

Figure 4.11 (Top) A simplified schematic showing the generation of an interferogram from monochromatic light by displacement of the moving mirror. (Modified from Coates, J., *Vibrational spectroscopy*, in Ewing, G.W., ed., *Analytical Instrumentation Handbook*, 2nd edn., Marcel Dekker, Inc., New York, 1997. With permission.) (Bottom) An enlarged view of the signal at the detector as a function of path difference between the moving and fixed mirrors for monochromatic light of wavelength λ . (© Thermo Fisher Scientific (www.thermofisher.com). Used with permission.)

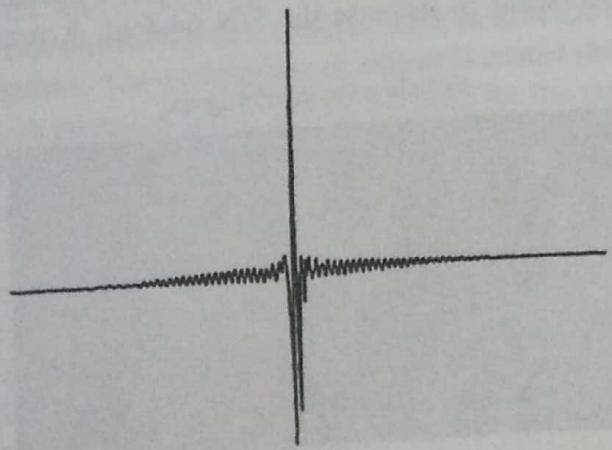


Figure 4.12 An idealized interferogram. (From Coates, J., *Vibrational spectroscopy*, in Ewing, G.W., ed., *Analytical Instrumentation Handbook*, 2nd edn., Marcel Dekker, Inc., New York, 1997. With permission.)

a record of intensity versus time based on the speed of the moving mirror. The spectral information about the sample is obtained from the wings of the interferogram.

If the unique cosine waves can be extracted from the interferogram, the contribution from each wavelength can be obtained. These individual wavelength contributions can be reconstructed to give the spectrum in the frequency domain, that is, the usual spectrum obtained from a dispersive spectrometer. A Fourier transform is used to convert the time-domain spectrum into a frequency-domain spectrum, hence, the term FTIR spectrometer for this type of system.

It is mechanically difficult to move the reflecting mirror at a controlled, known, steady velocity, and position variations due to temperature changes, vibrations, and other environmental effects must be corrected for. The position of the moving mirror must be known accurately. The position and the velocity are controlled by using a helium–neon (He–Ne) laser beam that is directed down the light path producing an interference pattern with itself. The cosine curve of the interference pattern of the laser is used to adjust the moving mirror in real time in many spectrometers. The He–Ne laser is also used to identify the points at which the interferogram is sampled for the FT, as shown schematically in Figure 4.13.

There are a number of advantages to the use of FTIR over dispersive IR. Because the sample is exposed to all source wavelengths at once, all wavelengths are measured simultaneously in less than 1 s. This is known as the *multiplex* or *Fellgett's advantage*, and it greatly increases the sensitivity and accuracy in measuring the wavelengths of absorption maxima. This multiplex advantage permits collection of many spectra from the same sample in a very short time. Many spectra can be averaged, resulting in improved signal-to-noise ratio. An FTIR is considerably more accurate and precise than a monochromator (*Connes' advantage*). Another advantage is that the intensity of the radiation falling on the detector is much greater because there are no slits; large beam apertures are used, resulting in higher energy throughput to the detector. This is called the *throughput* or *Jacquinot's advantage*. Resolution is dependent on the linear movement of the mirror. As the total distance traveled increases, the resolution improves. It is not difficult to obtain a resolution of 0.5 cm^{-1} . A comparison between FTIR and dispersive IR is given in Table 4.4.

