Hydride Generation Atomic Absorption Spectrophotometry (HGAAS) for the Determination of Lead (Pb)

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Introduction

Hydride generation atomic absorption spectrophotometry (HG-AAS) is a common technique for the determination of hydride forming metals. In HG-AAS, metals such as Se, As, Sn, Pb in solution are reacted with trace metal grade acid (HNO_3) along with sodium peroxysulfate ($Na_2S_2O_8$, an oxidizing reagent) and sodium borohydride ($NaBH_4$, a reducing reagent) to form volatile metal-hydride compounds that can be removed from solution by purging with an inert gas, such as Argon. The volatile hydride is then swept by the inert gas into a quartz-tube, mounted in a flame atomic absorption spectrophotometer. There, the metal-hydride compound is atomized and measured. The apparatus to be used for doing this experiment is vapor generator accessory (VGA-77). HG-AAS improves the limits of detection by a factor of 100 or more (into sub part-per-billion range) compared to flame AA, removes the analyte from most common matrix interferences present in the original sample, and speeds up the time of the measurement, offering advantages not found in the other techniques.

This technique is a vapor phase sample introduction method for AAS. In this method, lead hydride will be formed by the oxidation of aqueous Pb solution to Pb^{+4} in suitable acidic conditions and then further reduced in to PbH_4 using $NaBH_4$. Thus formed volatile plumbium is swept in to a quartz tube sitting over AA's flame using argon gas where PbH_4 is atomized to Pb^0 and hence the free gaseous lead atoms are measured by AA. The reaction is shown below.

1. $Pb^{+2}{}_{(aq)} \xrightarrow{\text{acid + sodium peroxysulfate}} Pb^{+4}$
2. $Pb^{+4} + BH_4^- \xrightarrow{\text{sodium borohydride}} PbH_{4\ (g)}$

The anticipated advantages of this method are:

1. Quicker approach than GFAAS
2. Comparable LODs to GFAAS
3. Less interferences issues

This lab exercise is designed to show you the general approach for vapor phase introduction and how it compares to flame AA or GFAAS of the hydride generation technique for the analysis of ultra-trace level metals. It will also help to demonstrate the concepts of limits of detection, and other figures of merit. Moreover, this approach will explore the benefits of using this technique over flame absorption and graphite furnace absorption techniques in terms of cost, time and better sensitivity in results.

