4.4 FTIR MICROSCOPY

FTIR instruments with sensitive MCT detectors have permitted the development of the IR microscope, which extends IR spectroscopy to the examination of very small samples with detection limits up to two orders of magnitude better than can be achieved with dispersive instruments. An IR microscope uses two light beams, one visible and the other IR, that travel through the microscope optics to the sample following identical paths, as shown in Figure 4.24. The sample is viewed optically and the exact region to be studied is centered and focused using the microscope controls. In some microscope designs, the visible beam is then moved out of the light path and the IR beam is moved in. Microscopes designed with dichroic optics allow both beams to reach the sample so that the analyst can view the sample while the IR spectrum is collected. It is possible to collect an IR spectrum in either transmission or reflectance mode from an area as small as 10 μm in diameter. The IR signal from the sample passes to a dedicated MCT detector designed for small samples.
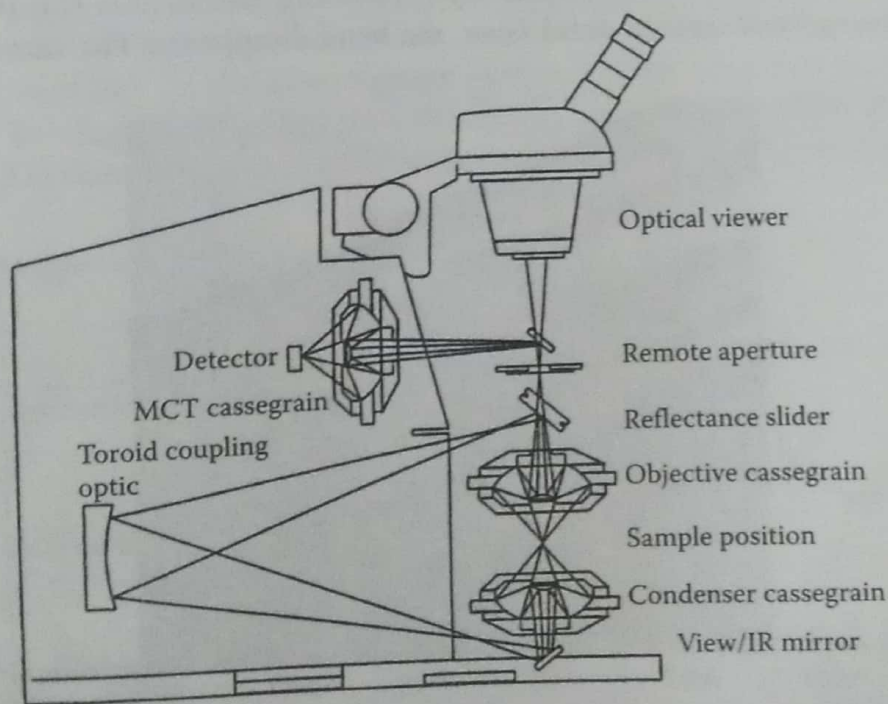

Figure 4.24 IR microscope schematic with the detector integrated into the microscope. The microscope is usually coupled to a light port on the side of the FTIR spectrometer. The FTIR spectrometer supplies a modulated, collimated beam of light to the microscope. [© 1997–2014 PerkinElmer, Inc. All rights reserved. Printed with permission. (www.perkinelmer.com).]

To obtain a transmission spectrum, the sample must be prepared. A microtome is used for cutting a very thin slice of the sample through which radiation can penetrate. Sample thickness must be in the range of 15 μm and the sample must be flat. The quality of the spectrum depends on the sample preparation. All of the reflectance modes are available for microscopy, including ATR and grazing angle analysis. These generally require little or no sample preparation. The sensitivity obtainable is subnanogram quantities of analyte.

Modern FTIR microscopes are available with computer-controlled microscope stages and video imaging systems that permit a 2D picture of the sample to be displayed, and areas containing a specified functional group to be highlighted using "false color" to show differences in composition with respect to position in the sample. Microscopes are available that allow the use of polarized light for imaging and that can obtain fluorescence images. These are useful to improve the contrast in samples that lack features under normal illumination.

A prime example of the use of FTIR microscopy is in the examination of polymers, a very important class of engineering materials. The physical properties of polymers are very dependent on their molecular structure. The presence of impurities, residual monomers, degree of crystallinity, size, and orientation of crystalline regions (the microstructure of a polymer) greatly affects their mechanical behavior. FTIR microscopy can identify polymers and additives and determine the presence of impurities.