The signal-to-noise improvement in FTIR comes about as a result of the multiplex and throughput advantages. These permit a rapid spectrum collection rate. A sample spectrum can be scanned and rescanned many times in a few seconds and the spectra added and averaged electronically. The IR signal (S) accumulated is additive, but the noise level (N) in the signal is random. The S/N ratio therefore increases with the square root of the number of scans (i.e., if 64 scans are accumulated, the S/N ratio increases eight times). FTIR has the potential to be many orders of magnitude more sensitive than dispersive IR. However, in practice, the sheer number of scans necessary to continue to improve the sensitivity limits the improvement. For example, 64 scans improve sensitivity eight times. It would require 4096 scans to increase the S/N 64-fold. A practical limit of one to two

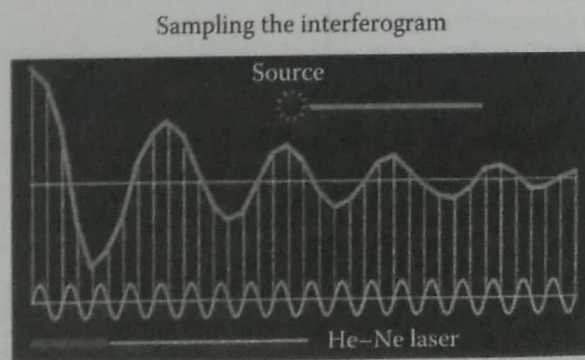


Figure 4.13 Schematic diagram showing how the interferogram is digitized by sampling it at discrete points based on the He–Ne laser signal, shown at the bottom. Each vertical line represents a sampling point. (© Thermo Fisher Scientific (www.thermofisher.com). Used with permission.)

Table 4.4 Comparison of Dispersive IR and FTIR Instruments

Dispersive IR	FTIR
Many moving parts result in mechanical slippage.	Only mirror moves during an experiment.
Calibration against reference spectra required to measure frequency.	Use of laser provides high frequency precision (to 0.01 cm^{-1}) (<i>Connes' advantage</i>).
Stray light within instrument causes spurious readings.	Stray light does not affect detector, since all signals are modulated.
In order to improve resolution, only a small amount of IR beam is allowed to pass through the slits.	Much larger beam aperture used; higher energy throughput (<i>throughput or Jacquinot's advantage</i>).
Only narrow-frequency radiation falls on the detector at any one time.	All frequencies of radiation fall on detector simultaneously; improved S/N ratio obtained quickly (<i>multiplex or Fellgett's advantage</i>).
Slow scan speeds make dispersive instruments too slow for monitoring systems undergoing rapid change (e.g., gas chromatography (GC) effluents).	Rapid scan speeds permit monitoring samples undergoing rapid change.
Sample subject to thermal effects from the source due to length of scan time.	Short scan times; hence, sample is not subject to thermal effects.
Any emission of IR radiation by sample will fall on detector due to the conventional positioning of the sample before the monochromator.	Any emission of IR radiation by sample will not be detected.
Double-beam optics permit continuous real-time background subtraction.	Single-beam optics; background spectrum collected separately in time from sample spectrum. Can result in error if background spectra not collected frequently.

orders of magnitude sensitivity increase is therefore normal unless circumstances merit the additional time. Of course, the ability to process many spectra rapidly is a result of the improvement in computer hardware and software that has occurred over the past decade or so. Inexpensive powerful computers and commercially available user-friendly software allow this technology to be used in undergraduate laboratories as well as in industrial and academic research labs.

4.2.2.2 Interferometer Components

The schematic interferometer diagrams given do not show most of the optics, such as beam collimators and focusing mirrors. Mirrors in an FTIR are generally made of metal. The mirrors are polished on the front surface and may be gold coated to improve corrosion resistance. Commercial FTIRs use a variety of flat and curved mirrors to move light within the spectrometer, to focus the source onto the beam splitter, and to focus light from the sample onto the detector.

The beam splitter can be constructed of a material such as Si or Ge deposited in a thin coating onto an IR-transparent substrate. The germanium or silicon is coated onto the highly polished substrate by vapor deposition. A common beam splitter material for the mid-IR region is germanium and the most common substrate for this region is KBr. Both the substrate and the coating must be optically flat. KBr is an excellent substrate for the mid-IR region because of its transparency and its ability to be polished flat. Its major drawback is that it is hygroscopic; this limits the use of KBr as a substrate for field or process control instruments, where environmental conditions are not as well controlled as laboratory conditions. Germanium on KBr is also used for the long-wavelength end of the NIR region, while Si coated on quartz can be used for the short-wavelength end of the NIR region. A thin film of Mylar is used as a beam splitter for the far-IR region. Other combinations of coatings and substrates are available, including complex multilayer materials, especially for applications where moisture may limit the use of KBr.

