hand-operated presses available for making KBr pellets, but the quality of the pellet obtained may not be as good as that obtained with an evacuable die. The pellet often will contain more water, which absorbs in the IR region and may interfere with the sample spectrum. There are several types of handheld presses available. A common design consists of two bolts with polished ends that thread into a metal block or nut. The nut serves as the body of the die and also as the sample holder. One bolt is threaded into place. The KBr mix is added into the open hole in the nut so that the face of the inserted bolt is covered with powdered mix. The second bolt is inserted into the nut. Pressure is applied using two wrenches, one on each bolt. The bolts are then removed; the KBr pellet is left in the nut and the nut is placed in the light path of the spectrometer. The pellet should appear clear; if it is very cloudy, light scattering will result, giving a poor spectrum. The pellet is removed by washing it out of the nut with water. One disadvantage of this type of die is that the pellet usually cannot be removed from the nut intact; if pellets need to be saved for possible reanalysis, a standard die and hydraulic press should be used. Micropellet dies are available that produce KBr pellets on the order of 1 mm in diameter and permit spectra to be obtained on a few micrograms of sample. A beam condenser is used to reduce the size of the IR source beam at the sampling point.

It is critical that the KBr be dry; even then bands from water may appear in the spectrum because KBr is so hygroscopic. The KBr used should have its IR spectrum collected as a blank pellet; reagent grade KBr sometimes contains nitrate, which has IR absorption bands. IR-grade KBr should be used when possible. The quality of the spectrum depends on having small particle size and complete mixing. A mortar and pestle can be used for mixing, but better results are obtained with a vibrating ball mill such as the Wig-L-Bug®. It is also very important that the polished faces of the anvils not be scratched. The anvils should never have pressure applied to them unless powdered sample is present to avoid scratching the polished faces.

In the third method, the solid sample is deposited on the surface of a KBr or NaCl plate or onto a disposable "card" by evaporating a solution of the solid to dryness or allowing a thin film of molten sample to solidify. IR radiation is then passed through the thin layer deposited. It is difficult to carry out quantitative analysis with this method, but it is useful for rapid qualitative analysis. The thin film approach works well for polymers, for example. It is important to remove all traces of solvent before acquiring the spectrum. Disposable salt "cards" are available for acquiring the IR spectrum of a thin film of solid deposited by evaporation. These cards have an extremely thin KBr or NaCl window mounted in a cardboard holder, but are manufactured so that atmospheric moisture does not pose a storage problem (Real Crystal™ IR cards, International Crystal Laboratories, Garfield, NJ). Water can even be used as the solvent for casting films of polar organic molecules on these cards.

A new approach to collecting transmission spectra of solids is the use of a *diamond anvil cell*. Diamond is transparent through most of the mid-IR region, with the exception of a broad absorption around 2000 cm^{-1}. A solid sample is pressed between two small parallel diamond "anvils" or windows to create a thin film of sample. A beam condenser is required because of the small cell size. Very high pressures can be used to compress solid samples because diamonds are very hard materials. As a result, the diamond anvil cell permits transmission IR spectra to be collected of thin films of very hard materials. Hard materials cannot be compressed between salt windows because the salt crystals are brittle and crack easily.

In general, spectra from solid samples are used for qualitative identification of the sample, not for quantitative analysis. The spectrum of a solid sample is generally collected when the sample is not soluble in a suitable IR-transparent solvent. There are

some problems that can occur with spectra from solid samples. Many organic solids are crystalline materials. The mull and pellet approaches result in random orientation of the finely ground crystals; deposition of thin films by evaporation may result in a specific crystal orientation with respect to the light beam. Hence, thin film spectra may look different from the spectrum of the same material collected as a mull or a pellet. When possible, spectra of known materials obtained by the same sample preparation method should be compared when trying to identify an unknown. Use of a high-pressure hydraulic press for KBr pellets may cause crystal structure changes in some materials; again, standards and samples should have the same sample preparation method used if spectra are to be compared.

4.3.1.2. Liquid Samples

The easiest samples to handle are liquid samples. Many liquids may be analyzed "neat", that is, with no sample preparation. Neat liquids that are not volatile are analyzed by pressing a drop of the liquid between two flat salt plates to form a very thin film. The salt plates are held together by capillary action or may be clamped together. NaCl, KBr, AgCl, and similar salts are used as the plates. Volatile liquids may be analyzed neat by using a pair of salt plates with a thin spacer in a sealed cell. The path length of these cells depends on the spacer thickness. For neat liquids very small path lengths, less than 0.05 mm, must be used to avoid complete absorption of the source beam. Sample sizes used for the collection of neat spectra are on the order of a few milligrams of material.