Food-packaging materials may be made up of several layers of different polymers, called a laminate, to provide a single plastic sheet with the desired properties. Typical layers are between 10 and 200 μm thick. Using an automated FTIR microscope, it is possible to obtain acceptable spectra from each layer and identify the polymers involved. As an example, a cross section of a polymer laminate, compressed between NaCl plates, is shown in Figure 4.25. Three layers were seen under magnification. The sample was moved in a straight line, as shown, and IR spectra were collected every 2 μm across the sample. The spectra collected from the laminate can be displayed in a variety of formats, such as the "waterfall display" presented in Figure 4.26. This display gives the analyst a very clear picture of the differences in the three layers. If we look at the band on the left, between 3200 and 3400 cm^{-1}, we see that it is high in the layer plotted at the front of the display and as we move back (along the sample), we reach the thin middle layer. Note that the band is still there but much less intense. Then, moving back into the third layer, the band disappears. The same thing happens to
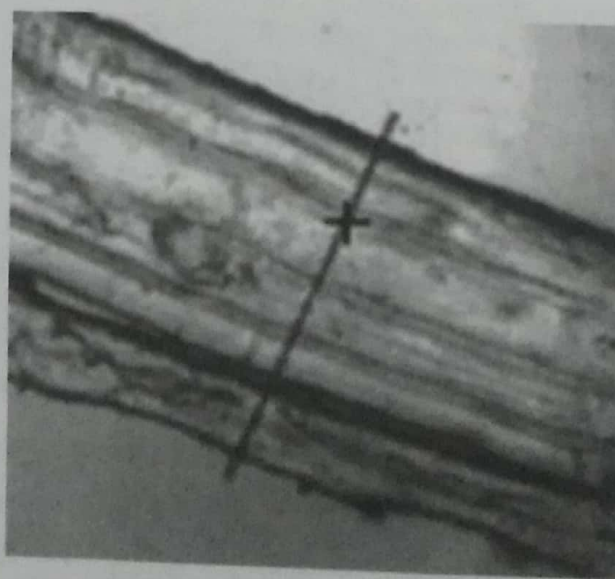

Figure 4.25 Micrograph of a polymer laminate, showing two broad layers and a narrow middle layer. The sample was mounted in a NaCl compression cell and spectra were collected automatically in 2 μm steps along the line indicated. A Centaurμs Analytical FTIR Microscope System from Thermo Fisher Scientific was used for the automatic data collection and results. (© Thermo Fisher Scientific (www.thermofisher.com). Used with permission.)
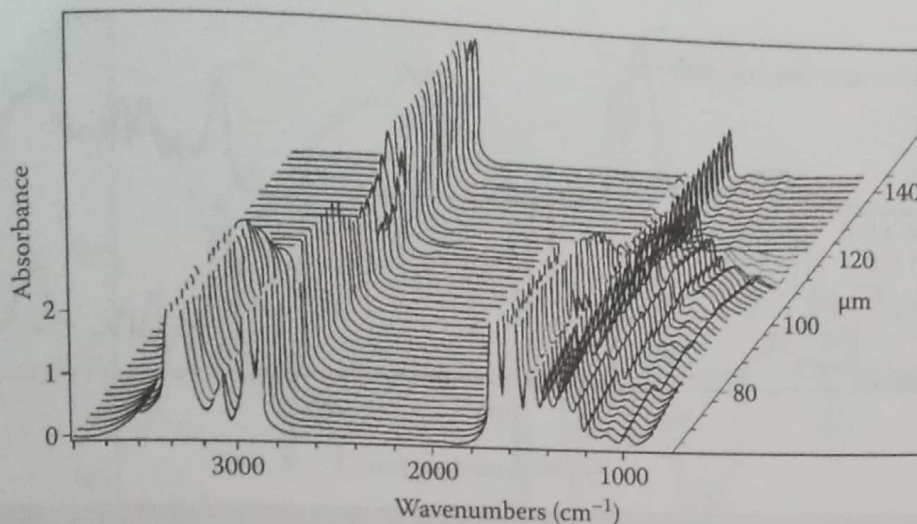
Figure 4.26 The spectra collected from the polymer laminate are displayed as a function of position along the sample, in a "waterfall display." The chemical differences in the layers are clearly seen. For example, the top layer has a large broad peak at about 3400 cm⁻¹ (the peak on the far left); that peak disappears as the middle and bottom layers are scanned. (© Thermo Fisher Scientific (www.thermofisher.com). Used with permission.)

the intense band at about 1700 cm⁻¹. Three distinct IR spectra were obtained, one from each layer (Figure 4.27). The front layer was identified as a polyamide polymer by matching its spectrum to a known spectrum. The back layer is identified as polyethylene—note that this spectrum does not show the bands seen in the polyamide spectrum at 3400 and 1700 cm⁻¹. The middle layer was not immediately identified. A search of a computerized IR spectral library matched the spectrum of the middle layer to a urethane alkyd, as shown in Figure 4.28. Figure 4.28 shows what a spectral search routine does—it picks a series of possible "fits" to the unknown from its database and assigns a goodness-of-fit or match number. In this case, the urethane alkyd spectrum has the highest match number, 77, of the spectra in this database.

