

# Atomic Absorption and Emission Spectrophotometry

**Objective:** The objective of this experiment is to use atomic absorption spectrophotometry (AAS) to determine the calcium concentration in a carbonated beverage using the calibration curve method. The effect of a releasing agent will also be studied. Atomic emission spectrophotometry (AES) will then be used to determine the sodium concentration using the standard addition method.

**Background:** In flame ionization AAS, the sample is nebulized into tiny droplets and then vaporized and finally atomized in a flame. Once in the atomic state, a particular analyte absorbs ultraviolet or visible radiation at very specific wavelengths. The characteristic wavelengths have such a narrow linewidth that there is very little chance that another species in the sample will absorb at the same wavelength. The technique is thus very selective for a particular analyte in a complex sample. The excitation source, a hollow cathode lamp, is constructed from the same material as the analyte and produces radiation with the exact wavelengths absorbed by the analyte. A monochromator is used to select the wavelength where absorption is greatest. The absorbance at this wavelength is proportional to the concentration of the analyte in the sample, provided the concentration is low enough.

The measurement of calcium by AAS is complicated by reaction with phosphates to form nonvolatile salts. This can be overcome by adding lanthanum to the sample because it reacts preferentially with the phosphate and releases the calcium atoms. In the laboratory procedure, 1 % lanthanum is added to all standards and the first sample solution. Lanthanum is left out of the second sample solution in order to observe its effect.

Alkali metals are usually measured using atomic emission rather than absorption. Due to their low ionization energies, a large fraction of alkali metal ions in flame atomization are in an excited electronic state in which they do not absorb the most intense wavelengths corresponding to ground-state atoms. For emission, no lamp is needed - the monochromator wavelength is simply set to select the most intense emission. The emission intensity is proportional to the concentration of analyte in the sample at low enough concentrations. The effect of chemical interferences on sodium AES will be minimized by using the standard addition method of calibration.

## Reagents

0.1 M HCl

Calcium standard solution (500 mg/L  $\text{Ca}^{+2}$ )

Sodium standard solution (100 mg/L  $\text{Na}^{+}$ )

Lanthanum solution (5%  $\text{La}^{+3}$  in 2 M  $\text{HNO}_3$ )

Degassed Coca-Cola

### Pre laboratory Assignment

1. How does Atomic Absorption spectroscopy "select" for a particular metal ion such as calcium in a complex solution that may contain several other metal ions?
2. A solution prepared from 5.00 mL of sample diluted to 100.0 mL had a sodium emission intensity of 0.095. A second 100.0 mL solution prepared from 5.00 mL of sample and 10.00 mL of 101.6 mg/L sodium standard solution had a sodium emission intensity of 0.141. What was the concentration of sodium in the original sample?

### Procedure

#### Calcium standard solutions

For AAS and AES solutions, glassware must be scrupulously clean and rinsed with MilliQ water. A stock solution of Ca at 500 mg/L in 0.1 M HNO<sub>3</sub> is provided. Be sure to note the exact concentration of this solution. Pipet 1 mL into a 500 mL volumetric flask and dilute to the mark with 0.1 M HNO<sub>3</sub>. Use this solution to prepare the following calibration standards: Pipet 15, 10, 5, 2, a mL into five 25 mL volumetric flasks, then add 5 mL of the lanthanum solution to each flask and fill each to the mark with 0.1 M HNO<sub>3</sub>. Cap the volumetric flasks and invert them several times to mix. Also prepare 100 mL of roughly 1 mg/L solution - a graduated cylinder is adequate for this solution.

#### Sample solutions

Obtain a sample of Coca-Cola that has been degassed. Prepare sample solution A by pipetting 5 mL of cola and 5 mL of lanthanum solution into a 25 mL volumetric flask and filling to the mark with 0.1 M HNO<sub>3</sub>. Prepare sample solution B the same way except do not add the lanthanum solution.

#### Sodium spiked samples

Prepare another sample of Coca-Cola with 10x dilution by pipetting 1 mL into a 100 mL volumetric flask and diluting to the mark with 0.1 M HNO<sub>3</sub>. Prepare a second sample with 1 mL of Coca-Cola but also pipet in 5 mL of the 100 mg/L sodium stock solution. Also prepare 100 mL of roughly 1 mg/L sodium solution from the stock solution.

#### AAS measurements

Set up the Perkin-Elmer AA and optimize for calcium AAS according to the following directions.

1. Turn on the AA instrument. After a minute or so, turn on the PC and monitor.
2. Run the AA\_INST.EXE program. Select Manual Control from the *Windows* menu. From the dialog box that appears choose Element File and select a method file for the desired element. To set up for calcium, for example, choose the file "CA.FEL". The instrument will take a minute or so to rotate the lamp into position and power it up.
3. Open the main valve on the acetylene tank (to the right of the instrument - turn the gray valve counter-clockwise). Press F8 on the keyboard to ignite the flame. Place the siphon tube into a bottle of deionized water and aspirate water for a few minutes to clean out the burner.

4. From the *Windows* menu select Continuous Graphics. From the *Continuous* menu select Autozero so that the absorbance reads zero while aspirating pure water.
5. Place the siphon tube in the roughly 1 a mg/L Ca solution and note the level on the graphics window. Adjust the burner in the horizontal (left front knob), vertical (right front knob), and twist (right rear knob) directions. Note that if the burner is raised too far, it blocks the light beam and a sharp rise in absorption occurs. Slowly lower the burner until the absorbance returns to reasonable values and continue to lower until a maximum is observed.
6. From the *Windows* menu, select Flame Control. Vary the acetylene flow rate in small increments (0.1 or 0.2) until a maximum in absorbance is observed. Close the Flame Control window. The instrument is now optimized. - be sure not to make any changes for the remainder of the experiment.
7. Aspirate 0.1 M HNO<sub>3</sub> for 30 seconds or so and zero the absorbance scale. Measure the absorbance of each standard and sample solution, going from low concentrations to high. Set the measurement time to 5 seconds and record three successive absorbance readings. Between each solution, aspirate 0.1 M HNO<sub>3</sub> for 1 a seconds to clean the burner, but do not rezero the absorbance.
8. Set up the instrument for Na emission by closing the Continuous Graphics window and then selecting from the menu bar File Open. Choose "NA.FEL" from the element file list. As the instrument sets up for AES, start aspirating the roughly 20 mg/mL Na solution. This is necessary because the instrument adjusts the detector gain based on the most concentrated sodium sample to be analyzed. When ready, use the 1 a mg/mL Na solution to optimize the burner position.
9. Aspirate 0.1 M HNO<sub>3</sub> to clean the burner, then record emission intensity for the sample solution, then the sample solution plus sodium spike.
10. When the experiment is concluded, aspirate deionized water for a minute or so, then close the valve on the acetylene tank. This will bleed the gas in the lines and produce a message that the flame is off. Turn off the instrument and shut down the PC.

### **Treatment of Data**

Plot a calibration curve for the calcium standard solutions to demonstrate that the absorbance follows Beer's Law. Perform a linear regression to determine the slope of the line and its standard deviation. Determine the amount of calcium in the original sample in mg/L based on the absorbances of both sample solutions and evaluate the effect of the releasing agent. For sodium, calculate the concentration in the original sample from your standard addition. Compare your value with that on the sample bottle. Be sure to report the uncertainties in your results.

### **Reference**

Chemistry Experiments for Instrumental Methods, Sawyer, Heineman, and Beebe, John Wiley & Sons, New York, 1984.