Ideally, the beam splitter should split all wavelengths equally, with 50% of the beam being transmitted and 50% reflected. This would result in equal intensity at both the fixed and moving mirrors. Real beam splitters deviate from ideality.

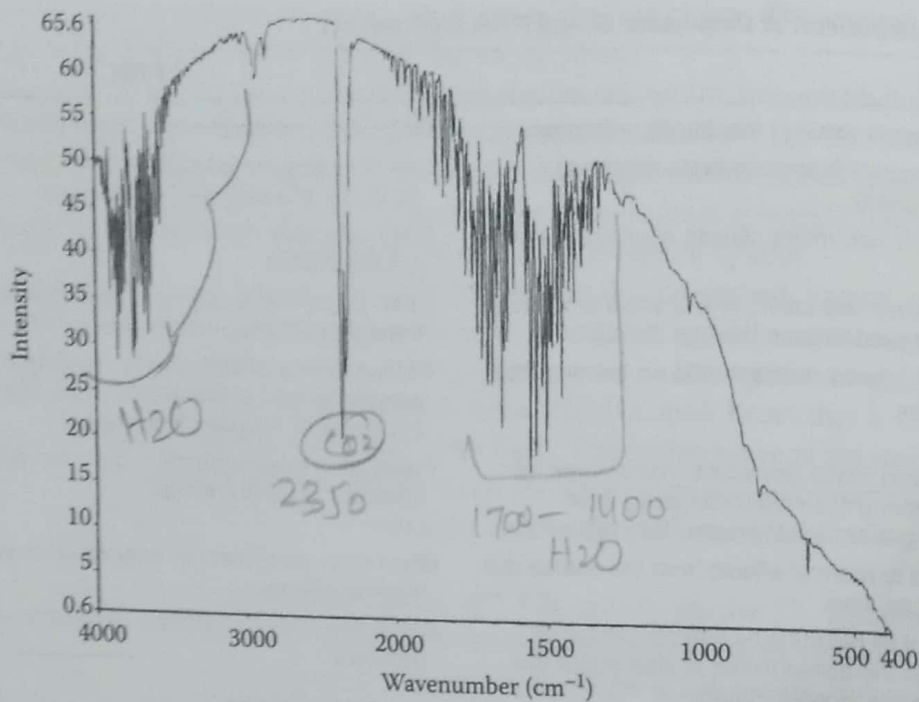


Figure 4.14 A background spectrum of air, showing the absorption bands due to water vapor and carbon dioxide. Collected on a Paragon 1000 FTIR spectrometer. [© 2012–2014 PerkinElmer, Inc. All rights reserved. Printed with permission. (www.perkinelmer.com).]

As noted earlier and discussed subsequently under background correction in IR spectroscopy, CO_2 and H_2O absorb IR radiation (Figure 4.14). To reduce the spectral background from CO_2 and H_2O and increase the light intensity in the regions where these gases absorb, many spectrometers have sealed and desiccated optical systems. Only a small air path in the sample compartment remains. Alternately, some spectrometers allow the optics and the sample path to be purged with dry nitrogen or other dry gas, decreasing the H_2O and CO_2 in the light path.

IR spectrometers must be calibrated for wavelength accuracy. FTIRs are usually calibrated by the manufacturer and checked on installation. Wavelength calibration can be checked by the analyst by taking a spectrum of a thin film of polystyrene, which has well-defined absorption bands across the entire mid-IR region, as seen in Figure 4.1. Polystyrene calibration standard films are generally supplied with an IR instrument or can be purchased from any instrument manufacturer. Recalibration of the spectrometer should be left to the instrument service engineer if required.