In forensic science, FTIR microscopy has been used extensively. Rapid chemical imaging of documents and paper currency allows an analyst to distinguish between various inks and the paper itself using ATR mode, which minimizes absorption from cellulose, enabling identification of counterfeit currency. In addition, modern currency often has small security fibers in the paper. These can be visually identified and chemically imaged to confirm authenticity. FTIR microscopy is used to examine paint chips from automobile accidents. An example of a paint chip
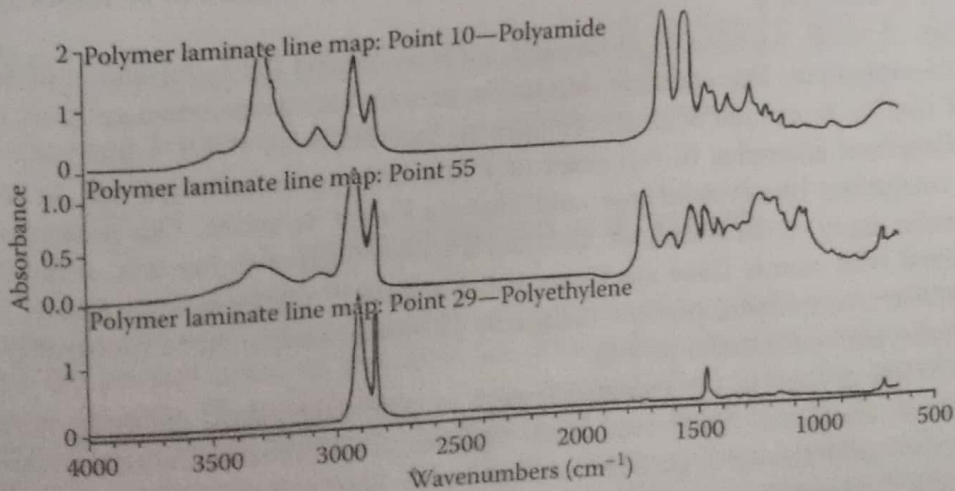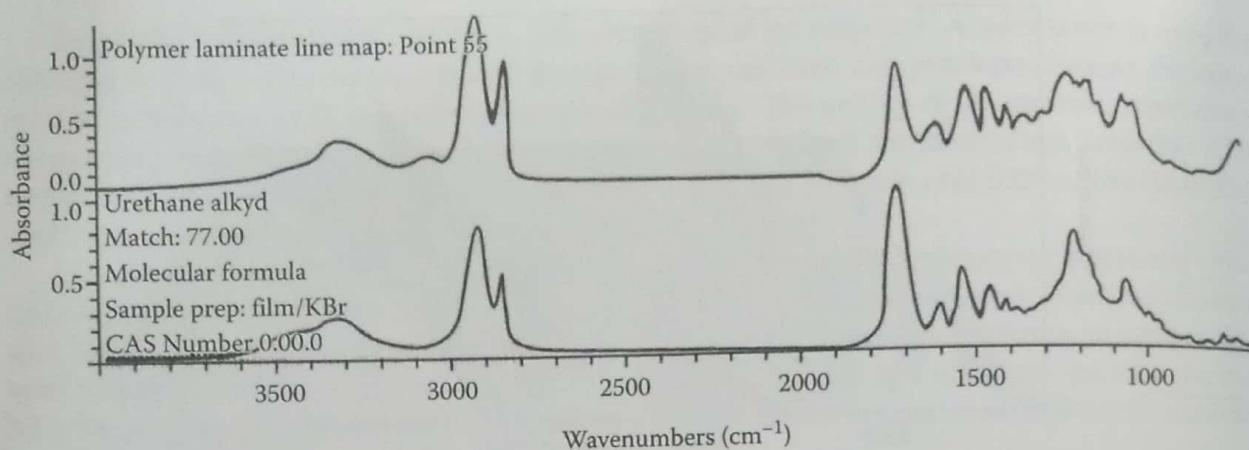

Figure 4.27 One spectrum from each layer is displayed. The spectrum from the top layer matches that of a polyamide; that on the bottom is the spectrum of polyethylene. The middle spectrum has not yet been identified. (© Thermo Fisher Scientific (www.thermofisher.com). Used with permission.)

Index	Match	Compound Name	Library Name
1 175	77.00	Urethane alkyd	HR Hummel Polymer and Additives
2 1767	76.48	PENTAERYTHRITOL MONORICINOLEATE #2	HR Polymer Additives and Plasticizers
3 1768	76.16	PENTAERYTHRITOL TETRARICINOLEATE	HR Polymer Additives and Plasticizers
4 1597	75.35	PROPYLENE GLYCOL MONOOLEATE	HR Polymer Additives and Plasticizers
5 1769	74.91	PROPYLENE GLYCOL MONORICINOLEATE	HR Polymer Additives and Plasticizers

Figure 4.28 The results of a library search of the spectrum from the middle layer of the laminate. The top spectrum is that collected from the sample; the bottom spectrum, urethane alkyd, is the best match found in the search of a polymer database. Other possible compounds are suggested by the search routine and listed in the box below the spectra. Note the match number—the higher the number, the better the agreement between the sample spectrum and the library spectrum. (© Thermo Fisher Scientific (www.thermofisher.com). Used with permission.)

spectrum is shown in Figure 4.29. The spectral region below 1000 cm^{-1} is where pigments absorb. Hit-and-run drivers frequently leave traces of paint on cars, structures, and victims with which they collide. Identification of the paint can help to identify the car. Both transmission and ATR sampling can be used in conjunction with optical microscopy and FTIR imaging. A typical paint chip will have layers of coatings, base coat, and binder, as well as possibly the substrate (plastic, fiberglass). In a real case, a jogger was intentionally struck by a car and killed. The driver of the car was convicted of murder based on the FTIR microscopy data from a tiny paint chip found on the victim's clothing. The tiny sample from the victim and a sample of paint from the car were mounted in paraffin and cross sectioned with a microtome. IR spectra were collected from five layers in each paint sample. Based on the data, the paints were shown to be identical and the hit and run driver found guilty.

