and systematic error, and estimate the sign and magnitude of the latter. You should also try to interpret any trends in your soil measurements. Either here or in the introduction, it might be useful to use references besides the Mielke paper.

Your report's **Conclusions** should summarize what you have accomplished in the experiment. Unlike the **Abstract**, the conclusion need not recapitulate every part of the paper. This section also should contain reflections on anything you would do differently if you had to repeat the experiment, and what hypothetical future experiments would be useful or interesting.

References: You do not need to cite course handouts, but you must cite all other sources you have used, including the Mielke article, your textbook and web pages. Insert a superscript

number the first time you cite a particular reference, and always use the same superscript number whenever you cite the same source in your report. Instead of using footnotes, collect all references in this final section. Follow the American Chemical Society's conventions:

Books without Editors: Author 1; Author 2; Author 3; Author 4. *Book Title*, number of ed.; Publisher: Place of Publication, Year; Number of Chapter(s) Cited. For example,

Masterton, W. L.; Slowinski, E. J.; Stanitski, C. L. *Chemical Principles*, 5th ed.; Saunders: Philadelphia, 1980; Chapter 23.

Books with Editors: Author 1; Author 2; Author 3; Author 4. Chapter Title. In *Book Title*, number of ed.; Editor 1; Editor 2, Eds.; Publisher: Place of Publication, Year; Number of Any Specific Chapter(s) Cited. For example,

Montgomery, M.; Norman, J. RNAi and Cosuppression: Double-stranded RNA as an Agent of Sequence-Specific Genetic Silencing in Animal and Plants. In *Molecular Biology of Double-stranded RNA: Concepts and Applications in Agriculture, Forestry, and Medicine*. Tavantzis, S., Ed.; CRC Press: New York, 2001. (This cites the entire book; "Chapters 3-5" would follow "2001," if only those chapters were relevant.)

Articles: Author 1; Author 2; Author 3. Title of Article. *Name of Journal* **Year**, *Volume*, Beginning – Ending Page. For example,

Kuwata, K. T.; Erickson, R. I.; Doyle, J. R. Improved Interatomic Potentials for Copper and Aluminum Sputter Atom Transport Simulations. *Nuclear Instruments and Methods in Physics Research B* **2003**, *201*, 566-570.

Web Sites: Cite their URL. Also note the last day you accessed the site. For example, <http://bcs.whfreeman.com/qca/> (accessed 2/17/2005).

Grading

This experiment will be worth **50 points** (or twice the value of a regular experiment), earned in the following ways:

3 points: Flowchart done before lab

5 points: Record-keeping and other notebook mechanics

2 points: Precision of calibration curve

40 points: Quality of your paper, and the accuracy of your calculations and data analysis.

Note that you and your partner will receive the same score for the precision of your results. If you choose to write your paper together, you will share that score as well. Each notebook's flowchart and record-keeping will be graded separately.

I would be happy to read a draft of your paper before you turn it in for grading. However, you must give it to me by 5 p.m. on Thursday, March 31. I will e-mail you comments by Saturday.