

# CHEM 334 Quantitative Analysis Laboratory

## *Determination of Calcium by Atomic Spectroscopy*

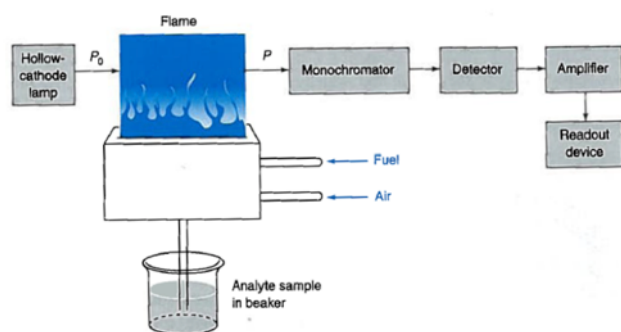
### Introduction

Atomic Spectroscopy is literally the spectroscopy (or spectrometry) of neutral atoms. It is made up of a group of methods suitable for elemental analysis, that is, the quantification of the amount of a particular element in an analyte. It offers little or no information on the state of the element in molecules or the molecules themselves.

Optical atomic spectroscopy, that is, using visible or near visible light as a probe, can be segregated into several broad types: atomic absorption spectroscopy (AAS), atomic emission spectroscopy (AES) and atomic fluorescence spectroscopy (AFS). These types differ in certain aspects of their fundamental principles, in the details of the instrumentation used and in the measurement details, for example, the limit of detection. In all cases, however, the spectroscopic absorption, emission and fluorescence lines are exceedingly narrow, typically a small fraction of a nanometer in contrast to the corresponding lines associated with liquid or solid species which start at widths of many nanometers and increase seemingly without limit.

Emission and fluorescence spectroscopies rely on the emission of specific wavelengths of light from the analyte in the gas phase. Absorption spectroscopy, in contrast, relies on the absorption of specific wavelengths of light by the analyte, also in the gas phase and requires a source of light to absorb.

No matter which type of atomic spectroscopy is performed it is necessary to form a gaseous cloud of neutral atoms from an analyte. The sample, dissolved in a solvent is nebulized, that is, reduced to a fine spray, by a turbulent flow of gaseous oxidant. It is then mixed with a gaseous fuel and carried into a flame where atomization, that is,



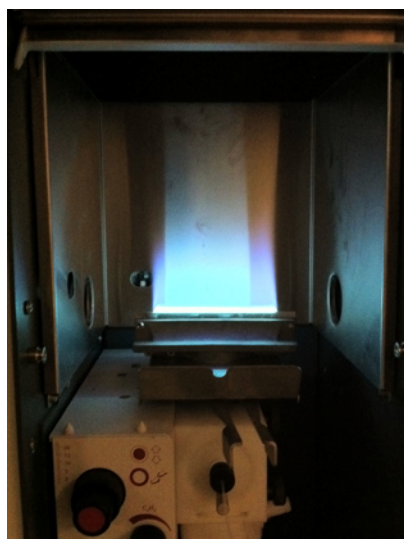
**Figure 2.** Schematic diagram of a flame atomic absorption spectrometer. An atomic emission would differ in the absence of the hollow cathode lamp since the atoms are emitting the light that the rest of the spectrometer is detecting.



**Figure 2.** The Varian SpectrAA 55B atomic absorption spectrometer. The user interface and display are located at the upper right, the light source at the lower left, the sample nebulizer, aspirator and reservoir at the lower left, the burner at the upper left and the exhaust chimney at the extreme upper left.

conversion to an atomic gas, occurs. A complex set of chemical and physical processes occurs in the flame. The first is desolvation where the solvent evaporates to produce a finely divided solid aerosol of molecules. The aerosol is then volatilized by elevated temperature to form a gas of molecules. Further elevated temperature causes dissociation of a fraction of the molecules into atoms to form a gas of atoms. Further elevated temperature causes ionization of a fraction of the atoms creating plasma. Some ions combine with free electrons and radicals present in the plasma to reform neutral atoms.

The light source used in atomic absorption spectroscopy deserves special mention. As previously mentioned, the width (in the wavelength dimension) of an atomic absorption is exceedingly narrow. In order for Beer's law to hold it is necessary for an analyte to absorb all of the light that falls upon the light detector. In other words, the width of the absorbance must be wider than the detector's width, which is almost always determined by the quality of the monochromator. It is almost impossible to achieve monochromator bandwidths in the range of 0.01 nm and narrower. Even if it were possible the amount of light reaching the detector would be infinitesimally small, resulting in very poor quality measurements. The solution to this problem is to use a light source that is based on the very element that is being analyzed. The so-called hollow cathode lamp is constructed of a metal cathode composed of the metal element to be analyzed and contained in a transparent tube filled with an inert gas, for example, neon or argon. A high voltage electrical discharge ionizes the filling gas and the ensuing plasma is effective in mobilizing metal atoms from the cathode which are then excited by the plasma and glow very brightly and with a band width as narrow as the absorbing atoms in the analyte thereby relieving the narrow bandwidth requirement of the monochromator.



**Figure 3.** The burner section with the cover removed and showing acetylene-air flame.



**Figure 4.** A hollow cathode lamp serving as a light source for absorption measurements installed in lamp position #1. Another lamp can be installed in position #2 to facilitate rapid switching between different elements.

## Procedures

**Preparation of Standard Calcium Solution:** Prepare 250 mL of solution of aqueous calcium nitrate that is approximately 5.0 mM but known accurately.