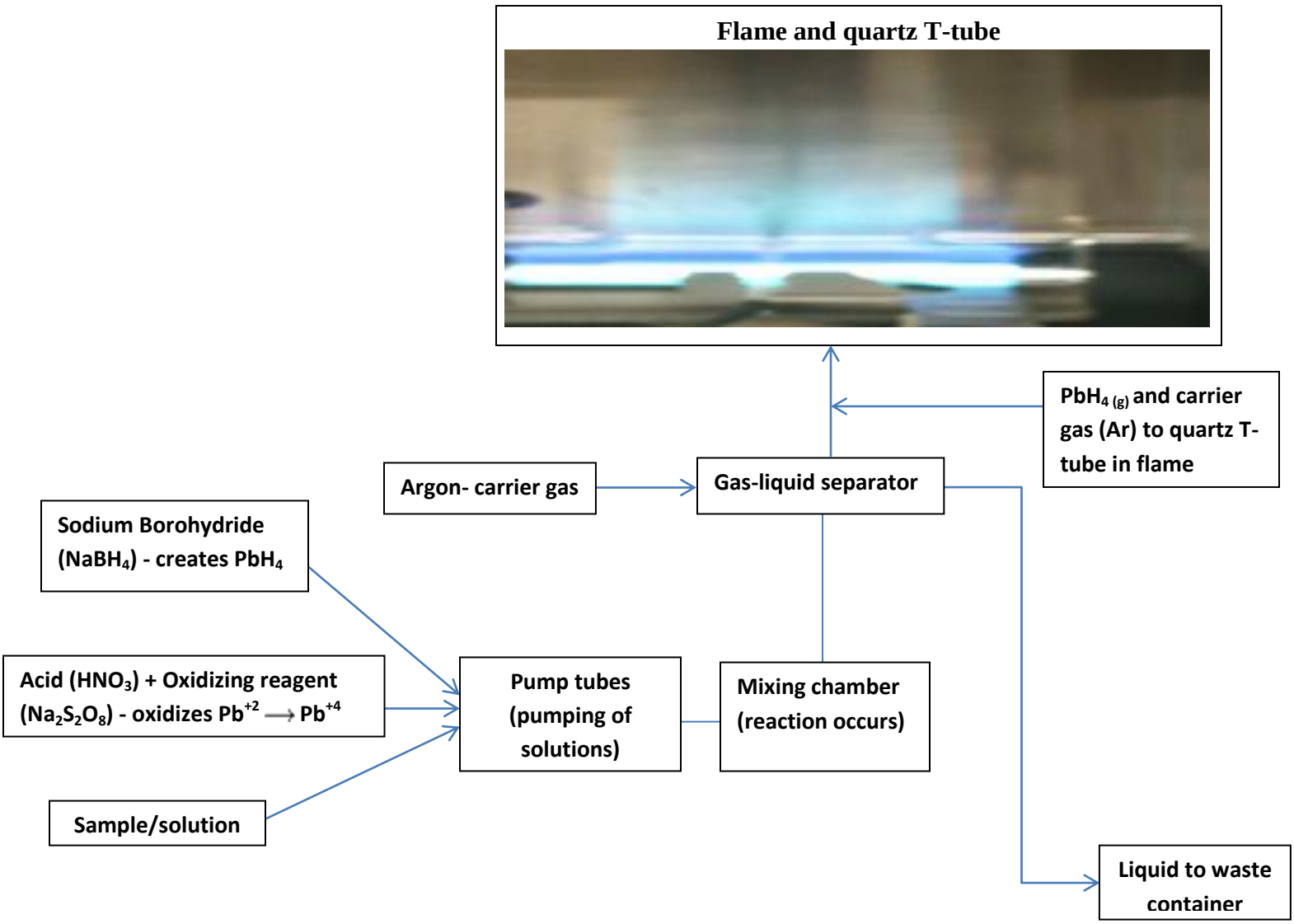


Figure 1: Schematic Diagram of HGAAS

Instrument Setup/Optimization

A] Instrument Preparation

1. Have VGA 77 accessories available in lab; uninstall furnace/autosampler per SOP by the instrument; set up flame unit as per directions.

2. Attach VGA 77 to the front of the instrument, as illustrated in figure 2.

3. Make sure VGA 77 is connected with power supply and that the argon supply line is open at required pressure.

4. Put holding bracket over burner to hold quartz tube for the transmittance of light; make sure quartz tube is clean and properly mounted on the bracket. Look figure 3.

5. Power on Instrument/VGA77.

6. Align tube for maximum hollow cathode throughput by adjusting the barrier positions.

7. Connect drain tubing to waste container.

8. Adjust the pump tubing using pressure adjust knobs.

B] Optimization

1. Have oxidant/fuel (acetylene or NO_2/air) flow on.

2. Ignite the flame (per SOP for flame instrument).

3. Open Spectra AA software; set up a method (per SOP) using Pb hollow cathode lamp (HCL).

4. Click on optimization.

5. Double check optimization of burner position and flame alignment for maximum signal.

6. Hit rescale once alignment has been completed.

7. Allow HCL to warm up for at least 15 minutes before measurements.

8. If using background correction, align the D2 (deuterium) arc lamp similarly to the hollow cathode.

9. Allow D2 lamp for warm up (~15 minutes).

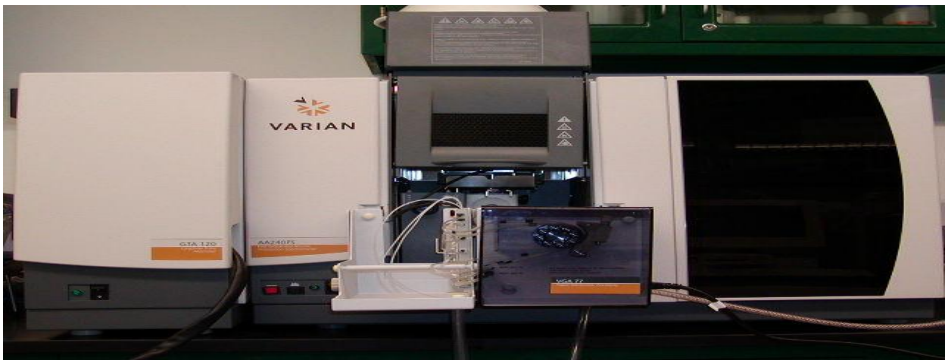


Figure 2: VARIAN 240FS Atomic Absorption Instrument (VGA 77 attached)

