Experiment 12A: Atomic Absorption Spectrometry: Graphite Furnace

SYNOPSIS Lead in liquid samples is injected into a small graphite tube which is resistively heated to dry and atomize the sample. The atom vapor is probed with a monochromatic beam of light specific for the excitation of valence electrons in Pb. Depending on the instrument used, automatic background correction is performed.

READINGS *Read pages* 293-301 in Critical Reviews. An attached article describes a method devised to overcome loss of the GFAA signal from $PbCl_2$ gas. A second article is interesting because it shows emission spectra obtained from Pb over a wide atomic spectroscopic range when using a laser for excitation.

INSTRUMENT

GLASSWARE Clean all Glassware *(WHY? - what chemical process can occur?)*

A. Wash with 6 M HNO_3
B. Rinse with de-ionized H_2O
C. Rinse with dilute basic EDTA
D. Rinse with de-ionized H_2O.

SOLUTIONS

A. Stock solution of: 0.2% HNO_3, 0.2 mg $NH_4H_2PO_4$, and 0.01 mg $Mg(NO_3)_2$ per injection. *What is the purpose of the $Mg(NO_3)_2$, HNO_3, and $NH_4H_2PO_4$?*

1. 1-2%HNO_3 per solution
volume = ((0.2%)(1000mL))/(70%) = 2.86 mL per 1 L

Steps 2&3 required only for GFAA not FAA

B. *0.3 mg $NH_4H_2PO_4$ per injection*
mg of modifier desired/ (volume of injection)(0.01) = 10 g/1L
0.02 mg $NH_4H_2PO_4$ /(20 µL)(0.01) = 1 g/100 mL = 10 g/1 L

3. *0.01 mg $Mg(NO_3)_2$ per injection*
mg of modifier desired/ (volume of injection)(0.01) = conc. in % (g/ 100 mL)
0.01 mg $Mg(NO_3)_2$/(20 µL)(0.01) = 0.05 g/100 mL = 0.5 g/1L

Make a 1 L solution by adding 10 g of $NH_4H_2PO_4$, 0.5 g of $Mg(NO_3)_2$, and 2.86 mL of HNO_3 and diluting to 1 L with de-ionized water.

4. Make up lead standards between 0.1 and 20 ppm in order to determine LOD by diluting stock standard with 1-2% HNO_3

PROCEDURE

Conditions used for Pb analysis by GFAA: 5/94

Step	Temp	Ramp Time	Hold Time	
1	120	1	25	
2	700	5	25	
3	2300	5	7	Mini-flow/read

Perkin Elmer 5000

Mode	AA-BG
	ABS
ë	283.3 nm
slit low	0.7 nm
signal	Peak Area
Time	7.0 seconds
Energy	60 (should be > 50)

C. Samples

1. Inject 10 µL of an intermediate standard into the furnace. Practice the injection as it will be variable. Hit the bottom button right hand side (missing cover) to initiate.

CAUTION

If you inject too forcefully you will **spatter** your solution to different regions of the tube. The tube heats inhomogeneously so that portion of your sample heated first will atomize first followed by a **second** peak. Your peak measurement will no longer be proportional to the amount of lead present, but only the amount of lead present in one of the peaks.
Do not push the injection tip to bottom of tube.
Do not leave injection tip outside of tube (will get sample exterior to tube).

2. When your physical technique is good run your standards from low to high

concentration using at least three injections per sample.

3. Run your soil extract unknown, the barley + no Pb sample, the barley + 10 ppm Pb sample, and the 10 ppm Pb sample.

For unknowns:, after every 10 samples, run an additional calibration curve.

REPORT In addition to materials, methods, and results your report should include the following information:

1. Compute the relative standard deviation of your injection technique.
2. What is the LOD, LOQ, linear range, and r value of your standard curve for this method? How does your LOD compare with the expected value (see Table in section "Selecting A Method for Lead Analysis").
3. Did your internal standards show your technique (digestion + GFAA) to be reliable?
4. Do you attribute all of the variation in your measurements to either the GFAA measurement and the digestion process?
5 What is the relative standard deviation for your measurement of 3 ppm Pb?
6. What is the purpose of the added HNO_3?
7. What is the main instrumental error? What causes the non-Gaussian shape (Absorbance vs time) of the absorbance peak?
8. How does sample matrix affect the atomization process?
9. Would you expect to be able to measure the emission of light by exciting lead in a flame? Consider which line you want to monitor and whether it can be successfully excited in a normal flame temperature.
10. With this instrument, as configured in the lab, what would be the best way of determining the background absorbance?
11. What was the estimated time for turn around in samples?
12. Are there any problems with disposal of hazardous materials?
13. How easy would it be to instruct a technician on this method?

