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. The 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 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 (Figure 4.19a). 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

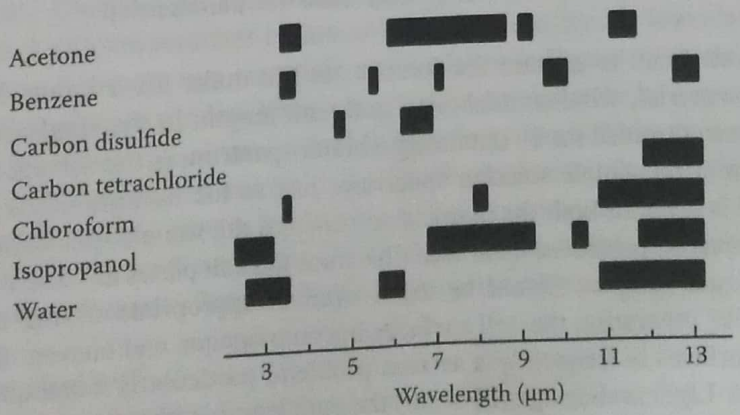


Figure 4.18 IR absorption characteristics of some common solvents. Regions of strong IR absorbance in 0.1 mm cells (except water, 0.01 mm cell) are shown as shaded areas. Longer cell paths will broaden the regions of absorption and in some cases introduce new regions where absorption is significant. (Reprinted from Aikens, D.A. et al., *Principles and Techniques for an Integrated Chemistry Laboratory*, Waveland Press, Inc., Prospect Heights, IL, 1978, Reissued 1984. All rights reserved. With permission.)