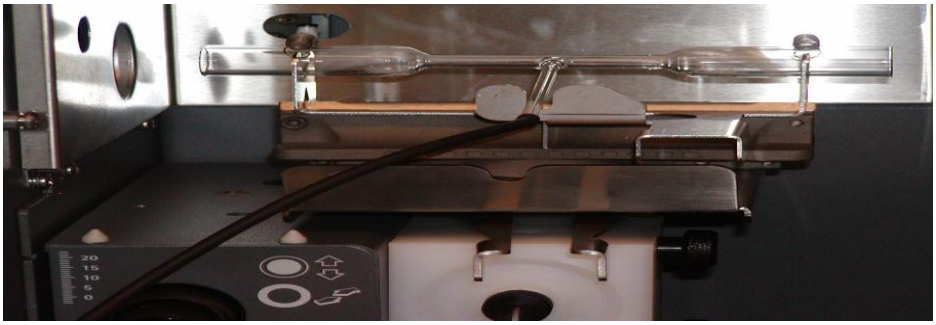


Figure 3: Quartz tube over the burner

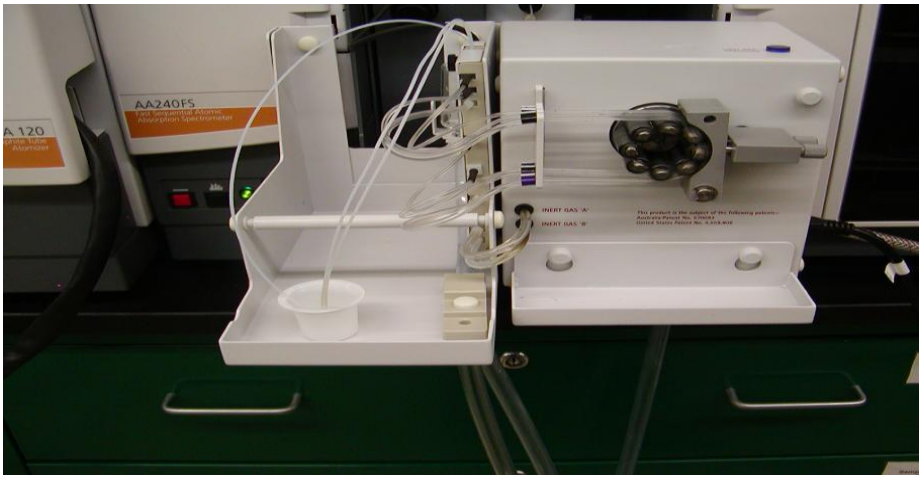


Figure 4: A closer look of VGA 77

Standard Preparation

a. Cleaning plastic bottles

i. Soak in soap water for 5 minutes

ii. Rinse with tap water followed by rinse with DDI water

iii. Soak in diluted cleaning ACS Reagent Grade HCL solution for ~20 minutes

iv. Rinse with 18 MΩ H_2O

v. Soak in diluted ACS Reagent Grade HNO_3 solution for ~20 minutes

vi. Rinse properly with 18 MΩ H_2O

vii. Let them dry (do not dry with towels or kimwipes)

b. Preparation of standards (ppb level) from 1000 ppm Pb stock standard

Create a series of concentrations in the range of 10-100 ng/g (ppb) using 18 MΩ H_2O, a top loading balance and serial dilutions.

c. Know the exact concentration of your standards (to at least 3 significant figures) prior to preparing instrument. Be sure to label all of your standard solutions.