Other uses of an IR microscope in forensic analysis include the examination of fibers, drugs, and traces of explosives. For example, oxidation of hair can occur chemically or by sunlight; oxidation of cystine to cysteic acid can be seen in hair fibers by FTIR microscopy (Robotham and Izzia). Excellent examples in full color of FTIR imaging microscopy can be found on the websites of companies like PerkinElmer and Thermo Fisher Scientific. Our limitations in use of gray scale make many of the examples unsuited for reproduction in the text. A novel IR microscope combined with atomic force microscopy, the nanoIR™ platform from Anasys Instruments (www.anasysinstruments.com), permits nanoscale IR spectroscopy, AFM topography, nanoscale thermal analysis, and mechanical testing.

IR microscopy is used in the characterization of pharmaceuticals, catalysts, minerals, gemstones, adhesives, composites, processed metal surfaces, semiconductor materials, fossils, and artwork. Biological samples such as plant leaves and stems, animal tissue, cells, and similar samples can be imaged. Frequently, such information cannot be obtained by any other means. A microscope that combines both IR and Raman measurements will be discussed in the section on Raman spectroscopy.
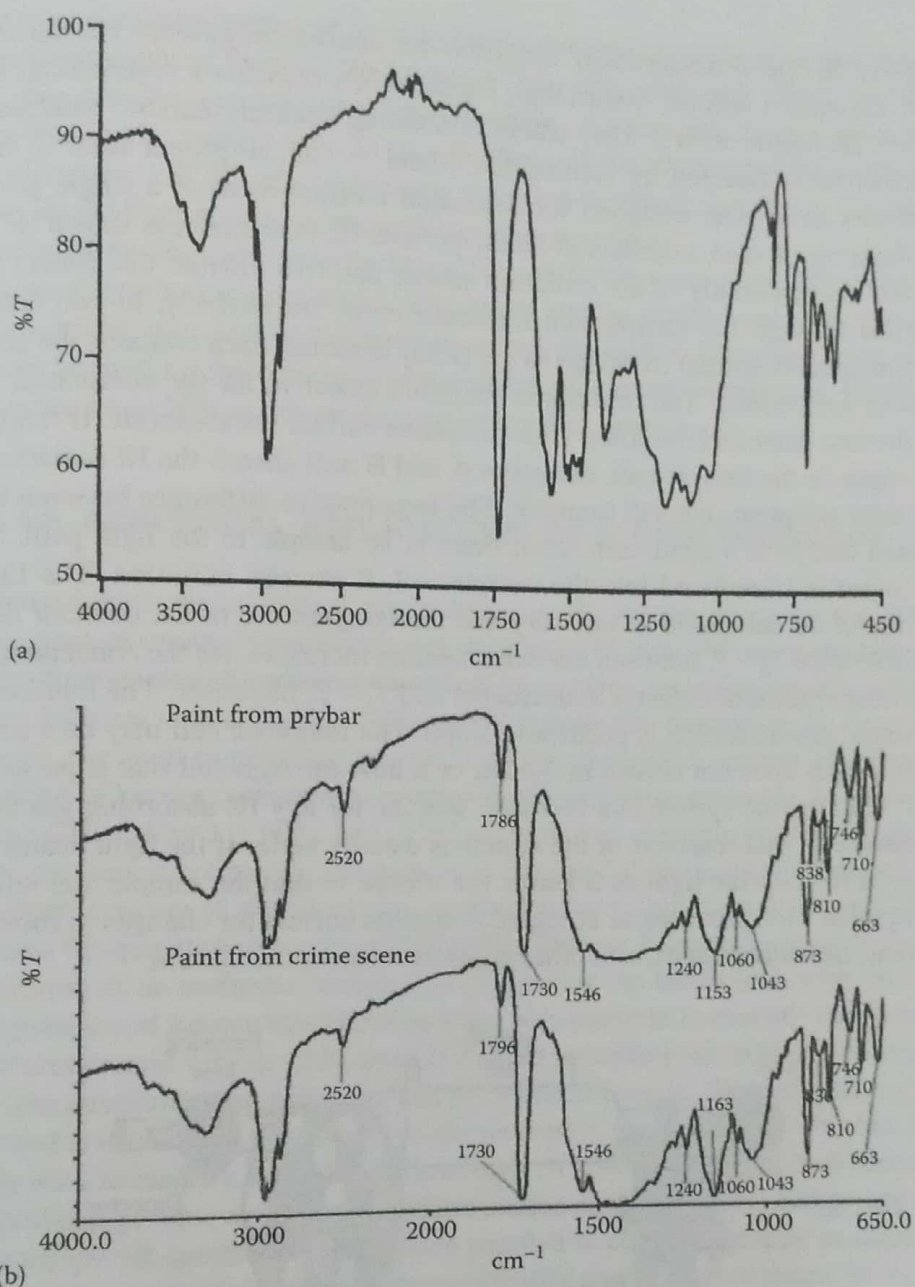
Figure 4.29 (a) Transmission spectrum of a blue paint chip from an American car measured using a miniature diamond anvil cell. (b) Comparison of microscopic paint chips taken from a crowbar and compared to paint from a window at the site of a burglary. [© 2000–2014 PerkinElmer, Inc. All rights reserved. Printed with permission. (www.perkinelmer.com).]