✓ 4.2.3 Detectors

Detectors for IR radiation fall into two classes: thermal detectors and photon-sensitive detectors. Thermal detectors include *thermocouples*, *bolometers*, *thermistors*, and *pyroelectric* devices. Thermal detectors tend to be slower in response than photon-sensitive semiconductors. The most common types of detectors used in dispersive IR spectroscopy were bolometers, thermocouples, and thermistors, but faster detectors are required for FTIR. FTIR relies on pyroelectric and photon-sensitive semiconducting detectors. Table 4.5 summarizes the wavenumber ranges covered by commonly used detectors.

✓ 4.2.3.1 Bolometer

A bolometer is a very sensitive electrical-resistance thermometer that is used to detect and measure weak thermal radiation. Consequently, it is especially well suited as an IR detector. The bolometer used in older instruments consisted of a thin metal conductor, such as platinum wire.

Table 4.5 Detectors for IR Spectroscopy

NIR (12,000–3,800 cm^{-1} ; 0.8 μm)	Mid-IR (4,000–400 cm^{-1} ; 2.5–25 μm)	Far-IR (400–20 cm^{-1} ; 25–500 μm)
InGaAs (12,000–6,000 cm^{-1})		
PbSe (11,000–2,000 cm^{-1})		
InSb (11,500–1,850 cm^{-1})		
mercury cadmium telluride (MCT) (11,700–400 cm^{-1})	MCT (11,700–400 cm^{-1})	
DTGS/KBr (12,000–350 cm^{-1})	DTGS/KBr (12,000–350 cm^{-1})	
	Photoacoustic (10,000–400 cm^{-1})	
	DTGS/CsI (6,400–200 cm^{-1})	
		DTGS/PE (700–50 cm^{-1})
		Si bolometer (600–20 cm^{-1})

Source: © Thermo Fisher Scientific (www.thermofisher.com). Used with permission.

Note: KBr, CsI, and PE (polyethylene) are the window materials for the DTGS detectors. The MCT detector can vary in its spectral range depending on the stoichiometry of the material.

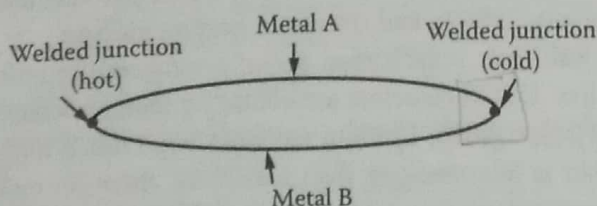
Incident IR radiation heats up this conductor, which causes its electrical resistance to change. The degree of change of the conductor's resistance is a measure of the amount of radiation that has fallen on the detector. In the case of platinum, the resistance change is $0.4\%/^{\circ}\text{C}$. The change in temperature depends on the intensity of incident radiation and on the thermal capacity of the detector. It is important to use a small detector and to focus the radiation on it. The rate at which the detector heats up or cools down determines how fast the detector responds to a change in radiation intensity as experienced when an absorption band is recorded. This constitutes the response time of the detector. For these older types of bolometers, the response time is long, on the order of seconds. Consequently, a complete mid-IR scan using a dispersive instrument and bolometer could take 20 min.

Modern bolometers are micromachined from silicon. This type of bolometer is only a few micrometers in diameter and is usually placed in one arm of a Wheatstone bridge for measurements. The modern microbolometer has a fast response time and is particularly useful for detecting far-IR radiation ($600\text{--}20\text{ cm}^{-1}$).

4.2.3.2 Thermocouples

A thermocouple is made by welding together at each end two wires made from different metals (Figure 4.15). If one welded joint (called the hot junction) becomes hotter than the other joint (the cold junction), a small electrical potential develops between the joints. In IR spectroscopy, the cold junction is carefully screened in a protective box and kept at a constant temperature. The hot junction is exposed to the IR radiation, which increases the temperature of the junction. The potential difference generated in the wires is a function of the temperature difference between the junctions and, therefore, of the intensity of IR radiation falling on the hot junction. The response time of the thermocouple detector is slow; thermocouples cannot be used as detectors for FTIR due to their slow response.