Preparation of the Hydride-Forming Reagents and Solutions for the Experiment

The required chemical reagents for doing the analysis using this approach are trace metal grade nitric acid, strong reducing agent sodium borohydride and strong oxidizing agent sodium peroxydisulfate. On optimizing the experimental conditions, the suitable concentration of reagents that would give best analytical signal is found to be 0.3M HNO_3 with 14% $Na_2S_2O_8$ and 10% $NaBH_4$ solutions. Prepare these solutions with18 MΩ H_2O using analytical balance in a properly cleaned reagent bottles. Blank reagent is 18 MΩ H_2O. After the preparation of standards, sample/s, blank solution and required chemical reagents solution, we are ready to perform analysis. One best calibration curve obtained using such experimental condition is shown in the result section.

Analysis (Determination of Pb in instructor provided sample)

1. Calibration and Detection Limit Study

No background correction.

Perform an analysis for Pb in sample provided by your instructor using a calibration curve made from aqueous standards. The instrument should be set up as described in setup mode. Use the 283.6 nm Pb line and a slit setting of 1 nm. Also, integrate signals for 3 repeat integrations at 15s each.

Measure the absorbance of a series of standard solutions using peak height measurements. Following the measurement of the standards, measure the sample (3 times) and a blank sample (five samples of 18 MΩ H_2O).

Create a calibration curve using your results and determine the Pb concentration in the water sample and in the tap water sample. Also, determine the detection limit for Pb using peak area measurements. Compare these detection limits value to that of flame atomic absorption and graphite furnace absorption.

2. Calibration with Background Correction

Now repeat the same analysis using background correction. Change the worksheet to allow for background correction, let D2 (deuterium) lamp warm up for at least 15 minutes. Perform a standard calibration curve followed by the analysis of your instructor provided sample. Observe the effect of using background correction on your results. What might be concluded about molecular absorption interferences based upon these results?

Removing the interferences present in the sample is an important footstep in the field of analytical chemistry. There are many reported examples of the use of separation techniques to eliminate interferences.

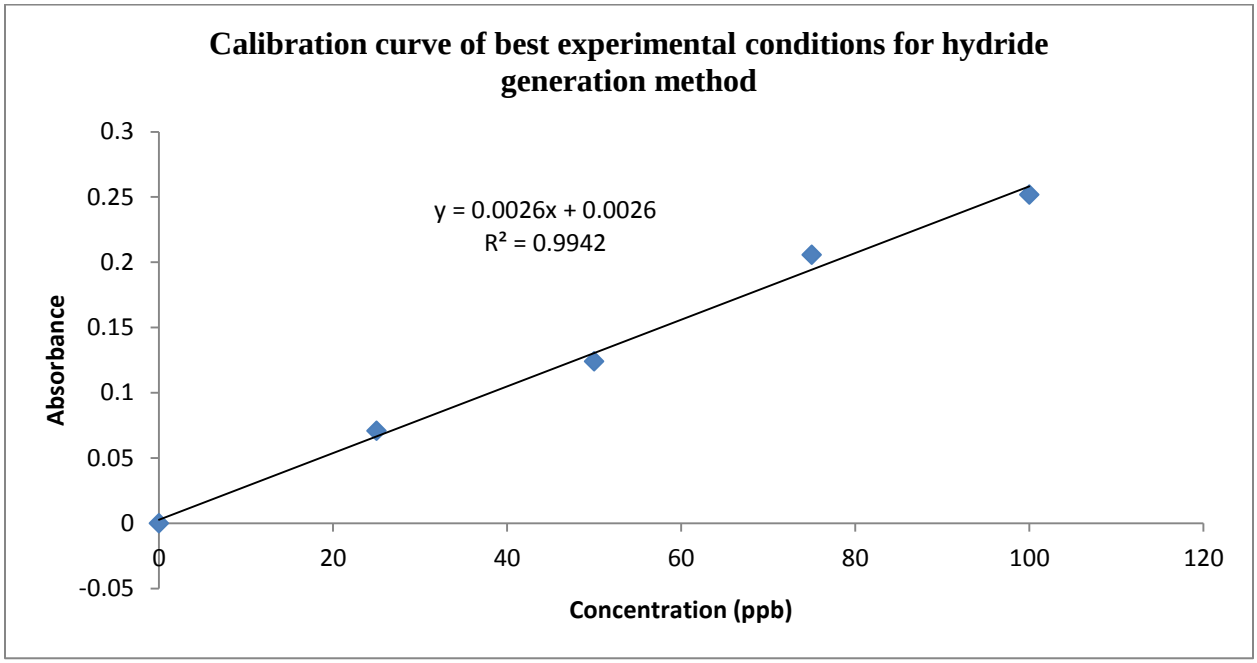
Note: If your instructor assigns you to provide your own analysis sample, then look for **TIPS/Recommendations** on the last page of this handout.