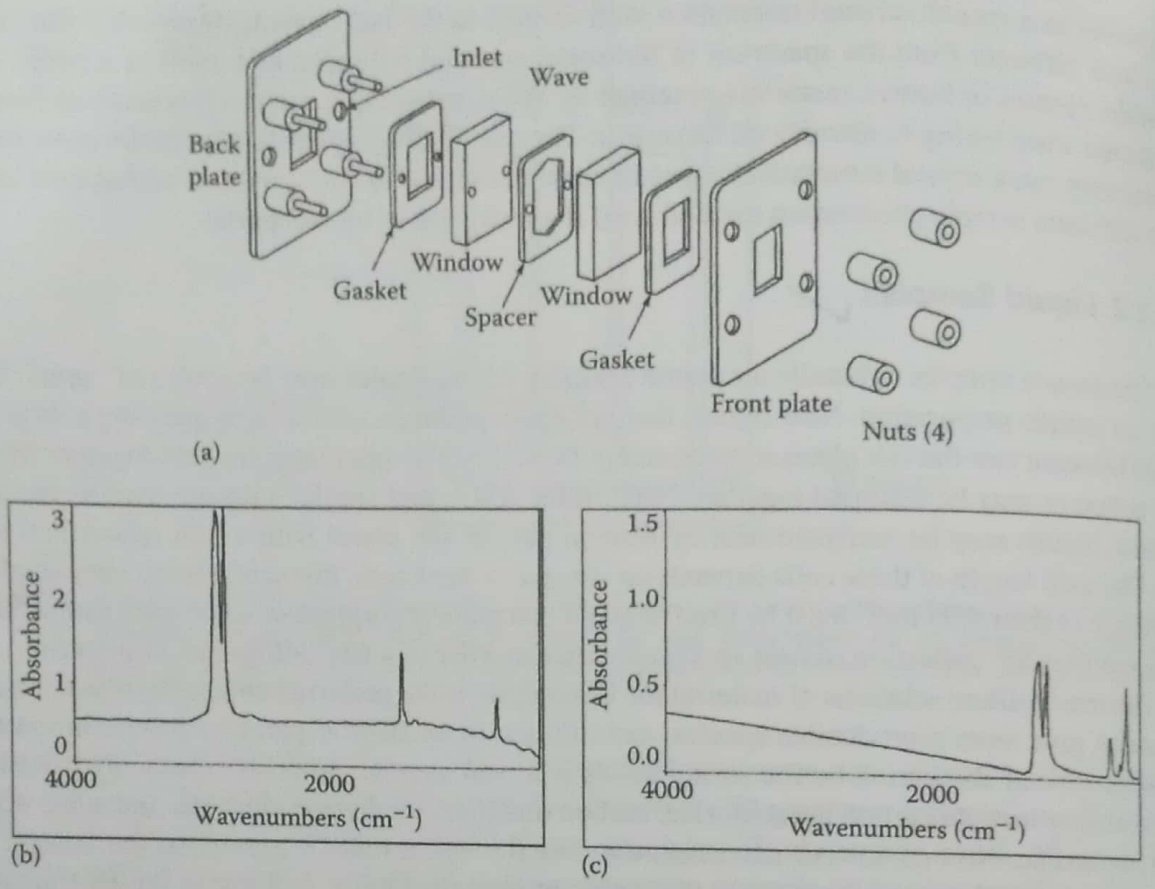


Figure 4.19 (a) Standard demountable cell for liquid samples, shown in an "exploded" view. The spacer is of Teflon or metal. The width of the spacer used determines the path length of the assembled cell. The nuts screw onto the four threaded posts to seal the assembled cell. Once the cell is assembled, 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. [] (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. Polytetrafluoroethylene (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. ()

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 is used for both the blank spectrum and the sample spectrum.

Most IR cells must be protected from water because the salt plates are water soluble and hygroscopic. Organic liquid samples should be dried over an appropriate drying agent before being poured into the cells; otherwise, the cell surfaces become opaque and uneven. Such etching of the internal window surfaces is frequently a serious problem, particularly when quantitative analyses are to be performed. Light scattering will occur; the path length within the cell becomes uneven and erroneous quantitative results may be obtained.

It will be remembered that Beer's law indicates that the absorbance = abc, where b is the path length through the sample or, in this case, the width of the empty cell. In order for quantitative data to be reliable, b must be a constant or at least measurable and correctable. A measurement of b may be performed by using a procedure based on interference fringes. An empty and dry cell is put into the light path, and the interferogram collected (or a suitable wavelength range is scanned

if a dispersive instrument is used). Partial reflection of the light takes place at the inner surfaces, forming two beams. The first beam passes directly through the sample cell, and the second beam is reflected twice by the inner surfaces before proceeding to the detector. The second beam therefore travels an extra distance $2b$ compared with the first beam. If this distance is a whole number of wavelengths ($n\lambda$), then the two emerging beams remain in phase and no interference is experienced. However, if $2b = (n + 1/2)\lambda$, interference is experienced and the signal reaching the detector is diminished. The interference signal generated is a sine wave, and each wave indicates an interference fringe. The path length of the sample holder can be measured by using the following formula:

$$b\,(\mu\text{m}) = \frac{n}{2\eta}\left(\frac{\lambda_1\lambda_2}{\lambda_2 - \lambda_1}\right) \tag{4.9}$$

where

n is the number of fringes

η is the RI of the sample (or air, if empty light path)

λ_1 and λ_2 are the wavelengths between which the number of fringes is measured

If λ is measured in μm, b also has units of μm. For example, if $n = 14$, $\lambda_1 = 2$ μm, and $\lambda_2 = 20$ μm, b can be calculated as

$$b = \frac{14}{2}\left(\frac{2\times 20}{20-2}\right) = 15.5\,\mu\text{m (assuming that } \eta = 1)$$

For quantitative analysis, it is necessary to measure the path length in order to use calibration curves obtained with the same cell but at different times. If the cell becomes badly etched, the interference pattern becomes noisy and the cell windows have to be removed and repolished.

IR spectra of samples containing water can be accomplished using special cells with windows of barium fluoride, silver chloride, or KRS-5. These materials are not very water soluble (see Table 4.3). However, a more useful technique is to measure attenuated total reflection (Section 4.3.3.1).

Disposable IR cards with a thin polymer film window are available for the qualitative analysis of liquids. (These cards were originally manufactured by 3M® but are now available from International Crystal Laboratories, Garfield, NJ, and other suppliers.) Two polymer substrates are available: PTFE for the 4000–1300-wavenumber region and polyethylene for the lower-wavenumber region. The absorption spectra for these two materials are displayed in Figure 4.19b and c. A thin film can be deposited onto the polymer window by evaporation from solution or by smearing the liquid onto the polymer. A major advantage of these cards is that the polymer films do not dissolve in water; therefore, 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,

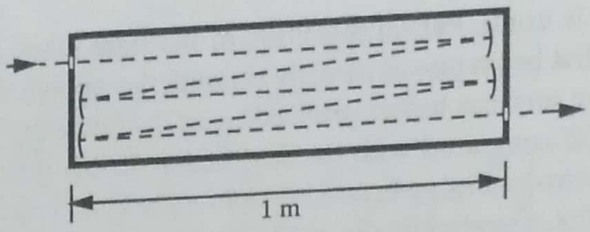


Figure 4.20 Schematic gas absorption cell. Reflection of the light beam through the cell makes the effective path length longer than the cell length.