Drawback:-



$P \cdot d/t \rightarrow \Delta T$ in 2 junctions
 \downarrow
 I of falling radiations

Figure 4.15 Schematic diagram of a thermocouple.

4.2.3.3 Thermistors

A thermistor is made of a fused mixture of metal oxides. As the temperature of the thermistor increases, its electrical resistance decreases (as opposed to the bolometer). This relationship between temperature and electrical resistance allows thermistors to be used as IR detectors in the same way as bolometers. The thermistor typically changes resistance by about 5% per °C. Its response time is also slow.

4.2.3.4 Golay Detector

The Golay detector was a pneumatic detector, a small hollow cell filled with a nonabsorbing gas such as xenon. In the center of the cell was a blackened film. Radiation was absorbed by the blackened film, causing an increase in temperature. In turn, the film heated the enclosed gas. Thermal expansion of the gas caused the internal pressure of the cell to increase. One wall of the cell was a thin convex mirror that was part of the optical system. As the pressure inside the cell increased, the mirror bulged. A change in radiation intensity falling on the Golay detector caused a change in the readout from the detector. An important advantage of this detector was that its useful wavelength range was very wide. The response was linear over the entire range from the UV through the visible and IR into the microwave range to wavelengths as long as 7.0 mm. The Golay detector's response time was about 10^{-2} s, much faster than that of the bolometer, thermistor, or thermocouple. The detector was very fragile and subject to mechanical failure. While this detector is no longer in use as an IR detector, a variation of the Golay detector, the photoacoustic detector, is used in photoacoustic spectroscopy, discussed later in this chapter.

4.2.3.5 Pyroelectric Detectors

Pyroelectric materials change their electric polarization as a function of temperature. These materials may be insulators (dielectrics), ferroelectric materials, or semiconductors. A dielectric placed in an electrostatic field becomes polarized with the magnitude of the induced polarization depending on the dielectric constant. The induced polarization generally disappears when the field is removed. Pyroelectric materials, however, stay polarized and the polarization is temperature dependent.

A pyroelectric detector consists of a thin single crystal of pyroelectric material placed between two electrodes. It acts as a temperature-dependent capacitor. Upon exposure to IR radiation, the temperature and the polarization of the crystal change. The change in polarization is detected as a current in the circuit connecting the electrodes. The signal depends on the rate of change of polarization with temperature and the surface area of the crystal. These crystals are small; they vary in size from about 0.25 to 12.0 mm².

The most common pyroelectric material in use as an IR detector is DTGS. The formula for triglycine sulfate is $(\text{NH}_2\text{CH}_2\text{COOH})_3 \cdot \text{H}_2\text{SO}_4$; replacement of hydrogen with deuterium gives DTGS. DTGS with a cesium iodide window covers the 6400–200 cm^{-1} range, which includes part of the NIR, all of the mid-IR, and some of the far-IR regions. With the use of a polyethylene window, a DTGS detector can be used as a far-IR detector (700–50 cm^{-1}). Other pyroelectric detectors for the mid-IR region include lithium tantalate, LiTaO_3 , and strontium barium niobate.

Pyroelectric materials lose their polarization above a temperature called their Curie point. For DTGS, this temperature is low. DTGS detectors are cooled by thermoelectric cooling to between 20°C and 30°C to prevent loss of polarization. Lithium tantalate has a much higher Curie temperature and does not require cooling, but is less sensitive than DTGS by about an order of magnitude. Lithium tantalate has a high linear response range, unlike DTGS. DTGS does not respond linearly over the IR frequency range. Its response is inversely proportional to the modulation frequency of the source, resulting in lower sensitivity at the high-frequency end of the spectral range than at the low-frequency end.

4.2.3.6 Photon Detectors

Semiconductors are materials that are insulators when no radiation falls on them but become conductors when radiation falls on them. Exposure to radiation causes a very rapid change in their electrical resistance and therefore a very rapid response to the IR signal. The response time of a semiconductor detector is the time required to change the semiconductor from an insulator to a conductor, which is frequently as short as 1 ns. The basic concept behind this system is that absorption of an IR photon raises an electron in the detector material from the valence band of the semiconductor across a band gap into the conduction band, changing its conductivity greatly. In order to do this, the photon must have sufficient energy to displace the electron. IR photons have less energy than UV or visible photons. The semiconductors chosen as IR detectors must have band gaps of the appropriate energy. The band gap of the detector material determines the longest wavelength (lowest wavenumber) that can be detected.