The use of dilute solutions of material for IR analysis is the preferred choice for several reasons. Solutions give more reproducible spectra, and dilution in an IR-transparent solvent eliminates the problem of total absorption by the strong bands in a neat sample. Solvents commonly used for IR spectroscopy include carbon tetrachloride, carbon disulfide, methylene chloride, and some alkanes such as hexane. No one solvent is transparent over the entire mid-IR region, so the analyst must choose a solvent that is transparent in the region of interest. Figure 4.18 shows the IR-transparent regions for

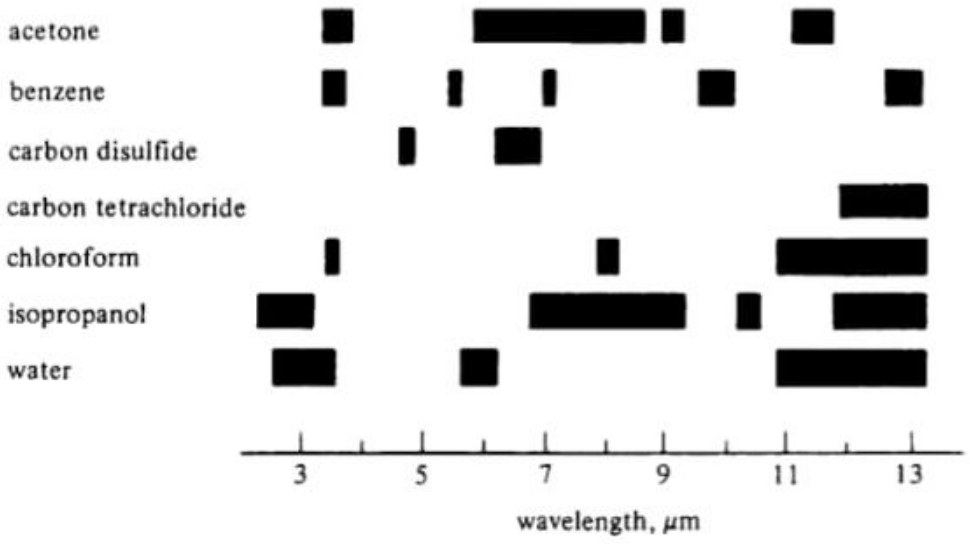


Figure 4.18 IR absorption characteristics of some common solvents. Regions of strong IR absorbance in 0.1 mm cells (except water, 0.01 mm cell) are shown as shaded areas. Longer cell paths will broaden the regions of absorption and in some cases introduce new regions where absorption is significant. (Reprinted from Aikens et al. by permission from Waveland Press, Inc. Long Grove, IL, 1984. All rights reserved.)

4.3.1. Techniques for Transmission (Absorption) Measurements

These are the oldest and most basic sampling techniques for IR spectroscopy and apply to both FTIR and dispersive IR systems. Transmission analysis can handle a wide range of sample types and can provide both qualitative and quantitative measurements. Transmission analysis provides maximum sensitivity and high sample throughput at relatively low cost. There is in some cases substantial sample preparation required.

The sample or the material used to contain the sample must be transparent to IR radiation to obtain an absorption or transmission spectrum. This limits the selection of container

materials to certain salts, such as NaCl or KBr, and some simple polymers. A final choice of the material used depends on the wavelength range to be examined. A list of commonly used materials is given in Table 4.3. If the sample itself is opaque to IR radiation, it may be possible to dissolve it or dilute it with an IR-transparent material to obtain a transmission spectrum. Other approaches are to obtain IR reflectance spectra or emission spectra from opaque materials.

4.3.1.1. Solid Samples

Three traditional techniques are available for preparing solid samples for collection of transmission IR spectra: mulling, pelleting, and thin film deposition. First, the sample may be ground to a powder with particle diameters less than 2 μm. The small particle size is necessary to avoid scatter of radiation. A small amount of the powder, 2–4 mg, can be made into a thick slurry, or *mull*, by grinding it with a few drops of a greasy, viscous liquid, such as Nujol (a paraffin oil) or chlorofluorocarbon greases. The mull is then pressed between two salt plates to form a thin film. This method is good for qualitative studies, but not for quantitative analysis. To cover the complete mid-IR region it is often necessary to use two different mulling agents, since the mulling agents have absorption bands in different regions of the spectrum. The spectrum of the mulling agents alone should be obtained for comparison with the sample spectrum.