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 Figure 4.20, where the multiple reflections make the effective path length five times 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 (Figure 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.

A second type of gas sampling FTIR is the open-path instrumentation used for the analysis of ambient air for environmental monitoring, chemical agent, and toxic vapor detection. These open-path systems are specifically designed for use in the field and are "hardened" against mechanical shock, vibration, temperature, and humidity changes. These systems use interferometry and either a passive mid-IR detector which measures IR signatures naturally emitted by chemicals or an active detector measuring absorption signatures using transmitted light from an active IR source. The systems can measure chemical agents and pollutants at distances of from one mile to several kilometers. They are used for smoke stack emission measurements, air pollution measurements, emissions for waste disposal sites, chemical accidents, or toxic agents deliberately released into the air. The Bruker website, www.bruker.com, has pictures and technical details of its HAWK First Responder and EM27 Open Path FTIR instruments, for example.

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. 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

The solvent absorption spectrum is measured by putting pure solvent in the liquid sample cell and recording its spectrum. This spectrum is stored by the computer under an assigned file name (e.g., Spectrum A). The cell (or an identical cell) is then filled with the sample solution in that solvent, its spectrum taken, recorded, and stored under a file name (e.g., Spectrum B). Spectrum A is then

subtracted from Spectrum B, giving the net spectrum of the sample. Of course, in this approach, any absorption by the air is also measured in both Spectrum A and Spectrum B, so the absorption by air is also corrected for.

4.3.2.2 *Air Absorption*

Gaseous CO_2 and H_2O vapor are both strong IR absorbers. Both occur in air in the optical light path and contribute to any IR absorption signal measured. This background signal may be corrected for in one of two ways. First, the air spectrum may be recorded by running a spectrum with no sample present. This constitutes the "blank" spectrum and is recorded and stored as a file (usually called BLANK). Samples of any type—mulls, pellets, or neat liquids—may be run and their total spectrum (air + sample) recorded and stored. The blank (air) spectrum is then subtracted by the computer, leaving the net sample spectrum. Any suspected changes in humidity or CO_2 content can be corrected by updating the blank spectrum at regular intervals. This is an easy and rapid measurement for an FTIR, and in routine analysis, the background spectrum should be collected and the file updated on a regular basis. The second method, *purging the optical path*, is more difficult. The optical system can be purged with dry N_2 or argon, removing CO_2 and H_2O in the process. This eliminates the necessity of correcting for the blank signal derived from impurities in the air if done effectively. However, the ease of collection and subtraction of the background with modern FTIR systems and the difficulty of purging the sample compartment completely makes the first option the more common approach.

A typical background spectrum of air taken by an FTIR spectrometer is shown in Figure 4.14. The bands above 3000 cm^{-1} and between 1400 and 1700 cm^{-1} are due to water; the main CO_2 band is the band at about 2350 cm^{-1}. The FTIR is a single-beam system; this background spectrum is collected and stored for subtraction from all subsequent sample spectra. However, the absorption of the source intensity by carbon dioxide and water reduces the energy available in the regions where they absorb. To reduce the spectral background from carbon dioxide and water and increase the light intensity in these regions, many spectrometers have sealed and desiccated optical systems or a means of purging the optical path to remove the air.

4.3.3 Techniques for Reflectance and Emission Measurements

The sample techniques just described are designed for collection of transmission (absorption) spectra. This had been the most common type of IR spectroscopy, but it was limited in its applications. There are many types of samples that are not suited to the conventional sample cells and techniques just discussed. Thick, opaque solid samples, paints, coatings, fibers, polymers, aqueous solutions, samples that cannot be destroyed such as artwork or forensic evidence samples, and hot gases from smokestacks—these materials posed problems for the analytical chemist who wanted to obtain an IR absorption spectrum. The use of reflectance techniques provides a nondestructive method for obtaining IR spectral information from materials that are opaque, insoluble, or cannot be placed into conventional sample cells. In addition, IR emission from heated samples can be used to characterize certain types of samples and even measure remote sources such as smokestacks. In reflectance and emission, the FTIR spectrometer system is the same as that for transmission. For reflectance, the sampling accessories are different and in some specialized cases contain an integral detector. The heated sample itself provides the light for emission measurements; therefore, there is no need for an IR source. There may be a heated sample holder for laboratory emission measurements.