4.5 NONDISPERSIVE IR SYSTEMS

In industry, it is often necessary to monitor the quality of a product on a continuous basis to make certain the product meets its specifications. This online, real-time approach to analysis is called **process analysis**. IR spectroscopy is often the method of choice for process monitoring of organic chemical, polymer, and gas production. It is usually not feasible to use laboratory IR instruments under production conditions because they are too delicate, too big, and too expensive. Nondispersive systems have therefore been developed that are much sturdier and can be left running continuously. Many nondispersive systems have been designed for the NIR region. These will be discussed in Section 4.7. The mid-IR region is used mainly for monitoring gas streams.

Nondispersive IR spectrometers may use filters for analysis of gaseous substances. Each filter is designed to measure a specific compound. Figure 4.30a presents a commercial filter photometer for the mid-IR region with a filter wheel containing multiple narrow bandpass filters. The compound measured is selected by turning the wheel to put the proper filter in the light path. Other photometers have been designed for dedicated measurement of a single gaseous species. A schematic diagram of such a dedicated nondispersive IR instrument is shown in Figure 4.30b. The system consists essentially of the radiation source and two mirrors that reflect two beams of light, which pass through the sample and reference cells, respectively, to two detectors. These detectors are transducers similar in design to the Golay detector; each contains the gas phase of the compound being determined. The detector is therefore selective for the compound. For example, imagine that the two detectors are filled with gas-phase carbon tetrachloride. If there is no carbon tetrachloride vapor in the sample call, detectors A and B will absorb the IR radiation equally and consequently their temperatures will increase. The temperature difference between the two detectors is measured and is at a minimum when there is no sample in the light path. When carbon tetrachloride vapor is introduced into the sample cell, it absorbs radiation. The light falling on detector A is therefore decreased in intensity and the temperature of the detector decreases. The temperature difference $T_2 - T_1$ between the two detectors increases. As the concentration of sample increases, the temperature of detector A decreases and $T_2 - T_1$ increases. The relationship between $T_2 - T_1$ and sample concentration is positive in slope. The reference cell may be a sealed cell containing N_2 gas, which does not absorb in the IR, or a flow-through cell that is purged with a non-absorbing gas. Clearly, the system can be made specific for any IR-absorbing gas by putting that vapor in the detectors. The response of the system is usually better if the light beams are chopped, and it is common to chop the light as it leaves the source so that the sample and reference beams are chopped equally. This provides an ac signal that helps correct for changes in room temperature during operation, instrument drift, and other types of noise in the system.
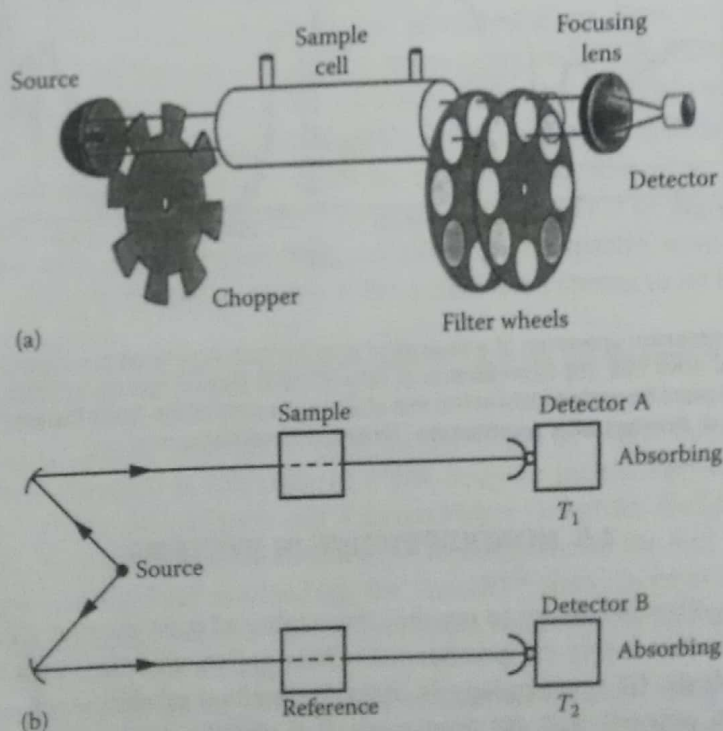

Figure 4.30 (a) Schematic of a two-filter wheel, multiwavelength filter photometer. (From Coates, J., Vibrational spectroscopy, in Ewing, G.W., ed., Analytical Instrumentation Handbook, 2nd edn., Marcel Dekker, Inc., New York, 1997. With permission.) (b) Schematic of a positive-filter nondispersive IR system.

A problem may be encountered if an interfering material is present in the sample that has absorption bands overlapping those of the sample. This will result in a direct interference in the measurement. The problem can be overcome by placing a cell containing a pure sample of the interfering material in the sample arm. In this fashion, all the absorbable radiation at a common wavelength is absorbed, and this eliminates any variation in absorption due to the impurity in the sample because all the light at this wavelength has been removed.

Nondispersive IR systems are good for measuring concentrations of specific compounds under industrial and other similar circumstances. As can be readily understood, they are not generally used as research instruments and do not have scanning capabilities. However, they are robust and enduring and can be used for the continuous monitoring of specific compounds. Nondispersive systems are very common in NIR applications, as discussed in Section 4.7.

