

Graphite Furnace Atomic Absorption Spectrophotometry

Graphite furnace atomic absorption spectrophotometry (GFAAS) is an analytical technique designed to perform the quantitative analysis of metals in a wide variety of samples. In comparison to standard flame atomic emission or flame atomic absorption methods for the determination of metals at the trace and ultra-trace level, it is an approach that is particularly attractive. The major reasons include:

1. The capability of using relatively small volumes or masses of samples.
2. It can allow the direct determination of solid samples with minimal sample preparation.
3. Relatively high S/N ratios are achieved by keeping the non-analyte background low and having highly efficient transport of the analyte into the measurement pathway.
4. It exhibits high sensitivity primarily because there are no flame gases to dilute the free, gaseous atoms that are analyzed.

The GFAA experiment is one that follows the laws of spectrophotometry, thus your knowledge of Beer's law should be applicable in this experiment. In this approach, microliter volumes of a sample are pipetted into a small graphite tube (the furnace) that can be heated electrically. A series of three heating steps are usually then applied to the sample contained in the graphite furnace. The first of these is the *drying stage*, designed to gently evaporate the solvent from the liquid sample (usually water) without splattering the sample. Following the drying stage, the temperature of the furnace is increased, often in the range of 400-800 ° C for a period of time called the *ashing (or charring) stage*. During this stage organic components (fats and oils) in the matrix can be charred, the composition of the sample can be changed chemically, or high boiling volatile components can be removed. The impact of this stage is one which further simplifies the sample matrix to help reduce interferences and make calibration easier. Finally, the *atomization stage* is applied. In this stage, the temperature of the furnace is very rapidly raised to temperatures often as high as 2700 ° C, effectively volatilizing the remaining components on the rod wall (mostly inorganic/metallic substances). Many of the volatilized metals will come off of the walls in the atomic form, creating a cloud of atomic vapor, trapped in a very small tube. The actual absorbance measurement that occurs during this stage by using a hollow cathode lamp shined through the furnace, creating the actual transmittance measurement that is common to all forms of spectrophotometry. A signal trace of absorbance versus time is the measurement that is used for quantitative purposes. The trace characteristically shows a transient absorbance signal as a function of time (similar to that of the Gaussian-like peaks observed in gas chromatography). For best consistency, the peak areas are integrated and these areas are directly proportional to the actual mass of the element deposited to the rod (or to the actual concentration if consistent volumes of sample are used). Calibrations are performed by measuring the areas of a number of standards.

This lab exercise will be one designed to show you the good sensitivity of the graphite furnace for the analysis of ultra-trace level metals. It will also help to demonstrate the concepts of limits of detection, background correction in atomic absorption (used to deal with complex sample matrix interferences), and the use of standard additions to correct chemical interferences that may not always be corrected by the instrument's background corrector. There are three parts to the lab.

Solution Preparation:

A bovine tissue sample will be prepared for you. You will need to prepare a 30 ppb standard Pb^{2+} solution from a 1000 ppm commercial lead standard. This preparation should be accomplished by performing serial dilutions by mass using a top-loading balance. To avoid error due to absorptive loss of lead, this 30 ppb solution must be made fresh each day.

1. Calibration and Detection Limit:

In this section, you are to perform an analysis for Pb in bovine tissue and tap water using a calibration curve made from aqueous standards. The [instrument](#) should be set up using the [worksheet](#) setup mode. Use the 283.6 nm Pb line and a slit setting of 1. Also use a 40 μL sized total sample injection volume.

Measure the absorbance of a series of standard solutions using peak area measurements. Following the measurement of the standards, measure the bovine tissue sample, a sample of tap water, the bovine tissue blank sample, and four samples of distilled deionized water.

Create a calibration curve using your results and determine the Pb concentration in the tissue sample and in the tap water sample. Also, determine the detection limit for Pb using peak area measurements. How do these detection limits compare to that of flame atomic absorption? Why would one want to use peak area measurements in GFAA instead of peak height measurements? How do your results compare to the "true" lead concentration reported on the NIST certificate for the bovine tissue reference material?

2. Calibration with Background Correction:

Next repeat the analysis of tap water and bovine tissue using background correction. Change the worksheet to allow for background correction, then perform a standard calibration curve followed by the analysis of your tissue, tissue blank and tap water samples. Explain why the uncorrected tissue absorbances are high. What effect does background correction have on the results of your tissue sample?

3. Method of Standard Additions:

Perform the lead determination of tissue using the method of standard additions.

In this approach, we will construct a calibration curve within the actual sample. Choose your blank to be the nitric acid solution and use 10 μL sized aliquots of the tissue sample. The add quantities should be 0, 5, 10, and 15 μL samples respectively. The aliquot of standard and sample should then be diluted to 40 μL total volume by the autosampler.

Determine the tissue Pb concentration using a standard additions calibration curve. Compare these results to that achieved in Parts 1 and 2. What differences, if any, do you note? What is the significance of each of these approaches of calibration in general? After performing this work, what advantages and disadvantages can you conclude are characteristic of GFAAS? Are there any other conclusions that you might make that could address the idea that "knowing your sample" is equally important as simply knowing how to do a measurement with a modern, computer-controlled instrument?