4.3.3.1 *Attenuated Total Reflectance*

ATR or internal reflectance uses an optical element of high RI. This optical element is called the internal reflection element (IRE) or the ATR crystal. Light traveling in a high-RI material is

reflected when it encounters an interface with a material of a lower RI. The amount of light reflected depends upon the angle of incidence at the interface. When the angle of incidence is greater than the *critical angle*, which depends on the ratio of the two RIs, complete reflection of light occurs at the interface (i.e., total internal reflection). If a sample of material, such as a squishy polymer or rubber or a liquid, is placed directly against the IRE, an interface is formed. The light beam traveling in the IRE will be completely reflected at the interface if the critical angle condition is met, but the beam of light actually penetrates a very short distance (generally less than 2 μm) into the lower RI material (in this case, the sample). This penetrating beam is called an **evanescent wave**. If the sample cannot absorb any of the light, all of the intensity is reflected. If the sample can absorb part of the light, the light beam is **attenuated**, that is, reduced in intensity, at the frequencies where the sample absorbs. This is the basis of the ATR sampling technique. A schematic representation of a multiple reflection ATR crystal is shown in Figure 4.21. The interaction of the evanescent wave with the sample essentially provides an IR absorption spectrum of the sample.

The selection of the ATR crystal material for a specific sample analysis depends on the crystal RI, its spectral range, and its chemical and physical properties. The crystal should have a higher index of refraction than the sample. The majority of organic samples have RIs of approximately 1.5. ATR crystals span a range of 2.4–4.0 in RI. If the RI ratio is not appropriate, spectral features may be distorted, with diminished peak symmetries, sharp baseline/peak shoulder transitions, and derivative-like features in the spectrum.

Typical ATR crystal materials are listed in Table 4.6. Samples must be in actual intimate physical contact with the ATR crystal. The first ATR systems were designed to analyze solids that could be pressed against the surface of the crystal: polymers, films, moldable resins, textiles, canvas paintings, and the like. Little or no sample preparation is required. For example, the IR spectrum of a

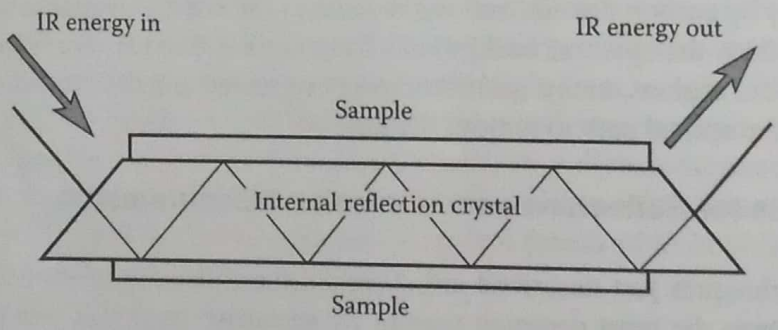


Figure 4.21 Schematic ATR sampling accessory. The internal reflection crystal permits multiple reflections. At each reflection, a small amount of IR energy penetrates the sample, and absorption occurs at the vibrational frequencies for the sample. (Courtesy of Pattacini Associates, LLC, Danbury, CT.)

Table 4.6 Common ATR IRE Materials

Material	Spectral Range (cm^{-1})	RI	Penetration Depth[a] (μm)	Uses
Germanium	5,500–675	4	0.66	Good for most samples; strongly absorbing samples such as dark polymers
Silicon	8,900–1,500	3.4	0.85	Resistant to basic solutions
AMTIR[b]	11,000–725	2.5	1.77	Very resistant to acidic solutions
ZnSe	15,000–650	2.4	2.01	General use
Diamond	30,000–200	2.4	2.01	Good for most samples, extremely caustic or hard samples

Source: © Thermo Fisher Scientific (www.thermofisher.com). Used with permission.
[a] Depth at 45° and 1000 cm^{-1}.
[b] AMTIR is an IR-transparent glass composed of Ge, As, and Se.