4.6 ANALYTICAL APPLICATIONS OF IR SPECTROSCOPY

The two most important analytical applications of IR spectroscopy are the qualitative and quantitative analyses of organic compounds and mixtures. We pointed out at the beginning of this chapter that the frequencies of radiation absorbed by a given molecule are characteristic of the molecule. Since different molecules have different IR spectra that depend on the structure and mass of the component atoms, it is possible, by matching the absorption spectra of unknown samples with the IR spectra of known compounds, to identify the unknown molecule. Moreover, functional groups, such as $-CH_3$, $-C=O$, $-NH_2$, and $-OH$, act almost as separate groups and have characteristic absorption frequencies relatively independent of the rest of the molecule they are part of. This enables us to identify many of the functional groups that are important in organic chemistry and provides the basis for **qualitative structural identification** by IR spectroscopy. By examining the absorption spectrum of an unknown sample and comparing the bands seen with the characteristic absorption frequencies of known functional groups, it is possible to classify the sample as, say, a ketone or a carboxylic acid very quickly, even if it is not possible to identify the compound exactly. In some cases, the structure of an unknown can be deduced from its IR spectrum, but this requires much practice and is not always possible, even for an expert. Computerized libraries of spectra are now commonly used to identify compounds from their IR spectra. In addition to identifying a molecule, or its functional groups, we can acquire information about structural and geometrical isomers from IR spectroscopy. IR spectroscopy has been coupled to chromatography to identify separated compounds and to thermogravimetric analyzers to identify compounds or degradation products that volatilize as a sample is heated.

We can measure the extent of absorption at a specific frequency for an analyte of known concentration. If now we were to measure the extent of absorption at the same frequency by a sample solution of unknown concentration, the results could be compared. We could determine the sample's concentration using Beer's law. Thus, as a *quantitative tool*, IR spectroscopy enables us to measure the concentration of analytes in samples.

The introduction and widespread use of FTIR has resulted in considerable extension of the uses of IR in analytical chemistry. With regard to wavelength assignment, speed of analysis, and sensitivity, FTIR has opened new fields of endeavor. Some of these uses are described.

Typical analyses include the detection and determination of paraffins, aromatics, olefins, acetylenes, aldehydes, ketones, carboxylic acids, phenols, esters, ethers, amines, sulfur compounds, halides, and so on. From the IR spectrum, it is possible to distinguish one polymer from another or determine the composition of mixed polymers or identify the solvents in paints. Atmospheric pollutants can be identified while still in the atmosphere. Another interesting application is the examination of old paintings and artifacts. It is possible to identify the varnish used on the painting and the textile comprising the canvas, as well as the pigments in the paint. From this information,

fake "masterpieces" can be detected. Modern paints and textiles use materials that were not available when many masterpieces were painted. The presence of modern paints or modern synthetic fabrics confirms that the painting must have been done recently. In a similar manner, real antiques can be distinguished from modern imitations.

As already discussed, paints and varnishes are measured by *reflectance analysis*, a process wherein the sample is irradiated with IR light and the reflected light is introduced into an IR instrument. The paint, or other reflecting surface, absorbs radiation in the same manner as a traversed solution. This technique can be used to identify the paint on appliances or automobiles without destroying the surface. Tiny scraps of paint from automobiles involved in accidents can be examined. From the data obtained, the make and year of the car may be able to be determined and matched to that involved in a hit and run, for example, or to a car involved in a crime.

Forensic science makes use of IR spectroscopy and IR microscopy, not only for paint analysis but for analysis of controlled substances. IR can be used to detect the active compounds in hallucinogenic mushrooms, for example. IR is often used to confirm the identity of controlled substances such as cocaine. It has the advantage of being able to differentiate isomers that cannot be distinguished by mass spectrometry (MS), for example, ephedrine and pseudoephedrine.

In industry, IR spectroscopy has important uses. It is used to determine impurities in raw materials. This is necessary to ensure good products. It can be used for QC by checking the composition of the product, either in batch mode or continuously (online or process analysis). Online IR analyzers can be used to control the process in real time, a very cost-effective way of producing good products. IR spectroscopy is used in the identification of new materials made in industrial research laboratories and in the analysis of materials made or used by competitors (a process called "reverse engineering"). New handheld portable FTIR systems are available and can be used in manufacturing plants to identify incoming raw materials and finished products on site, to identify coatings (composition, thickness, homogeneity), in the field to identify minerals, to characterize materials, to evaluate surface cleanliness, and to determine cure times for polymer coatings in real time. A handheld instrument can evaluate pieces too large or too valuable to be analyzed in a laboratory setting. The handheld instrument in Figure 4.31 is a Michelson interferometer system, weighs 7 lb; is battery powered; has both DR and single-reflection diamond ATR sampling heads and a DTGS detector; covers the 4000–650 cm^{-1} range, is water, shock, and vibration resistant; and can operate from 32°F to 120°F (0°C–50°C).
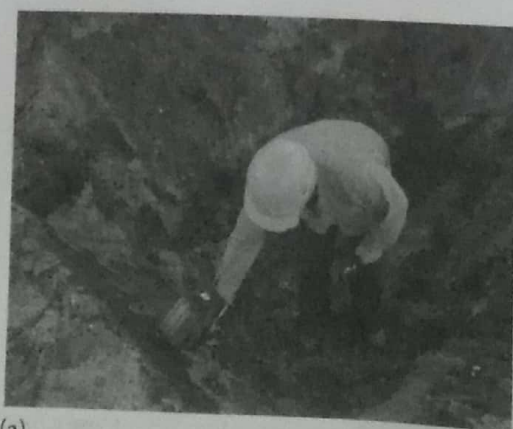
(a)
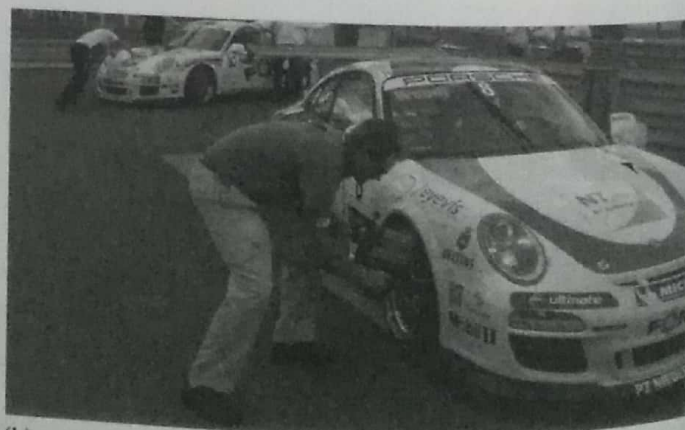
(b)

