

Determination of Lead in Paint Chip Samples Using Flame Atomic Absorption Spectrophotometry.

The objective of this laboratory experiment will be to quantitatively determine the lead (Pb) content of paint chip samples. This lab experiment will require you to decompose paint samples using mineral acids, prepare appropriate dilutions of the decomposed samples, and measure these paint samples by aspirating them into an air-acetylene flame for atomic absorption measurements.

Experimental Procedure:

Note: Any glassware used for this lab should be soaked for 5 minutes in dilute nitric acid to remove trace amounts of metal adsorbed to the glass before a final rinse with 18 M Ω distilled water.

Part A – Sample Preparation:

Obtain a sample of paint chips from some location in which you are interested. In addition, your instructor will furnish a sample of paint, known as a Standard Reference Material, supplied by the National Institute of Standards and Technology (NIST). Take note of the pertinent information from this NIST Pb in Paint Standard, including the SRM number. Further information on the exact Pb content in this paint sample can be found at www.nist.gov. Each of these paint samples should be dried for 1 hour at 110-120 °C. Please note: As the NIST paint samples are very expensive, please carefully remove your paint sample from the bulk container by rocking the bottle (don't insert a spatula into the jar), estimating a mass of no more than 0.4 g on the top-loading balance OR your instructor may dispense your sample to you.

There are two possible methods of sample preparation. One is a microwave digestion (described below) and the second is a longer method done on a hot plate in the hood (described in the appendix to this experiment). You should write up both procedures so that you will be prepared depending on what equipment is available.

MICROWAVE DIGESTION

Accurately weigh out triplicate samples of about 0.1 g (to the nearest 0.1 mg) of your dried paint chip samples and NIST reference samples. You should weigh by difference directly into the Teflon vessels of the microwave digestion bombs.

Add approximately 2 mL of concentrated nitric acid (trace metal grade) and 1 mL of 30 % H₂O₂ to each vessel. Seal the vessels in the microwave after replacing the rupture membranes on the lids. Make sure that one sample is connected to the control lid to allow for pressure monitoring. Heat these samples in the microwave using the program called "PAINT." After heating, allow the samples to cool for approximately 10 minutes and then carefully vent in the hood. While the

digestion and cooling steps are proceeding, begin preparing the standards as described in Part B.

Once the samples have cooled, quantitatively transfer each sample to a clean, dried and tared plastic bottle and dilute so that the final mass of the solution is between 10 and 11 grams and record the final mass of solution (you may use a top-loading balance and retain four significant figures). After transfer, be sure to rinse the bombs very well with water before returning them to minimize carryover of undissolved material to the next sample. Note that not all of the sample may have dissolved. If so, after mixing thoroughly, transfer a portion of the sample to a centrifuge tube and centrifuge for 5 minutes at about 1000-1500 rpm to separate the particulate matter. Directly analyze the supernatant by AA as described below. If the Pb content is high, you may be required to further dilute your sample to be sure it falls within the range of your calibration standards.

Part B: Preparation of Aqueous Pb Calibration Standards

A stock standard Pb solution of 1000 $\mu\text{g/mL}$ (which is equivalent to 1000 $\mu\text{g/g}$) will be provided to you to prepare calibration standard solutions. You will need to prepare five Pb calibration standard solutions of in concentrations ranging from approximately 4 - 40 $\mu\text{g/g}$. These solutions should be prepared in clean, dried and tared plastic bottles using dilution by mass on a top-loading balance.

To perform these dilutions and maintain reasonable precision, a minimum mass of 1.00 gram of concentrated sample should be used for each dilution. For example, to dilute the 1000 ppm standard to ~ 10 ppm, ~ 1.00 gram of the 1000 ppm solution should be transferred to a plastic bottle and diluted to a total mass of ~ 100.00 grams. Note that it is not worth your time to measure exactly 1.00 or 100.00 grams (or whatever mass you calculated). As long as you know the initial concentration and the precise masses used, you can calculate the concentration of the dilute solution. To keep the total mass or volume of the solution reasonable (< 125 mL), it may be necessary to prepare these solutions using serial dilution.

A word of reminder in performing determinations of metals at the low ppm level is needed. It is recommended that the standard solutions be prepared on the same day of use and never be stored in glass containers. With time, the integrity of the solution concentrations will be at risk, usually a result of adsorption of metal to the container walls.

Part C: Analysis of Pb in Paint Samples

FLAME START-UP PROCEDURE: Before you begin the experiment, it is extremely important to point out the precautions and rules to follow when using the Varian AA-1475 atomic absorption/emission spectrophotometer. **FAILURE TO OBSERVE ANY OF THE FOLLOWING PRECAUTIONS CAN AND WILL RESULT IN A VIOLENT EXPLOSION.**