The second technique is the KBr pellet method, which involves mixing about 1 mg of a finely ground (<2 μm diameter) solid sample with about 100 mg powdered dry potassium bromide. The mixture is compressed under very high pressure (>50,000 psi) in a vacuum to form a small disk about 1 cm in diameter. An evacuable die is designed for use in a hydraulic press. A die consists of a body and two anvils that will compress the powdered mixture. The faces of the anvils are highly polished to give a pressed pellet with smooth surfaces. A schematic of an evacuable die is shown in Fig. 4.17. When done correctly, the KBr pellet looks like glass. The disk is transparent to IR radiation and may be analyzed directly by placing it in a standard pellet holder. There are small,

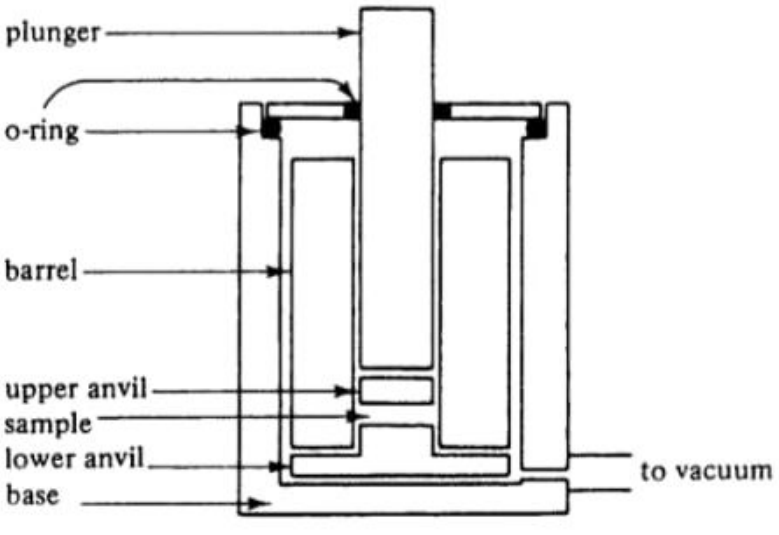
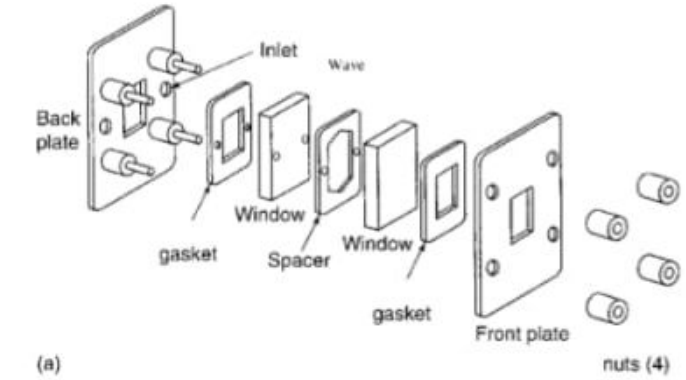


Figure 4.17 Schematic drawing of a typical IR pellet die showing the arrangement of the major

some common solvents. Liquid cells for solutions are sealed cells, generally with a path length of 0.1–1 mm and two salt windows. The path length is fixed by a spacer placed between the two salt windows. Some cells come with a single fixed path length; other cells can be purchased with a variety of spacers. These cells can be disassembled and the path length changed by inserting a different spacer [Fig. 4.19(a)]. The windows and spacer are clamped into a metal frame that has two ports: one inlet and one outlet port. The cell is filled by injecting sample solution with a syringe into one port and allowing it to flow until the solution exits the other port. Solution concentrations of 1–10% sample are used for most quantitative work. Solvent absorption peaks are compensated for in a double-beam dispersive IR by using matched cells. One cell is used to contain the sample solution, and the other cell to contain the solvent used to make the solution. Matched cells have the same window material, window thickness, and path length. In the single-beam FTIR, solvent absorption bands are corrected for by obtaining a blank spectrum of the solvent and subtracting the blank spectrum from the sample solution spectrum, just as the background is subtracted. In this case, the same cell can be used for both the blank spectrum and the sample spectrum.