Experiment 12B: Atomic Absorption Spectrometry: Flame

SYNOPSIS Lead in liquid samples is aspirated into a flame to dry and atomize the sample. The atom vapor is probed with a monochromatic beam of light specific for the excitation of valence electrons in Pb. Depending on the instrument used, automatic background correction is performed.

READINGS *Read pages* 293-301 in Critical Reviews.

INSTRUMENT

GLASSWARE Clean all Glassware *(WHY? - what chemical process can occur?)*

A. Wash with 6 M HNO_3
B. Rinse with de-ionized H_2O
C. Rinse with dilute basic EDTA
D. Rinse with de-ionized H_2O.

SOLUTIONS

A. Stock solution of: 0.2% HNO_3, 0.2 mg $NH_4H_2PO_4$, and 0.01 mg $Mg(NO_3)_2$ per injection. *What is the purpose of the $Mg(NO_3)_2$, HNO_3, and $NH_4H_2PO_4$?*

1. 1-2%HNO_3 per solution
   volume = ((0.2%)(1000mL))/(70%) = 2.86 mL per 1 L

2. Make up lead standards between 0.1 and 20 ppm in order to determine LOD by diluting stock standard with 1-2% HNO_3

PROCEDURE

Mode	AA-BG
	ABS
ë	283.3 nm
slit low	0.7 nm
signal	Peak Area
Time	7.0 seconds
Energy	60 (should be > 50)

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1. *Turn on the Power to the main instrument control panel.*
2. *Turn on the "stand-by" switch to run.*
3. *Turn on the Power switch to the automatic burner control system.*

4. *Turn on Acetylene gas tank and adjust for proper gas flow.*
5. *Retighten air release vale on the air compressor and start the air compressor.*
6. *If needed, insert the proper hollow cathode lamp into the turret and plug the lamb into the corresponding receptacle (Note location of lamp).*
7. *Enter in the proper lamp #, and then press* ***Lamp #*** *key.*
8. *Enter the operating current, and press the* ***LAMP MA*** *key.*
9. *Enter the desired wavelength (ë), and press the* ***ë slew*** *key*
10. *Enter the desired slit width, and press the* ***slit high*** *key.*
11. *Press the* ***ë Peak*** *key. Allow the instrument to adjust the wavelength until the wavelength appears on the board.*
12. *Enter the desired integration time (sec) and then press the* ***t*** *key.*
13. *Press the* ***Set Up*** *key. Maximize the Lamp intensity by adjusting the x, y, and z position of the lamp. (Your T.A. should do this for you.)*
14. *Select the appropriate mode of operation. Press the* ***AA-BG*** *key for atomic absorption with background correction.*
15. *Aspirate the blank or wash solution for 2 min to remove any memory effect from previous experiments.*
16. *Run Experiment.*

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C. Samples

1. Run your standards from low to high concentration. For the lowest standard or for the blank aspirate the solution three separate times.

If you have unknowns:, after every 10 unknown or samples, run an additional calibration curve.

REPORT In addition to materials, methods, and results your report should include the following information:

1. Compute the relative standard deviation of your injection technique.
2. What is the LOD, LOQ, linear range, and r value of your standard curve for this method? How does your LOD compare with the expected value (see Table at front of this book).
3. If you used internal standards, did your internal standards show your technique (digestion + FAA) to be reliable?
4. Do you attribute all of the variation in your measurements to either the FAA measurement and the digestion process?

5 What is the relative standard deviation for your measurement of the lowest standard and/or the blank?

6. What is the purpose of the added HNO_3?
7. What is the main instrumental error? What causes the non-Gaussian shape (Absorbance vs

time) of the absorbance peak?

8. How does sample matrix affect the atomization process?
9. Would you expect to be able to measure the emission of light by exciting lead in a flame? Consider which line you want to monitor and whether it can be successfully excited in a normal flame temperature.
10. With this instrument, as configured in the lab, what would be the best way of determining the background absorbance?
11. What was the estimated time for turn around in samples?
12. Are there any problems with disposal of hazardous materials?
13. How easy would it be to instruct a technician on this method?