4.2: Specialized Infrared Methods

Non-Dispersive Infrared Spectroscopy

One technique is called non-dispersive infrared (NDIR) spectroscopy. NDIR is usually used to measure a single constituent of an air sample. Think what the name implies and consider how such an instrument might be designed. The word non-dispersive implies that the instrument does not use a monochromator. The design of a NDIR is illustrated in Figure 4.2.6. Common things that are often measured using NDIR are the amounts of carbon monoxide and hydrocarbons in automobile exhaust.

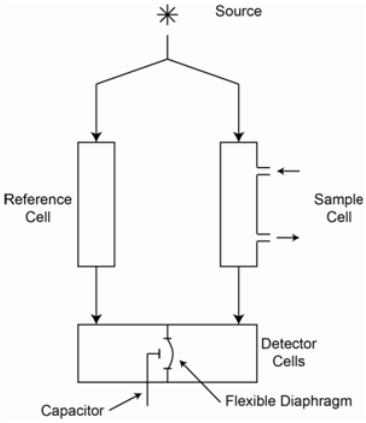

Figure 4.2.6. Diagram of the components of a non-dispersive infrared spectrophotometer.

The device either splits the beam or uses two identical sources, one of which goes through a reference cell and the other of which goes through the sample cell. The sample of air (e.g., auto exhaust) is continually drawn through the sample cell during the measurement. The reference cell is filled with a non-absorbing gas. The detector cell is filled with the analyte (i.e., carbon monoxide, which has an IR absorption band in the region from 2050-2250 cm^{-1}). If the system is designed to measure carbon monoxide, the reference cell does not absorb any radiation from 2050-2250 cm^{-1}. The sample cell absorbs an amount of radiation from 2050-2250 cm^{-1} proportional to the concentration of carbon monoxide in the sample. The two detector cells, which are filled with carbon monoxide, absorb all of the radiation from 2050-2250 cm^{-1} that reaches them. The infrared energy absorbed by the detector cells is converted to heat, meaning that the molecules in the cell move faster and exert a greater pressure. Because the reference cell did not absorb any of the radiation from 2050-2250 cm^{-1}, the detector cell on the reference side will have a higher temperature and pressure than the detector cell on the side with the sample. A flexible metal diaphragm is placed between the two cells and forms part of an electronic device known as a capacitor. Note that the capacitor has a gap between the two metal plates, and the measured capacitance varies according to the distance between the two plates. Therefore, the capacitance is a measure of the pressure difference of the two cells, which can be related back to the amount of carbon monoxide in the sample cell. The device is calibrated using a sealed sample cell with a known amount of carbon monoxide. When measuring hydrocarbons, methane (CH_4) is used for the calibration since it is a compound that has a C-H stretch of similar energy to the C-H stretching modes of other hydrocarbons. Another common application of NDIR would be as a monitoring device for lethal levels of carbon monoxide in a coal mine.

Another specialty application is known as **attenuated total reflectance spectroscopy (ATR)**. ATR involves the use of an IR transparent crystal in which the sample is either coated or flows over both sides of the crystal. A representation of the ATR device is shown in Figure 4.2.7.

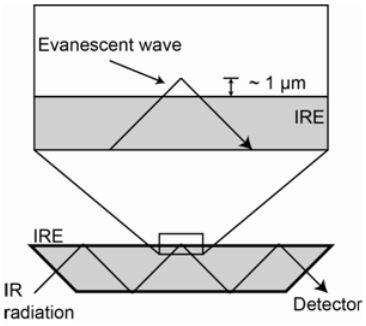

Figure 4.2.7. Representation of a device for measuring attenuated total reflectance spectra.

The radiation enters the crystal in such a way that it undergoes a complete internal reflection inside the crystal. The path is such that many reflections occur as the radiation passes through the crystal. At each reflection, the radiation slightly penetrates the coated material and a slight absorption occurs. The reason for multiple reflections is to increase the path length of the radiation through the sample. The method can be used to analyze opaque materials that do not transmit infrared radiation.

An inconvenience when recording IR spectra is that glass cells cannot be used since glass absorbs IR radiation. Liquid samples are often run neat between two salt plates. Since solvents absorb IR radiation, IR cells usually have rather narrow path lengths to keep solvent absorption to acceptable levels. Solid samples are often mixed with KBr and pressed into an IR transparent pellet.

Another way to record an IR spectrum of a solid sample is to perform a **diffuse reflectance** measurement. The beam strikes the surface of a fine powder and as in ATR some of the radiation is absorbed. Suitable signal-to-noise for diffuse reflectance IR usually requires the use of Fourier transform IR methods.