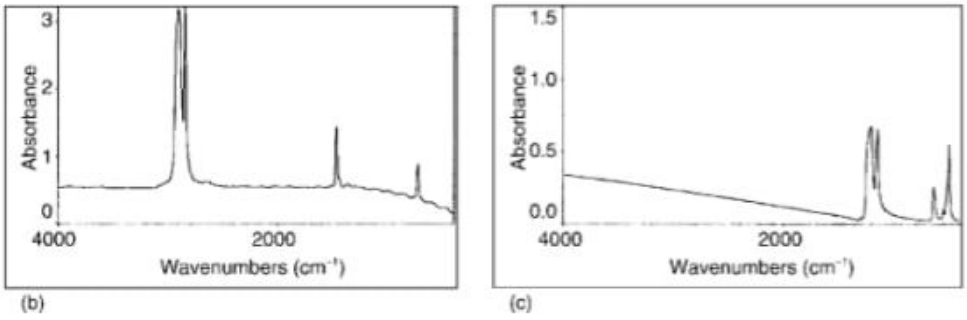


Figure 4.19 (a) Standard demountable cell for liquid samples, shown in an "exploded" view. The spacer is of Teflon or metal. The width of the spacer used determines the pathlength of the assembled cell. The nuts screw onto the four threaded posts to seal the assembled cell. Once the cell is assembled, it is filled via syringe. The inlet port on the back plate is equipped with a fitting for a syringe (not shown); the outlet port is the hole in the back plate opposite the inlet hole. Sample is injected until the liquid appears at the top of the outlet port. Plugs are put into both inlet and outlet ports to seal the cell. Courtesy of PerkinElmer Instruments, Shelton, CT (www.perkinelmer.com). (b) and (c) show the absorbance spectra for two commercial disposable IR cards with polymer film windows. The choice of polymer depends on the region of the spectrum to be studied. PTFE (c) would be used if the C—H stretch region needs to be measured, while clearly polyethylene (b) is not suited for that use. [Courtesy of ThermoNicolet, Madison, WI (www.thermo.com).]

samples containing water can be analyzed. Absorption bands from the polymer substrate are subtracted from the sample spectra by running a blank card spectrum.

Microcells are available for the analysis of as little as 0.5 μL of liquid sample. These microcells also require a beam condenser as described for solid microsamples.

4.3.1.3. Gas Samples

Gas sample cells have windows of KBr and cell bodies made of glass or metal, along with two ports with valves for evacuating the cell and filling the cell from an external gas source. Gases are much more dilute than liquids or solids; a gas has many fewer molecules per unit volume than does a condensed phase. To compensate for the small concentration of sample molecules in a gas (the c term in Beer's Law), the gas cells have longer path lengths (b is increased). The sample cavity of an IR spectrometer is generally about 10 cm long. There are gas cells with a single-pass 10 cm path length, but most gas cells make use of multiple reflections to increase the effective path length. Commercial gas cells with effective path lengths of 2, 10, 20, 40, and up to 120 m are available. The IR beam is reflected multiple times from internal mirrors in the cell. Such a cell is shown schematically in Fig. 4.20, where the multiple reflections make the effective path length 5× longer than the actual physical length of the cell. A single-pass 10 cm cell requires about 50 torr of sample pressure to obtain a good IR spectrum. However, multiple reflection cells with long path lengths permit the analysis of ppm concentrations of gases. Gas cells are also used to obtain the vapor-phase spectrum of highly volatile liquids. A drop or two of liquid is placed in the cell, the valves are closed and the sample is allowed to come to equilibrium. The vapor phase spectrum of HCl (Fig. 4.2) was collected by placing a few drops of concentrated hydrochloric acid in a 10 cm gas cell with a glass body and KBr windows. The gas sample must not react with the cell windows or surfaces. Temperature and pressure must also be controlled if quantitative measurements are being made.

4.3.2. Background Correction in Transmission Measurements

The two main sources of background absorption (i.e., absorption from material other than the sample) are the solvent used for liquid solutions and the air in the optical light path. In a conventional double-beam dispersive system, comparing the sample beam to the reference beam and recording the difference spectrum in real time automatically eliminate absorption from air and solvent. If the sample is a liquid solution, a matching liquid cell with pure solvent is placed in the reference beam. The absorption from the solvent and from the air is measured simultaneously and subtracted from the sample beam signal.

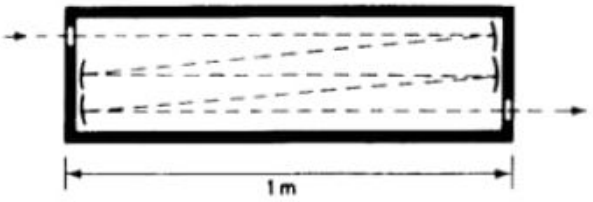


Figure 4.20 Schematic gas absorption cell. Reflection of the light beam through the cell makes the effective path length longer than the cell length.

However, FTIR is a single-beam system and both air and solvent contribute to the signal, so corrections must be made in several steps.

4.3.2.1. Solvent Absorption