valuable painting could be obtained without destroying the painting. This is essential in examining artwork and in other applications such as forensic science, archaeology, and paleontology. Very hard materials such as minerals could not be pressed against traditional ATR crystals because the IRE would be damaged. Designs of ATR probes include cylindrical probes used for analysis of liquids and diamond ATR probes for hard materials. The diamond ATR probes permit analysis of hard, rigid samples and probes with inert diamond tips are available for direct insertion into process streams. The ATR crystal chosen must be chemically and physically compatible with the sample. Some crystal materials may react with certain samples, damaging the crystal and in some cases, producing dangerous side effects. For example, ZnSe cannot be used in acidic solutions, because solutions with pH < 5 will etch the crystal and very strong acids will generate toxic hydrogen selenide. The crystal KRS-5 is not only soft but somewhat soluble in water and should be used only in the pH range of 5–8. Other crystals are susceptible to temperature and pressure changes.

ATR can be used to monitor organic reactions and processing of organic materials. For example, if an ATR probe is put into a mixture of reacting organic compounds, one particular wavelength can be monitored to indicate the disappearance of one of the reactants or the appearance of a product as the reaction proceeds. This eliminates the need to remove samples from the reaction vessel or process line in order to obtain an IR spectrum and permits continuous monitoring of the reaction without disturbing the system. ATR systems are also available with heaters to monitor processes at elevated temperatures and to study reaction kinetics and thermal degradation. Making quality chocolate is an example of a process that can be monitored by ATR at elevated temperature. ATR can be applied to the study of fossils. IR spectra can be obtained from the surface of fossilized plants or animals. The method is nondestructive, and the samples need not be removed from the fossil surface. The method is of particular interest to paleontologists and archeologists. Fossilized leaves, amber, bone, fish, trilobites, teeth, and many other sample types have been examined.

Remote mid-IR probes such as the PIKE FlexIR™ Hollow Waveguide Accessory (Pike Technologies, www.piketech.com) permit *in vivo* studies, such as investigations of chemical diffusion through the skin, residual chemicals on skin from personal care type products, analysis of large painted panels, and similar studies which could not be done in the sampling compartment of an FTIR. The hollow waveguide consists of hollow silica tubing coated on the inside with a highly reflective, smooth Ag/AgI dielectric layer and on the outside with a polymer coating for strength (Figure 4.22a and b). The spectral range spanned by hollow wave guides is from 11,000 to 400 cm^{-1} and remote probes are available for ATR, specular reflectance, and DR measurements. The ATR crystals available are ZnSe, Ge, and diamond/ZnSe composite. As an example, the FlexIR™ ZnSe ATR probe was used to study the effect of sunscreen on skin. Untreated skin measured directly with the probe showed the amide I and amide II bands at 1650 and 1550 cm^{-1}. Spectral subtraction of the untreated skin spectrum from the sunscreen treated skin permitted the residual chemicals from the sunscreen to be studied (Briggs; www.piketech.com).

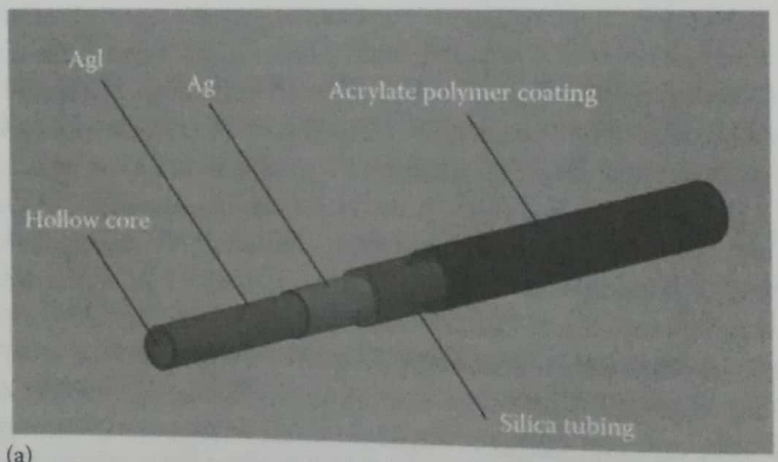
4.3.3.2 *Specular Reflectance*

When light bounces off a smooth polished surface, specular reflection occurs. By specular reflection, we mean that the angle of reflected light is equal to the angle of incident light just as happens with a mirror. Specular reflectance is a nondestructive way to study thin films on smooth, reflective surfaces. The measurement is a combination of absorption and reflection. The IR or NIR beam passes through the thin coating where absorption can occur. The beam is reflected from the polished surface below the coating and then passes through the coating again on its way out. Spectra can be obtained from inorganic and organic coatings from submicrometer to 100 μm in thickness. An angle of incidence of 45° from the normal is typically used for thin films. Ultrathin films, as thin as 20 Å, may be studied using a much larger angle of incidence, such as 80° from normal. This technique is called grazing angle analysis.

