Chem 321 Lecture 20 - Atomic Absorption Spectrophotometry

11/7/13

Student Learning Objectives

Although the basic principles, especially Beer's law, apply, the instrumentation for doing atomic absorption spectrophotometry (AAS) differs in some significant ways from what is used for conventional UV-VIS spectrophotometry. The main differences are the radiation source and sample holder that are used. As the name suggests, AAS involves absorption by analytes that are atoms (in the gas phase). These atoms are usually produced in a flame from solutes in aqueous solution. A schematic diagram of a typical AAS instrument is shown in Figure 13.1.

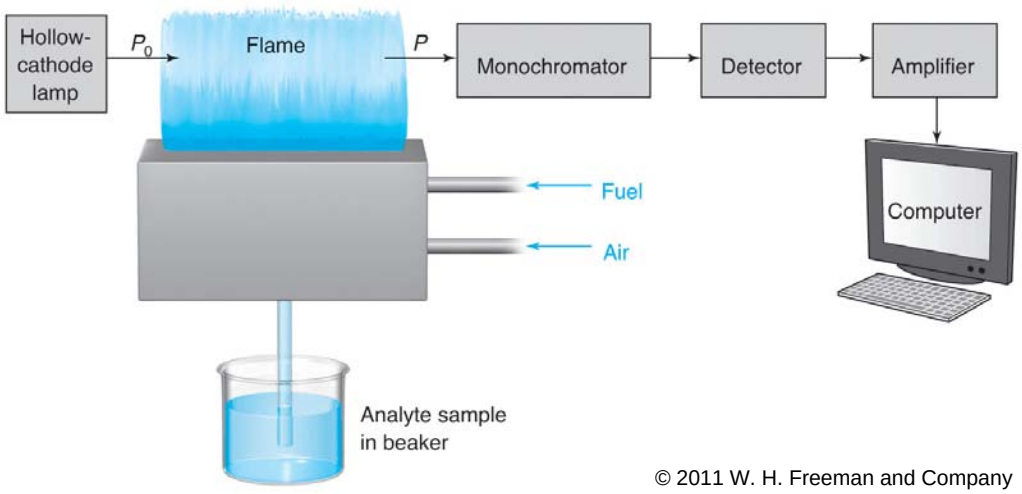

Figure 13.1 Schematic diagram of an atomic absorption spectrophotometer

The flame not only produces the atomic species, but also serves as the sample holder. The aqueous sample is drawn up into a mixing chamber through a capillary tube where it becomes an aerosol, is mixed with the burner gases and drawn into the burner. The following sequence, using calcium as the analyte, describes the production of the light-absorbing analyte atoms in the flame.

$$CaCl_2(aq) \rightarrow CaCl_2(s) \rightarrow CaCl_2(g) \rightarrow Ca(g) + 2Cl(g)$$

The formation of Ca(g) is not the only possible fate for this analyte. It could also be ionized or form a polyatomic species, both of which will absorb differently than the calcium atoms. Proper choice of the burner gases and adjustment of the gas mixture composition can optimize the production of analyte atoms in the gas phase. In our experiment, an acetylene/air mixture is used. One assumption made in this experiment is that the same fraction of analyte is converted to atoms in the gas phase for all samples.

An “exploded” view of a mixing chamber in an AAS instrument is shown in Figure 13.2. Notice the drain outlet at the rear of the mixing chamber. Most of the aspirated sample never makes it into the flame and is removed through the drain. Another assumption made in this experiment is that the sample uptake into the flame is the same for all samples.