Materials such as lead selenide (PbSe), indium antimonide (InSb), indium gallium arsenide (InGaAs), and mercury cadmium telluride (HgCdTe, also called MCT) are intrinsic semiconductors commonly used as detectors in the NIR and mid-IR regions. Cooling of these detectors is required for operation. MCT requires operation at 77 K and must be cooled with liquid nitrogen; other detectors such as InGaAs can operate without cooling but show improved S/N if cooled to -30°C or so with thermoelectric cooling. For the far-IR region, extrinsic semiconductors such as Si and Ge doped with low levels of copper, mercury, or other dopants are used. The dopants provide the electrons for conductivity and control the response range of the detector. These doped germanium or silicon detectors must be cooled in liquid helium but are sensitive to radiation with wavelengths as long as 200 μm. The spectral response curves of some semiconductor detectors are shown in Figure 4.16. The MCT material used is nonstoichiometric and can be represented as $Hg_{(1-x)}Cd_xTe$. The actual spectral range of an MCT detector can be varied by varying the Hg/Cd ratio.

Semiconductor detectors are very sensitive and very fast. The fast response time has permitted rapid-scan IR to become a reality, as is needed in FT spectrometers and coupled techniques such as GC-IR that generate transient peaks. The sensitivity of these detectors has opened up the field of microsampling, IR microscopy, and online IR systems for process control.

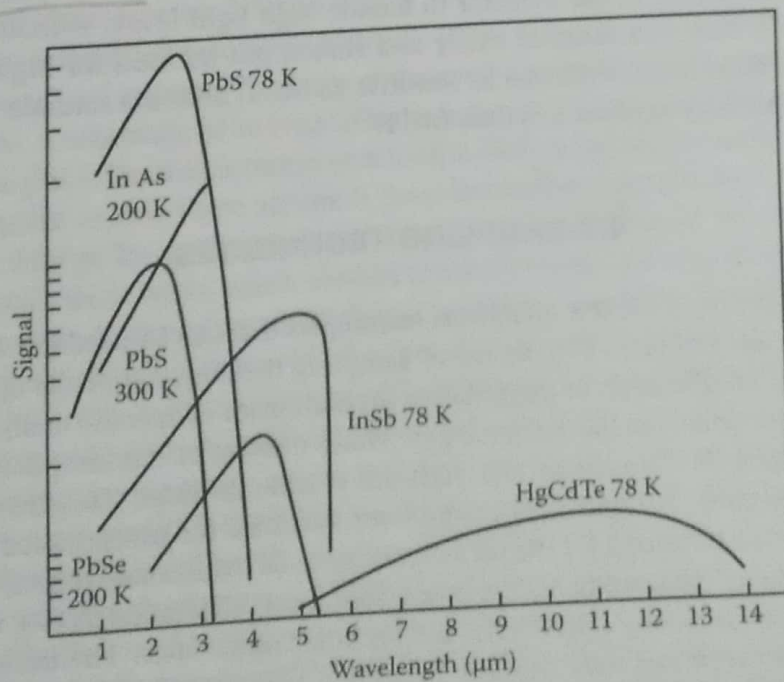


Figure 4.16 Spectral response of various semiconductor detectors. The operating temperature in kelvin is given next to the material.

4.2.4 Detector Response Time

The length of time that a detector takes to reach a steady signal when radiation falls on it is called its *response time*. This varies greatly with the type of detector used and has a significant influence on the design of the IR instrument. Thermal detectors such as thermocouples, thermistors, and bolometers have very slow response times, on the order of seconds. Consequently, when a spectrum is being scanned, it takes several seconds for the detector to reach an equilibrium point and thus give a true reading of the radiation intensity falling on it. If the detector is not exposed to the light long enough, it will not reach equilibrium and an incorrect absorption trace will be obtained. It was normal for dispersive IR instruments with older-style thermal detectors to take on the order of 15 min to complete an IR scan. Attempts to decrease this time resulted in errors in the intensity of the absorption bands and recording of distorted shapes of the bands.