The thin films or coatings can be studied nondestructively, with no sample preparation other than deposition on a polished metal surface if necessary. Specular reflectance has been used to study lubricant films on computer disks, oxide layers on metal surfaces, paint curing as a function of time, and molecules adsorbed on surfaces. For example, the IR absorption spectrum of proteins adsorbed onto a polished gold surface can be studied. This spectrum from an adsorbed layer can form the basis of sensors for compounds that will bind to the proteins and change the spectrum. The use of a polarizer in conjunction with grazing angle analysis can provide information about the orientation of molecules adsorbed onto surfaces.

4.3.3.3 Diffuse Reflectance

DR, also called DRIFTS, is a technique used to obtain an IR or NIR spectrum from a rough surface. The rough surface may be a continuous solid, such as a painted surface, fabric, an insect wing or a piece of wood, or it may be a powder that has just been dumped into a sample cup, not pressed into a glassy pellet. The incident light beam interacts with the sample in several modes. Specular reflectance from the surface can occur; this is not desired and samples may need some preparation or dilution with KBr to minimize the specular component. The desired DR occurs by interaction of the incident beam with the sample. Ideally, the beam should penetrate about 100 μm into the sample and the reflected light is scattered at many angles back out of the sample. A large collecting mirror or, for NIR, an integrating sphere is used to collect the scattered radiation.



(a)

(b)

Figure 4.22 (a) Hollow wave guide schematic and (b) mid-IR FlexIR™ with remote probes.

