Graphite-Furnace Atomic Absorption Spectrophotometry

I. Introduction

Atomic absorption spectrophotometry (AAS) has become a routine method for the determination of many trace elements in a variety of sample matrices. One of the limitations of flame AAS is the sensitivity of the method. However, the sensitivity of detection for most elements is significantly improved using a graphite furnace in place of the flame to atomize the sample. In this approach, the liquid sample is placed on a small platform or in a small cup in the furnace and heated in a series of progammed steps to dry, pyrolyze and ultimately atomize the sample. Frequently, a matrix modifier is added to the sample prior to heating so that the chemical form of the analyte is controlled during the heating sequence. Although solid samples can also be analyzed with the furnace, it is generally more desirable to dissolve such samples to minimize matrix effects. In this experiment, a sample of wheat flour will be wet ashed to dissolve the material and the resulting solution containing ppb of Mn will be analyzed using graphite furnace AAS and the method of standard addition.

II. Equipment

A. Perkin Elmer 3300 AA spectrophotometer with HGA-600 graphite furnace
B. 25-mL round bottom flask (obtain from instructor)
C. water bath with adjustable temperature controller (obtain from instructor)
D. 50-mL volumetric flask
E. two 100-mL volumetric flasks
E. 1-mL adjustable volume pipet (obtain from instructor)
F. plastic sampling vials
G. plastic storage bottle
H. glass stirring rod

III. Reagents

A. manganese standard solution, 100 ppm
B. wheat flour (obtain from instructor)
C. conc. H_2SO_4, ultrapure
D. 30% H_2O_2, high purity
E. 1% HNO_3

IV. Procedure

A. Wet Ashing of Wheat Flour Sample

1. Accurately weigh out about 0.2 g of the wheat flour and quantitatively transfer it to a 25-mL round bottom flask.

2. Add 2-3 mL of conc. H_2SO_4. Use a glass stirring rod to ensure that the entire sample is completely wet. Rinse the stirring rod with drops of conc. H_2SO_4 before removal from the flask. Heat the flask with sample in the water bath for about 15 minutes using a water temperature of 90-95EC. Control the heating so that the reaction is not too vigorous and the sample does not splatter.

3. Slowly add 1-2 mL 30% H_2O_2 to completely dissolve the blackened sample. The H_2O_2 must be added dropwise to avoid splattering of the sample.

4. When the sample has dissolved completely (a clear, light yellow solution remains), quantitatively transfer the solution to a 50-mL volumetric flask and dilute to the mark with deionized water.

5. While the wheat flour sample is digesting, clean your plastic storage bottle using 1% HNO_3 and thoroughly rinse it with deionized water.

6. Rinse the storage bottle with a few milliliters of the dilute sample solution and transfer the sample solution to the bottle for storage.

B. Preparation of Standard Mn Solution

1. Carefully prepare a 40 ppb solution of Mn by succesive dilutions of the 100 ppm Mn standard solution. Do not use less than 1.0-mL aliquots for these dilutions. Store this solution in a plastic storage bottle that has been cleaned as described in IV.A.5 above.

C. Furnace AAS

Your instructor will demonstrate the basic use of the software used for data collection and printing. Take careful note of all settings. Before running the software, the instrument must be turned on. If the instrument has not been turned on, refer to the start-up directions in the front of the log book.

1. On the Windows Desktop screen, double click the **AAWinLab Analyst** icon. Click on **Use a custom-designed workspace**. Select **322L_Mn.frn** and click **OK**.

2. Click the **Lamps** button at the top of the screen. Click on the **Set-up** button for Mn. After the lamp is set up, click on the **Bkgnd. Corr.** button at the bottom of the window. When the background signal is displayed on a bar graph, close the Align Lamps window.

3. In the **Automated Analysis** window, locate the column entitled **Use Autosampler Locations Listed Below**. Click once in the cell in this column opposite the Mn method. Enter the number **3** and press **Enter** on the keyboard. Scroll to the bottom of this window and click on the **Analyze** tab.

4. Prepare a series of plastic sampling vials (3 total) by filling each to the line with either deionized water, the 40 ppb Mn standard solution or the wheat flour sample solution and place them in locations 1,2 and 3, respectively, in the autosampler tray. Replace the autosampler cover.

5. **Verify the proper alignment of the robotic sampling tube with your instructor BEFORE you begin any runs.**

6. Click the **Analyze All** button. The standard addition method used for this experiment analyzes the following five 20-µL samples that are placed on the platform in the graphite furnace.

Sample 1:	5 µL H_2O	+	15 µL H_2O		
Sample 2:	5 µL unknown	+	15 µL H_2O		
Sample 3:	5 µL unknown	+	10 µL H_2O	+	5 µL standard
Sample 4:	5 µL unknown	+	7 µL H_2O	+	8 µL standard
Sample 5	5 µL unknown	+	5 µL H_2O	+	10 µL standard

   As each sample is analyzed, absorption data will be printed out and a standard addition calibration curve will be plotted on screen. Note the adjusted peak area for the blank. It should be less than 0.01. When all of the analyses are finished, the approximate concentration of your diluted sample is displayed. This is only approximate because the standard solution is assumed to be exactly 40 ppb.

7. When finished, carefully remove all samples from the autosampler tray and replace the cover.

8. **Do not discard your wheat flour sample solution.** This will be further analyzed in the ICP-MS experiment.

V. Treatment of Data

A. Prepare a standard addition calibration curve by plotting the net peak area versus the concentration of the added Mn in the 20-µL sample for samples 2-5. Fit these data points with a linear least-squares line. Print this graph with the equation for the line.

B. Calculate the concentration of Mn in the dilute wheat flour solution from the equation for the standard addition calibration curve and the dilution factor associated with the graphite furnace analysis.

C. Calculate the concentration (in ppm) of Mn in the solid wheat flour sample. Report this result.

D. Identify the most likely sources of error in this experiment. Which error is likely to be the largest?

Lab Cautions for Graphite-Furnace AAS

1. **Before turning on the instrument, ensure that the argon gas and cooling water are turned on.**

2. **Before running any samples, ensure that the autosampler is properly aligned to deliver sample to the furnace platform.**

3. **After placing sampling vials in the autosampler, make sure the lid is properly aligned so that the robotic sampling tube can access the liquid in the sampling vials.**

4. **The last user of the day should turn off the power to the main unit and the furnace power supply, then turn off the argon gas and the cooling water. Do not exit the software completely; exit to the Windows Desktop before quitting.**

5. **When finished, remove all sampling vials from the autosampler and dispose of the solutions.**