Figure 4.31 The Agilent 4100 ExoScan FTIR, used (a) to characterize minerals in the field and (b) to evaluate rubber tire condition in real time. (© 2013 Agilent Technologies, Inc., www.agilent.com/chem. Used with permission.)

4.6.1 Qualitative Analyses and Structural Determination by Mid-IR Absorption Spectroscopy

Qualitative analysis of unknown samples is a major part of the work of an analytical chemist. Since it is better to give no answer than an incorrect answer, most analytical chemists perform qualitative analysis using an array of techniques that overlap and confirm each other, providing in the sum more information than could be obtained with the separate individual methods. For qualitative analysis of an unknown organic compound, the most commonly used spectroscopic methods are as follows: IR spectroscopy to see which functional groups are present, nuclear magnetic resonance (NMR) to indicate the relative positions of atoms in the molecule and the number of these atoms, and MS to provide the molecular weight (MW) of the unknown and additional structural information. UV spectroscopy was used in the past to study unsaturated or substituted compounds; it has been almost entirely replaced for qualitative structural information by NMR and MS, which are commonly available in undergraduate chemistry labs. Each technique provides an abundance of valuable information on molecular structure, but a combination of methods is used to ensure more reliable identification. In addition to spectroscopy, real samples may be submitted to chromatography to determine if the unknown is a pure substance or a mixture, to determine the number of compounds present, and to separate and purify the compound of interest. *Sample nature :*

The value to qualitative analysis of prior knowledge about the sample cannot be overemphasized. Before trying to interpret an IR spectrum, it is important to find out as much as possible about the sample, For example, to identify the products of an organic reaction, it is very valuable to have information about the materials that were present before the reaction started, the compounds the reaction was expected to produce, the possible degradation products that may come about after the reaction, and so on. Armed with as much of this information as possible, we may be able to identify the molecules in the sample from their IR spectra.

The general technique for qualitative analysis is based on the characteristics of molecular structure and behavior mentioned at the beginning of the chapter. That is, the frequency of vibration of different parts of a molecule depends on the weight of the vibrating atoms (or groups) and the bond strength. Many groups can be treated as isolated harmonic oscillators and their vibrational frequencies calculated. More commonly, vibrational frequencies for functional groups are identified by the collection of spectra from hundreds of different compounds containing the desired functional group. These characteristic group vibrational frequencies are tabulated in correlation tables or correlation charts. Table 4.2 is a short list of functional groups and their relevant vibrational frequencies. Since the absorption frequency is the same as the vibration frequency, the presence of absorption at a given frequency is an indication that the functional group may be present. More tables are found later and very detailed tables are found in the references listed in the bibliography by Silverstein and Webster, Pavia et al., Lambert et al., Colthup et al., Dean, Robinson, and in the *CRC Handbook of Chemistry and Physics.*

Qualitative analysis is carried out by matching the wavelengths of the absorption bands in the spectrum of the sample with the wavelengths of functional groups listed in a correlation table. Before a positive identification can be made, all the absorption bands typical of the functional group must be observed. More importantly, the lack of an absorption band where one should be can be used to rule out certain functional groups. For example, as we will see later, if there is no strong absorption at about 1700 cm^{-1} due to the C=O stretch in a pure unknown compound, we can state with certainty that the compound does not contain a C=O group and therefore is not a ketone, aldehyde, amide, ester, or carboxylic acid. *Comparision with reference :*