**Preparation of Unknown Sample Solutions:** Obtain one antacid tablet and record the manufacturer's identification and tablet's characteristics. Place the tablet into 250-mL beaker and add a few milliliters of water. Calculate the

volume of 1 M hydrochloric acid required to completely react with the manufacturer's reported amount of calcium carbonate in the tablet. Slowly and carefully add 110% of this volume of acid to the beaker. Considerable foaming will occur from the carbon dioxide evolution. The solution may be turbid or contain bits of residual tablet coating at this point. Bring the suspension just to a boil using a hot plate set to 200 °C to remove any remaining traces of carbon dioxide. Cool then quantitatively transfer the beaker's contents to a 250 mL volumetric flask and make up



**Figure 5.** Display, control and readout section showing the **Signal** screen. The spectrometer has not yet been zeroed and displays a non-zero absorbance.



**Figure 6.** Detail of the sample area. The Erlenmeyer flask is the distilled water reservoir. While the flame is burning water must flow continuously into the nebulizer and the drain tube must be unobstructed.

the volume with water. This is named the “undiluted unknown sample solution.” Solutions with high turbidity require filtration to remove the particles that will clog the spectrometer inlet. Use a simple gravity filter made up of either a single folded piece of filter paper or a small ( $\sim 2 \text{ cm}^2$ ) piece of filter loosely balled up in the top of the stem of a funnel to filter a small quantity of the undiluted unknown sample solution ( $\sim 10 \text{ mL}$ ). Dilute this filtered solution by a factor of one hundred (100) to obtain a “diluted unknown sample solution.” (Compute the approximate  $[\text{Ca}^{2+}]$  of both the undiluted and diluted unknown sample solutions.)

**Preparation of Calibration Curve Measurement:** Prepare a series of solutions, each with a volume of fifty milliliters. Add various volumes of the Standard Calcium Solution so that the set contains a series of known, calcium concentrations excluding zero. The calcium concentration in any solution must not exceed 1.0 mM. Transfer these solutions to a labeled set of fifty-milliliter Erlenmeyer flasks. Measure the absorbance of each of these solutions in the spectrophotometer as described below. Prepare these solutions and measure them one at a time or at most two at a time. For example, start with 0.5 and 1.0 mM. (Are the absorbances in the spectrophotometer’s linear region?) Make additional solutions of different calcium concentration accordingly and collect at least four (4) good data points for a linear calibration curve.

**Unknown Sample Measurement:** Measure the absorbance of the diluted unknown sample solution in the spectrophotometer. If the absorbance is above of the maximum found in the calibration curve then estimate a suitable dilution factor and dilute until a solution is obtained that displays an absorbance less than the maximum found in the calibration curve. Do not discard the undiluted and the diluted unknown sample solutions just yet.

**Standard Addition Method:** Prepare a series of standard addition solutions, each with a volume of fifty milliliters. Select a volume of one of the diluted unknown sample solutions that when added to these standard addition

solutions will contribute approximately 0.1 to their total absorbance. Add various volumes of the Standard Calcium solution to the series so that it contains several known calcium concentrations yet remains in the spectrophotometer's linear range. Prepare and measure their absorbance of these solutions one-at-a-time not all at once. Collect at least three and no more than five measurements.

Measure the absorbance of each of the six solutions in the spectrophotometer.

**Atomic Absorption Spectrophotometer Measurement:** Teaching staff will provide specific instructions on the operation of the spectrometer. The following is a brief synopsis of the required steps.

1. Aspirate a sample of distilled water from the reservoir. Press the **Optimize** button, select the **Signal** setting and then hold down the **Alt** button and press the **Read** button. The spectrometer will then report zero absorbance.
2. Aspirate the most concentrated calcium solution. Ensure that the instrument reads an absorbance of approximately but no more than one.
3. Aspirate a sample of distilled water from the reservoir. Press the **Results** button followed by the **Read** button. The spectrometer will wait roughly five seconds to permit the analyte solution to flow to the flame then it will make several multiple-second measurements of the absorbance. Record the averaged absorbance and its %RSD.
4. Aspirate all of the solutions in turn, pressing the **Read** button and recording the averaged absorbance and its %RSD.
5. Return the sample tube to the distilled water reservoir.

## Results

Report the results of the both the calibration curve and the standard addition measurements in tabular form. Be certain to carefully compute the actual concentration of added calcium (in appropriate units of molarity) for each solution. Prepare a figure showing the results of the calibration curve and standard addition on the same graph. (Remember to always use the known analyte concentration on the x axis.) Compute a least squares fit for each of the two sets of data using a linear function and draw the resulting lines with the experimental data points. Extrapolate the standard addition data to zero absorbance, calculate the unknown calcium concentration in the solutions in mM and estimate its uncertainty.

Do not forget (!) to report the result of your unknown sample measurement.

Report the measured amount of calcium carbonate in a tablet. Include a suitable uncertainty analysis.

## Discussion

In addition to a now customary discussion of the results presented in this Report compare and contrast the results of the method used in this experiment and with the previous determination of calcium concentration of the same supplement tablet by titration - this includes the presence (or not) of a matrix effect.

Are any effects of the sample matrix observed in your data? Explain.

## References

Harris, D., *Quantitative Chemical Analysis*, 8<sup>th</sup> ed.; Freeman & Co.: NY; 2010; Chapter 20.

Skoog, D. Holler, F.J. and Crouch, R., *Principles of Instrumental Analysis*, 6<sup>th</sup> ed.; Thomson Brooks/Cole: CA; 2010; Chapter 9.

*Flame Atomic Absorption Spectrometry - Analytical Methods*. User Manual #8510000900; 8<sup>th</sup> edition; 2010. [Online] Agilent Technologies, Inc. Literature Library. <https://www.chem.agilent.com/Library/usermanuals/Public/0009.pdf> (accessed 9 Oct, 2011).