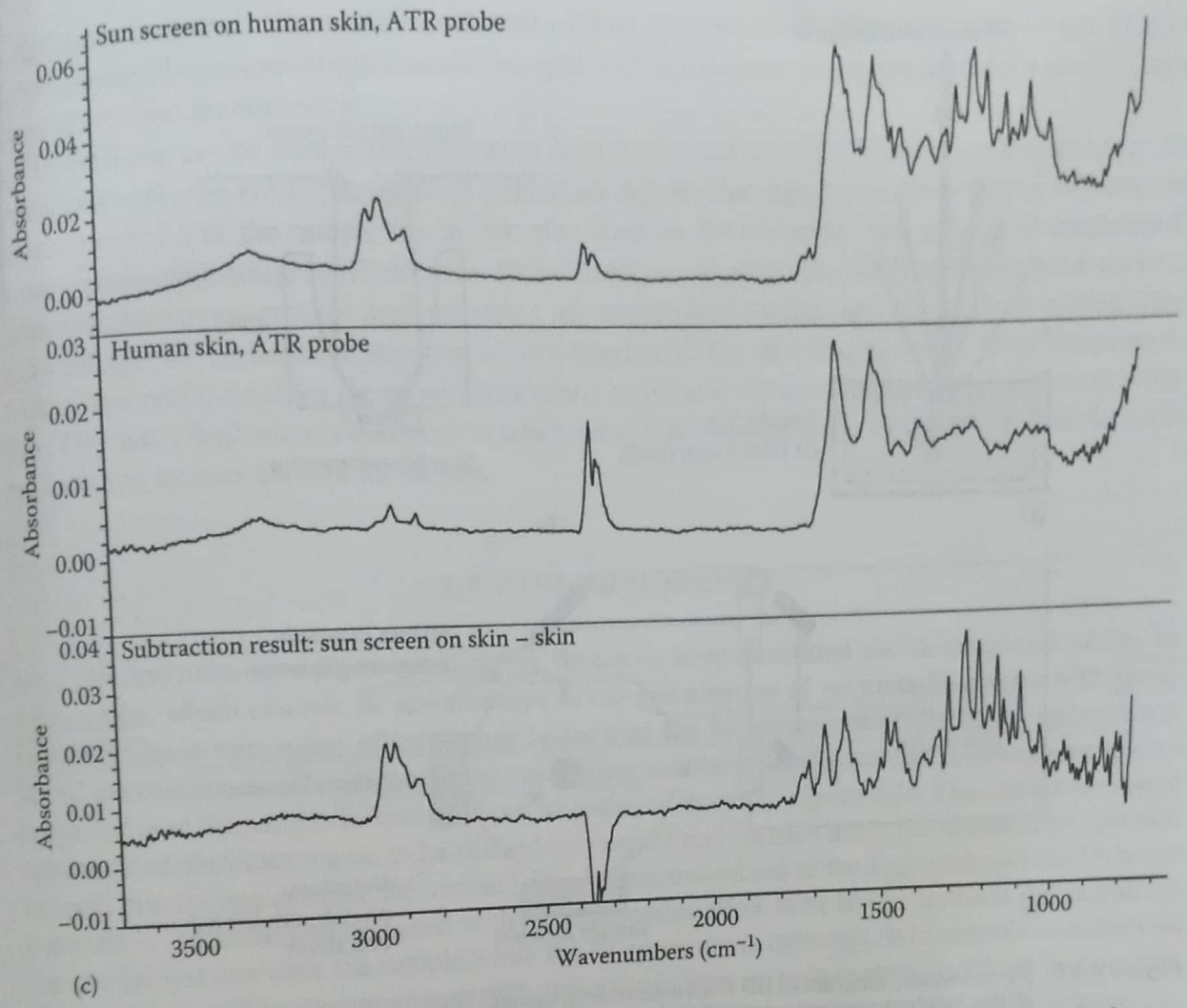


Figure 4.22 (continued) (c) ATR spectra of human skin, skin treated with sunscreen and the result of spectral subtraction of the skin spectrum (middle spectrum) from the top spectrum. (Courtesy of PIKE Technologies, www.piketech.com. Used with permission.)

DRIFTS works very well for powdered samples. The sample powder is generally mixed with loose KBr powder at dilutions of 5%–10% and placed into an open sample cup. A commercial DR arrangement for the mid-IR region is shown in Figure 4.23a and b. Other types of probes, including fiber-optic probes, are available for DR measurements in the NIR region. A commercial IR integrating sphere for NIR DR measurements is diagrammed in Figure 4.23c.

The DR experiment requires that the incident beam penetrate into the sample, but the path length is not well defined. The path length varies inversely with the sample absorptivity. The resulting spectrum is distorted from a fixed path absorbance spectrum and is not useful for quantitative analysis. Application of the Kubelka–Munk equation is a common way of making the spectral response linear with concentration.

The Kubelka–Munk relationship is

$$f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = K'C \tag{4.10}$$

where

R_∞ is the ratio of the sample reflectance spectrum at infinite sample depth to that of a nonabsorbing matrix such as KBr