1. Pull off the burner head to check if the liquid trap is filled. Check by pouring distilled water into the spray chamber through the burner head collar until you observe water running through the drain tube into the waste bucket. Replace the burner head, making sure that it is secure.
2. Make certain the waste bucket has been emptied before you start. After emptying the bucket, replace the drain tube. When replacing the tube, make sure that the end of the tube is not submerged and that there are no places in which a lower portion of the tube rises to a higher elevation than a portion of the tube closer to the spray trap on the burner assembly.
3. Turn on the exhaust hood before any fuel or oxidant lines have been opened. Also, turn on the power switch on the Varian spectrophotometer.
4. Open the oxidant supply (tank or building air line). With the oxidant switch on the AA-1475 open, make sure the oxidant supply pressure is about 50 psi and that there is at least 500 psi total pressure in the air supply tank (if house air is not used). Then check to be sure that the oxidant flow gauge ball is even or slightly above the red line.
5. Open the valve on the acetylene tank. Open and adjust the fuel flow so that it reads between 3 and 4 on the flow scale. Once adjusted, return to the acetylene tank and check the tank pressure. It should read between 8 and 10 psi with the fuel valve adjusted as previously requested. The acetylene tank should be changed if the total pressure in the tank is less than 50 psi.
6. With both the air and acetylene lines open, press the ignite button on the instrument's front panel. A bright yellow-white flame should result. Adjust the fuel control so that less acetylene is allowed into the combustion mixture. You should continue the adjustment until you see a crisp blue feather and non-luminous flame (the feather should be sharp and well-defined).
7. Aspirate distilled deionized water for ~5 minutes to allow the flame and instrument to stabilize. Aspiration of water also serves to clean out the spray chamber and nebulizer, which may have residue left from previous samples.

SHUT-DOWN PROCEDURE: To shut down the instrument's flame, the following procedure should be used.

1. At the end of use, aspirate distilled deionized water for ~5 minutes.
2. To shut off the flame, turn the fuel flow gauge control off (completely to the right, BUT DO NOT OVERTIGHTEN). Once the flame has extinguished, open the acetylene flow again, then turn off the valve at the acetylene tank to bleed the fuel lines out. Let the air run about 1 minute beyond the time at which the acetylene pressure has dropped to 0 to flush any remaining acetylene from the system.
3. Then shut the valve on the air tank off with the air control on the instrument still open. Allow the air pressure in the oxidant line to reach 0, too.
4. Turn off instrument.
5. Turn off fume exhaust hood when complete.

ANALYSIS OF Pb IN SAMPLES:

Refer to the procedure in the Varian AA-1275/1475 operating manual for specific directions for the operation of this instrument in flame AA mode. Your instructor or TA will assist you with the set-up of instrumental conditions. You should use the 283.3 nm Pb wavelength and an instrument slit width (band width) of 0.5 nm. The D₂ – arc background corrector will be used in this experiment. Don't forget to adjust the burner position to obtain the highest and most stable absorbance using your high standard solution.

When the instrument has been set-up, compare the absorbance of your high standard solution to that of one of each of your unknown samples (use 1 s integrations for this). If the absorbance of your unknown is higher than that of the high standard solution, then you must dilute your unknown sample further (in a quantitative fashion). If not, then you can measure all your samples.

Switch the integration time to 5s, then measure a 0 µg/mL solution, all your Pb standards, and your unknown samples. To make a measurement for any sample, you must aspirate the sample, wait until the signal maximizes then record at least 3 back-to-back integration signals. Average these signals and create a calibration curve of Absorbance versus the concentration of Pb. Determine the concentration of each unknown solution. Then determine the original Pb concentration in your paint sample and in the standard reference material. Ultimately you will express the Pb content in each sample in terms of the weight percent Pb.

Part D: Discussion and Reporting Results

In your results and discussion, show the calculations you used to determine the percent Pb in each paint sample, by weight, as well as the 95% confidence interval. For the NIST paint samples, you should compare your results' accuracy to that of the certified values for that sample, found on the NIST website (do not use the label values, as they are only estimates). Use this result to make some assumptions about the accuracy of your unknown paint sample.

Questions:

1. Based on your results, what specific sources of determinate error are most likely?
2. Are any of these determinate error sources likely to also impact the precision of these data?
3. In what ways might the confidence limit of your results be improved?
4. NIST reference materials are often used to help validate analytical methods. Can you think of any other approaches that might be used to help you validate the results you obtain on an unknown sample?

Appendix

Microwave Program "PAINT"

	(1)	(2)	(3)	(4)
Power	39	0	90	100
PSI	40	40	40	40
Time	2:00	3:00	4:00	10:00
TAP	0	0	0	0
Fan	100	100	100	100

Alternative hot plate digestion

Accurately weigh out triplicate samples of about 0.1 g (to the nearest 0.1 mg) of both your dried paint chip samples and NIST reference samples. You should weigh by difference into 6" test tubes that have been cleaned using soap and water and a brief (~ 5 minute) soaking in dilute nitric acid.

Add approximately 5 mL of concentrated nitric acid (trace metal grade) into each test tube, place in a boiling water bath on a hot plate and digest in boiling water for at least 30 minutes. After decomposition, evaporate the remaining liquid in each test tube to dryness, using a Bunsen burner. The test tube should be clamped into a ring stand inside of a fume hood to evaporate to dryness. (Remember to point the test tube toward the back of the hood and to avoid heating too rapidly as spray loss due to excessive splattering of Pb analyte will result). NO_x gases will be evolved in this step and it is of high importance that it be done in a fume hood.

After evaporated, add exactly 10 mL of 0.5 M HCl to the dry sample, cover each test tube, and mix the sample thoroughly. Allow to sit for 10 minutes, then mix again, transfer a portion of the solution into a centrifuge tube and centrifuge for 5 minutes at about 1000-1500 rpm to separate particulate matter. You should directly analyze the supernatant (or dilute the sample using the supernatant if necessary). If the Pb content is high, you may be required to further dilute your sample to be sure it falls within the range of your calibration standards.