6.1: Introduction to Atomic Spectroscopy

Earlier we discussed the difference between atomic spectra, which only consist of electronic transitions and therefore appear as sharp lines, and molecular spectra, which because of the presence of lower energy vibrational and rotational energy states appear as a broad continuum. Provided we have atoms present in a sample, it is possible to analyze them spectroscopically using either absorption or emission measurements. One problem is that most samples we analyze do not consist of atoms but instead consist of molecules with covalent or ionic bonds. Therefore, performing atomic spectroscopy on most samples involves the utilization of an **atomization source**, which is a device that has the ability to convert molecules to atoms.

It is also important to recognize that the absorption or emission spectrum of a neutral atom will be different than that of its ions (e.g., Cr^0, Cr^{3+}, Cr^{6+} all have different lines in their absorption or emission spectra). Atomic absorbance measurements are performed on neutral, ground-state atoms. Atomic emission measurements can be performed on either neutral atoms or ions, but are usually performed on neutral atoms as well. It is important to recognize that certain metal species exist in nature in various ionic forms. For example, chromium is commonly found as its +3 or +6 ion. Furthermore, Cr^{3+} is relatively benign, whereas Cr^{6+} is a carcinogen. In this case, an analysis of the particular chromium species might be especially important to determine the degree of hazard of a sample containing chromium. The methods we will describe herein cannot be used to distinguish the different metal species in samples. They will provide a measurement of the total metal concentration. Metal speciation would require a pre-treatment step involving the use of suitable chemical reagents that selectively separate one species from the other without altering their distribution. Metal speciation is usually a complex analysis process and it is far more common to analyze total metal concentrations. Many environmental regulations that restrict the amounts of metals in samples (e.g., standards for drinking water, food products and sludge from wastewater treatment plants) specify total metal concentrations instead of concentrations of specific species.

The measurement of atomic absorption or emission requires selection of a suitable wavelength. Just like the selection of the best wavelength in molecular spectroscopic measurements, provided there are no interfering substances, the optimal wavelength in atomic spectroscopic measurements is the wavelength of maximum absorbance or emission intensity.