K' is a proportionality constant

C is the concentration of absorbing species

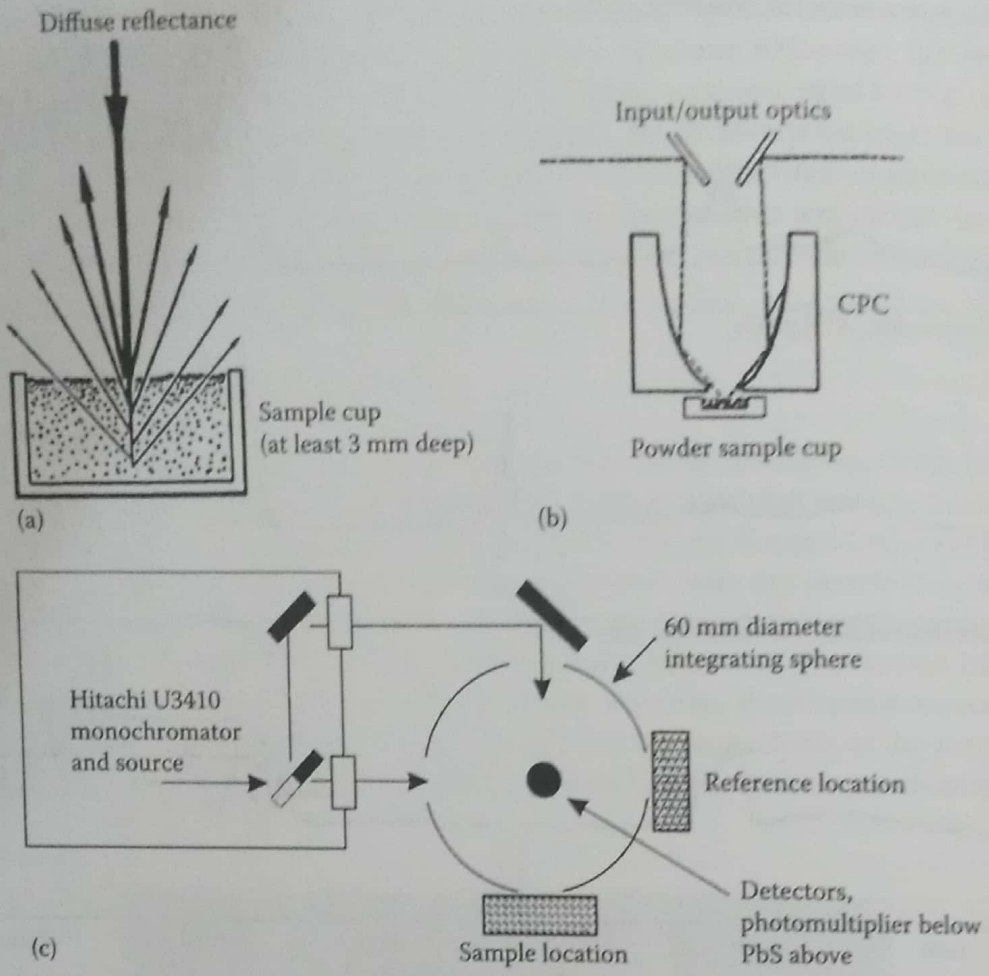


Figure 4.23 (a) Schematic diagram of DR from a powdered sample in a cup, showing the depth of penetration of the incident and reflected beams. Ideally, specular reflectance should be minimized to prevent distortion of the DR spectrum. (From Coates, J., Vibrational spectroscopy, in Ewing, G.W., ed., *Analytical Instrumentation Handbook*, 2nd edn., Marcel Dekker, Inc., New York, 1997. With permission.) (b) A DRIFTS sampling accessory with a compound parabolic concentrator (CPC) design. The CPC design minimizes specular reflection from the sample surface, reduces sample packing and height effects, and avoids damage to the optics from sample spills by placement of the sample below the optics. (© Thermo Fisher Scientific (www.thermofisher.com). Used with permission.) (c) Schematic diagram of an NIR integrating sphere for DR. The sphere is placed in the sample compartment of a dispersive UV/VIS/NIR spectrophotometer. The sphere design permits only DR to reach the detector; the specular component is reflected out through the same opening the light enters. (Courtesy of Hitachi High Technologies America, Inc., Pleasanton, CA, www.hitachi-hhta.com.)

The Kubelka–Munk equation gives absorbance-like results for DR measurements, as can be seen by comparing it to Beer's law, $A = abc = Kc$ for a fixed path length. In Beer's law, K is a proportionality constant based on the absorption coefficient and the path length. K' is also a proportionality constant, but based on the ratio of absorption coefficient to scattering coefficient. The term $f(R_\infty)$ can be considered a "pseudoabsorbance."

4.3.3.4 IR Emission

Some samples are not amenable to transmission/absorption or reflectance spectroscopy. Samples can be characterized by their IR emission spectrum under certain conditions. If the sample molecules are heated, many will occupy excited vibrational states and will emit radiation upon returning to the ground state. The radiation emitted is characteristic of the vibrational levels of the molecule, that is, the IR spectrum, and can be used to identify the emitting sample. The IR emission from the sample is directed into the spectrometer instead of the usual IR light source. Very small

samples can have their IR emission collected with an IR microscope, discussed later in this chapter. Large, physically remote samples can be imaged with a telescope arrangement and the emitted light directed into the spectrometer.

IR emission can be used in the laboratory to study heated samples. Most modern research-grade instruments offer an emission sampling port as an option. One significant advantage of IR emission spectrometry is that the sample can be remote—such as the emission from a flame or smokestack. Some typical applications of IR emission include analysis of gases, remote flames and smokestacks or other hot discharges, process measurements, photochemical studies, and the analysis of thin films and coatings. IR emission measurements are nondestructive and do not suffer from atmospheric background problems since the room temperature water and carbon dioxide in air do not emit radiation. The major limitation is that thick samples cannot be measured due to reabsorption of the emitted radiation by cool parts of the sample.