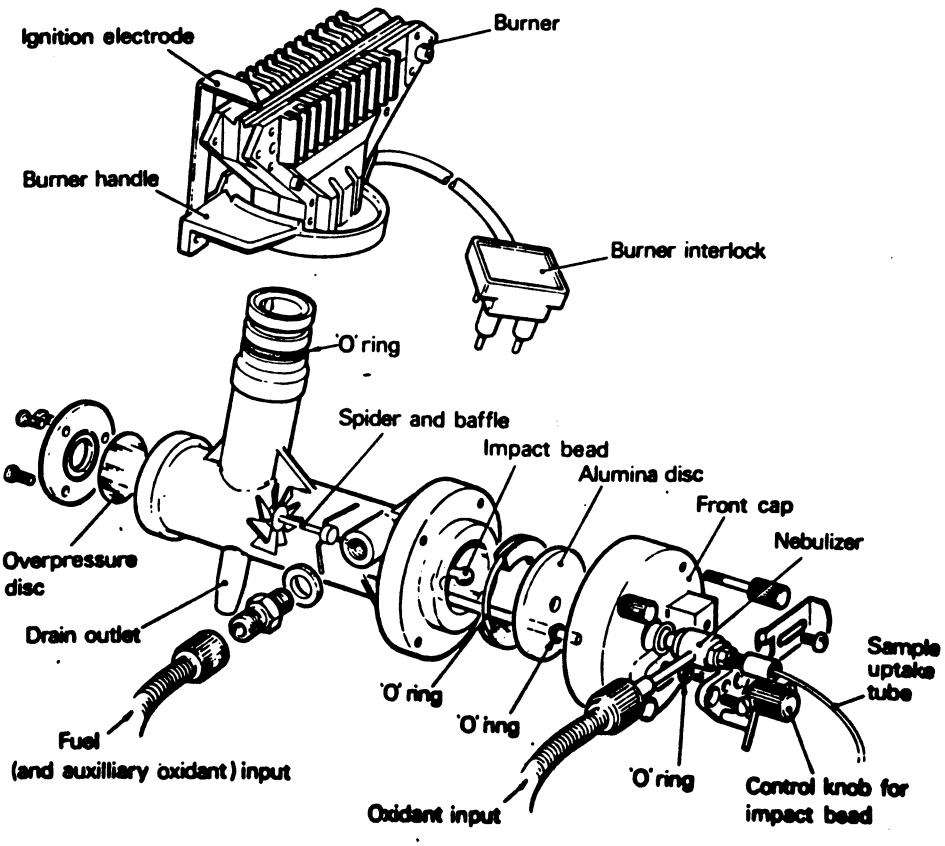

Figure 13.2 An “exploded” view of the mixing chamber in an AAS instrument

During the absorbance measurement, aqueous sample is continuously drawn into the flame at a rate of several milliliters per minute. A steady-state level of the gas-phase analyte atoms is eventually established in the flame. These atoms absorb a portion of the radiation that is directed through the flame. This process is monitored for a preset interval (4 seconds in our experiment) and the light intensity reaching the detector (P) is determined. A blank solution that is run in a similar way serves to establish P_0 (recall $A = -\log P/P_0$).

Since the light-absorbing species is an atom in the gas phase, radiation absorption occurs in very narrow bands at discrete wavelengths corresponding to the electronic excitations in the atom. These absorption bands are much narrower than the band of radiation that is typically selected by a monochromator. However, Beer's law holds only if the band of radiation passing through the sample is narrow compared to the absorption band. Thus, a different type of radiation source must be employed for AAS. The radiation source in an atomic absorption spectrophotometer is a **hollow cathode lamp** (Fig. 13.3). This source, unlike the tungsten lamp and deuterium lamp, does not emit all wavelengths in a specific spectral region. Instead, the output is the atomic emission line spectrum of the element specific to the lamp. In the hollow cathode lamp, electronically excited atoms of the cathode material are produced in the gas phase. These atoms then emit photons as they return to the ground state. By selecting a lamp with a cathode made of the same material as the analyte, the lamp emissions will be at exactly the wavelengths absorbed by the analyte. The width of these emission lines is sufficiently narrow compared to the absorption band of the analyte for Beer's law to hold. The monochromator in an atomic absorption instrument is used to isolate only one emission line from the hollow cathode lamp and to reject as much of the emissions from the flame as possible. Usually a different hollow cathode lamp is used for each analyte.

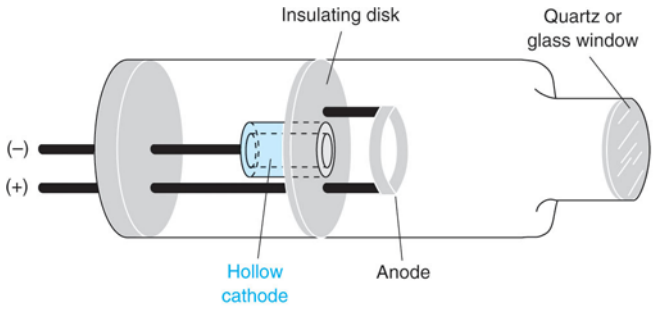

Figure 13.3 Diagram of a hollow cathode lamp

It is important to note that AAS is a total element method. That is, you are able to determine how much of an element is present, but not what chemical form is present. Because AAS is a rather sensitive technique (it can detect ppm levels for most metals) and the instrumentation is rather inexpensive ($20,000 and up), this has been a widely used method for trace element analysis. The disadvantages with flame AAS are that the samples are usually limited to aqueous solutions or other easily aspirated liquids, it is not suitable nonmetal analysis and a different lamp is often needed for each element analyzed.

The spectrophotometric determination of iron and the atomic absorption experiment with magnesium are both done in the linear range for these analytes. Consequently, the calibration curves (plots of absorbance versus concentration of standard) are quite linear. If your standard data points do not all fall on or very near the linear least-squares line fit, consider rejecting one of the data points or remaking one or more of the standards. The AAS determination of calcium, however, uses analyte concentrations slightly outside the linear range for calcium. Consequently, the calcium calibration curve is not quite linear and is better fit with a quadratic least-squares line (a polynomial equation of order 2). Once again, reject a standard point that deviates markedly from the line fit, or remake standards if necessary. For all of these experiments, it is appropriate to include a (0,0) data point when preparing each calibration curve. The best results are obtained when the standards and samples are all run at the same time (identical instrument conditions).

Exercises for Atomic Absorption Spectrophotometry