Results

To explore reaction chemistry that generates PbH_4, best reagent combination is shown in table below:

Chemical Reagents	Chemical Compounds	Concentration
Reducing agent (hydride-forming)	$NaBH_4$	10%
Oxidizing agent	$Na_2S_2O_8$	14%
Acid (trace metal grade)	HNO_3	0.3M

Experimentally, using Pb standard solutions in the range of 10-150 ppb, we have investigated the variations in the concentration of peroxydisulfate, nitric acid, and borohydride that give the best analytical performance. A calibration curve under such experimental condition is presented here as an example.



LOD	LOQ	RSD (%)
0.06	0.2	0.3

Figure 5: Calibration curve obtained using hydride generation technique under suitable experimental conditions

Conclusion

Thus, the basic goal of this experiment is to be able to use hydride generation sample introduction method for the detection of heavy metal (Pb) by atomic absorption spectrophotometry. VGA-77 apparatus is used for the generation of volatile metal hydride. Using this technique, better sensitivity in the result is obtained as expected. Comparison of results obtained using this approach with graphite furnace method would prove the success of doing analysis using this method. Moreover, this method is fast and economical comparing to furnace absorption method. Detection limit obtained is as good as or slightly better than GFAAS.

Successful optimization of experimental conditions gave us the easy way for preparing chemical reagents which provided linear calibration behavior. However, one can always observe the difference in result upon varying the concentration of reagents. Consult with your instructor if you want to vary the concentration of reagents.

Discussion

Analyze all the results obtained with analytical performance using this approach. Save all absorbance values of your standards and sample/s. Create a calibration curve using thus obtained absorbance value and concentration value of your standards. Use this calibration curve for the calculation of concentration of your unknown sample. Perform calculations for LOD, LOQ and estimate LOL. Compare the results with graphite furnace absorption methods. Also, compare the results obtained with or without background correction absorption. Notice any matrix interference issues or any spectral, physical or chemical interference involved. Observe any random or systematic error in the result. Discuss the possible ways for the improvement of results in the future.

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TIPS/RECOMMENDATIONS for Non-Instructor Provided Sample Preparation

The main aim of sample preparation is to create an analyte of interest in the physical and chemical form required by the instrument. It should be free of interfering substances, and in the concentration range of your standards.

a) Sample Creation and Collection: Sample origination is basically important step of sample preparation. Sample collection is another step of sample preparation that can be carried out by using contaminants free collection tool to prevent the sample from being contaminated. Phase of the sample (liquid, solid, gas) affects the precision of our method, so it is necessary to prepare sample in the phase required by the instrument. Generally, this method requires sample in forms of solution.

b) Number of lab analysis samples: For assembling the accuracy and precision for the standards that company desires, one should ensure that numbers of lab samples prepared are appropriate. Moreover, it is necessary to take adequate amount of sample that will be sufficient to carry out duplicate or triplicate analysis if required.

c) Sample Reduction or Decomposition: Sample decomposition is required to reduce the gross size sample in to lab size. This approach requires sample in solution form, so liquid sample are good, however, solid samples need to be reduced or decomposed. Solid samples are usually lees homogenous and most difficult to sample. Solids should change in form of solution which requires crushing and decomposition. Depending upon the hardness of material to be ground, we can choose grinders and crushers available. Sometimes, oven dry might be necessary before sampling to remove adsorbed water to obtain a representative sample. This techniques use wet-sample digestion (e.g., nitric- perchloric acid) to destroy organic matter. The lead hydride is thermally decomposed and atomized in the sample beam of the atomic absorption spectrophotometer. Nitric-perchloric acid is commonly used for the digestion step. Nevertheless, perchloric acid is potentially explosive, so use of phosphoric acid is also common.

d) Sample Storage: If samples cannot be analyzed immediately, they must be stored. During storage composition of sample might get changed due to reaction with air, light or container material, so lid of sample container should be keep tight and stored in refrigerator. When ready for analysis, take out the stored sample and perform the measurement of sample to get results.