Because the IR spectrum of each compound is unique, matching the IR spectrum of an unknown peak for peak to a reference spectrum of a known material is a very good way to identify the unknown. This is often done with the aid of computerized spectral libraries and search routines, as we saw for the polymer laminate (Figure 4.28). A number of companies, instrument manufacturers, government agencies, and other sources publish collections of reference spectra in electronic format

and in hardcopy. These spectral databases may contain spectra of more than 200,000 compounds, with subsets of the database available for specific fields of endeavor, such as environmental chemistry, pharmaceuticals, polymers, and forensic science. The unknown spectrum or some predetermined number of the strongest absorption bands from the unknown spectrum may be entered into a computerized search routine, which compares the unknown with stored spectra. It then retrieves all compounds from the database that may match the unknown spectrum, assigning a goodness of fit or probability to the suggested matches. The analyst then identifies the spectrum of the unknown based on spectral matching and chemical knowledge of the sample to rule out improbable compounds suggested by the search routine. A short list of reference spectra suppliers is located at the end of the bibliography. Most large spectral databases are expensive to buy. Many small companies or individuals can now access these by a "pay for what you use" approach. The KnowItAll™ system from the Informatics Division, Bio-Rad Laboratories (www.bio-rad.com) and the FTIR/Raman system from Thermo Fisher Scientific (www.ftirsearch.com) are two examples of this very new and cost-effective approach to spectral matching. In addition, there are some free databases that allow the user to view spectra of known compounds. These sources include FTIR and FTNMR spectra from Sigma-Aldrich (www.sigma-aldrich.com), gas-phase IR spectra from National Institute of Standards and Technology (NIST) in the United States (www.nist.gov), and a comprehensive spectral database, including IR spectra, from the Japanese National Institute of Advanced Industrial Science and Technology (www.aist.go.jp/RIOBD/SDBS/menu-e.html). If a database or spectral library is not available or the spectra do not match exactly, the analyst must try to identify the compound from its spectrum. Even when electronic databases are available, it is useful for the analyst to understand how to look at and interpret an IR spectrum. This process is described subsequently for common classes of organic compounds. Only a limited number of examples of the most common types of compounds are discussed here. For detailed basic IR spectral interpretation, the texts by Colthup et al., Pavia et al., Lambert et al., or Silverstein and Webster should be consulted. The ability to interpret an IR spectrum and deduce molecular structure requires a great deal of practice and experience as well as detailed correlation tables and knowledge of organic chemistry and molecular geometry. But even experienced analysts never try to assign every peak in an IR spectrum!

The first region to look at is the 4000–1300 cm^{-1} region, called the **functional group region**. This is the region where strong absorptions due to stretching from the hydroxyl, amine, carbonyl, and CH$_x$ groups occur. The region also has areas of weak absorptions that are nonetheless very informative. The 2000–1660 cm^{-1} region will show a set of weak overtone/combination bands if an aromatic ring is present. The intensity pattern of these weak bands can identify how the ring is substituted (i.e., *ortho*, *meta*, or *para*). Weak absorptions from triple bonds occur in this region, identifying alkynes (C≡C), cyano groups (C≡N), and diazonium salts (N≡N); also occurring in the region are absorptions by single-bonded heteroatom groups such as S–H, Si–H, and P–H.

The region 1300–910 cm^{-1} is called the **fingerprint region** because the complex absorption patterns are really what make the IR spectrum unique—a molecular "fingerprint." These absorptions are not easily interpreted because they arise from interactions between vibrations. There are some very important bands in this region, especially the C–C–O band of alcohols and the C–O–C band of esters. These should be confirmed in conjunction with the appropriate bands (OH or C=O) in the functional group region of the spectrum. *Aromatic region:*

The low-frequency end of the spectrum, 910–650 cm^{-1}, is sometimes called the aromatic region. If there are no strong absorptions in this region, the structure is probably not aromatic. Strong absorptions in this region are due to oop bending of aromatic ring C–H bonds. Broad absorption bands in this region are usually due to nonaromatic amines and amides or due to carboxylic acid dimers. Below 800 cm^{-1}, absorption due to C–Cl and C–Br bonds occurs.

Before trying to interpret an IR spectrum, there are some things the analyst should note. The method of collecting the spectrum should be stated—mull, thin film, KBr pellet, solution, and the solvent—because the appearance of the spectrum may change as has been discussed earlier. The

method of collecting spectra :

analyst should compare reference spectra collected under the same conditions when possible. Older spectra were printed with the spectrum displayed linear in wavelength (on the x-axis); modern grating and FTIR spectra are generally plotted linear in wavenumber. The two plots look very different for the same spectrum; for example, bands will appear to have expanded or contracted depending on their position in the spectrum. It is important that the analyst pay attention to the scale when comparing spectra from the older literature. It should also be noted that in grating IR spectra, the scaling changes at 5 μm. The spectrum should be of a pure compound (at least 95% pure when possible), should have adequate intensity and resolution, and should have been collected on a wavelength-calibrated instrument in order for the interpretation to be useful. The y-axis units should also be noted. Until recently, the y-axis for IR absorption spectra was "transmittance" or "% transmittance," with 100%T at the top of the spectrum. Transmittance is the ratio of radiant power transmitted by the sample to the radiant power incident on the sample, P/P_0 or I/I_0. 100%T is the transmittance multiplied by 100. Transmittance ranges from 0 to 1.0; %T ranges from 0 to 100. The absorption peaks therefore are pointing toward the bottom of the spectrum as printed. The y-axis could be given in A, where A is defined as $-\log T$. If 0.00 absorbance is at the top of the y-axis, the spectrum is similar to the standard %T plot, but the contrast between strong and weak bands is not as good because A ranges from infinity to 0. However, it is becoming more common to see IR spectra plotted with A on the y-axis and with 0.00 A at the bottom of the y-axis, resulting in the peaks pointing up to the top of the plot. This is the inverse of the traditional %T spectrum. One reason for this is that Raman spectra are plotted with peak intensity increasing from bottom to top of the plot; having the complementary IR spectrum in the same format may make comparisons easier.