The slow response time of thermal detectors is due to the fact that the detector temperature must change in order to generate the signal to be measured. When there is a change in radiation intensity, the temperature at first changes fairly rapidly, but as the system approaches equilibrium, the change in temperature becomes slower and slower and would take an infinitely long time to reach the true equilibrium temperature. It should also be remembered that when an absorption band is reached, the intensity falling on the detector decreases and the response depends on how fast the detector cools.

Semiconductors operate on a different principle. When radiation falls on them, they change from a nonconductor to a conductor. No temperature change is involved in the process; only the change in electrical resistance is important. This takes place over an extremely short period of time. Response times of the order of nanoseconds are common. This enables instruments to be designed with very short scanning times. It is possible to complete the scan in a few seconds using such detectors. These kinds of instruments are very valuable when put onto the end of a GC and used to obtain the IR spectra of the effluents. Such scans must be made in a few seconds and be completely recorded before the next component emerges from the GC column.

Response time is not the only detector characteristic that must be considered. Linearity is very important in the mid-IR region where wide variations in light intensity occur as a result of absorption by a sample. The ability of the detector to handle high light levels without saturating is also important. The MCT detectors saturate easily and should not be used for high-intensity applications; DTGS, on the other hand, while not as sensitive as MCT, does not saturate readily. DTGS can be used for higher intensity applications than MCT.

4.3 SAMPLING TECHNIQUES

IR spectroscopy is one of the few analytical techniques that can be used for the characterization of solid, liquid, and gas samples. The choice of sampling technique depends upon the goal of the analysis, qualitative identification, or quantitative measurement of specific analytes, upon the sample size available, and upon sample composition. Water content of the sample is a major concern, since the most common IR-transparent materials are soluble in water. Samples in different phases must be treated differently. Sampling techniques are available for transmission (absorption) measurements and, since the advent of FTIR, for several types of reflectance (reflection) measurements. The common reflectance measurements are attenuated total reflectance (ATR), diffuse reflectance (DR) or DR-IR-FT spectroscopy (DRIFTS), and specular reflectance. The term reflection may be used in place of reflectance and may be more accurate; specular reflection is actually what occurs in that measurement, for example. However, the term reflectance is widely used in the literature and will be used here.

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. Substantial sample preparation may be required.

The sample and 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 Figure 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, 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.

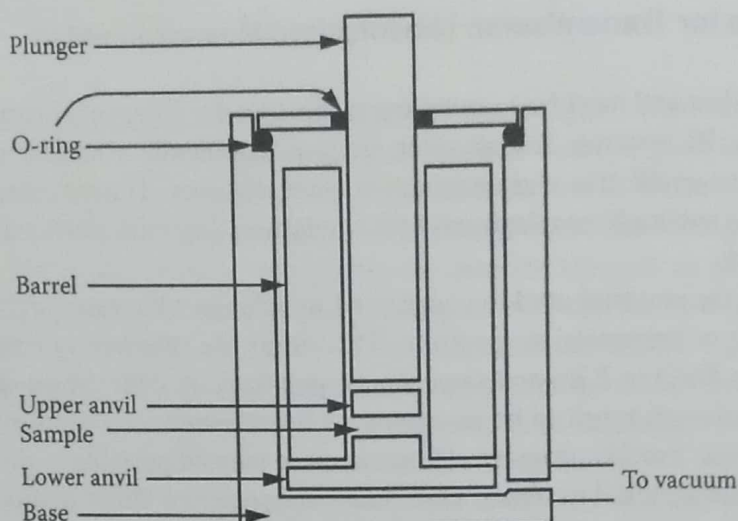


Figure 4.17 Schematic drawing of a typical IR pellet die showing the arrangement of the major components. (Reprinted from Aikens, D.A. et al., *Principles and Techniques for an Integrated Chemistry Laboratory*, Waveland Press, Inc., Prospect Heights, IL, 1978, Reissued 1984. All rights reserved. With permission.)

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