

5 Diffuse Reflectance Spectroscopy

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5.1 INTRODUCTION

The optical phenomenon known as diffuse reflectance is commonly used in the UV-visible, near-infrared (NIR), and mid-infrared (sometimes called DRIFT or DRIFTS) regions to obtain molecular spectroscopic information. It is usually used to obtain spectra of powders with minimum sample preparation. A reflectance spectrum is obtained by the collection and analysis of surface-reflected electromagnetic radiation as a function of frequency (ν , usually in wavenumbers, cm^{-1}) or wavelength (λ , usually in nanometers, nm). Two different types of reflection can occur: regular or specular reflection usually associated with reflection from smooth, polished surfaces like mirrors, and diffuse reflection associated with reflection from so-called mat or dull surfaces textured like powders. Techniques such as external reflectance and total internal reflectance spectroscopy use the phenomenon of specular reflection to obtain spectroscopic information. In

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diffuse reflectance spectroscopy, electromagnetic radiation reflected from dull surfaces is collected and analyzed. If a sample to be analyzed is not shiny, and for whatever reason is not amenable to conventional transmission spectroscopy, diffuse reflectance spectroscopy is a logical alternative.

To explain what diffuse reflectance is, consider a white wall illuminated by sunlight. The wall appears equally bright regardless of whether you stand directly in front of it, or at any other angle. The surface of the wall reflects the incident sunlight at angles independent of the angle of incidence. In other words, the surface of the wall scatters the incoming radiation. Ideal diffuse reflection requires that the angular distribution of the reflected radiation be independent of the angle of incidence. In contrast to this example, consider a mirror illuminated by sunlight. At most angles of observation, the sunlight will not be visible to the observer. However, at a very specific angle, the reflected sunlight will provide a direct image of the source (the sun). This specularly reflected radiation is characterized by the angle of reflection being equal to the angle of incidence. Specular and diffuse reflections are illustrated in Fig. 5.1.

Whereas specular reflectance can be rigorously treated theoretically using the Fresnel equations, many complex processes produce the phenomenon called diffuse reflection. When light is shined on a dull surface, such as a densely packed powdered sample for diffuse reflectance spectroscopy, the sample will result in a combination of reflection, refraction, and diffraction (i.e., scattering) of the impinging light. Of course, if the sample is of spectroscopic interest, light will also be absorbed by the sample at selected wavelengths or frequencies. Samples of interest for diffuse reflectance spectroscopy are therefore simultaneous scatterers and absorbers of electromagnetic radiation. These complicated and related phenomenon are generally treated with so-called two-constant theories, where the two constants

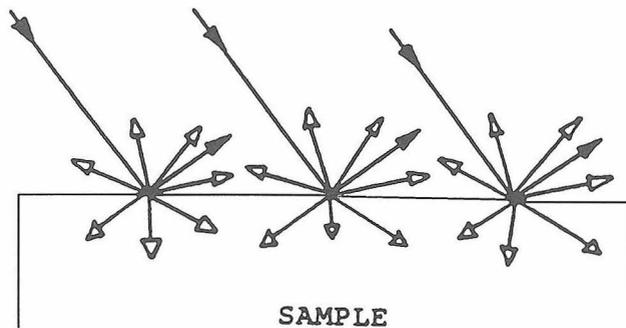


Fig. 5.1 Specular reflection, denoted by the shaded arrows, is radiation whose angle of reflection equals the angle of incidence. Diffuse reflection, denoted by hollow arrows, is radiation whose angle of reflection is independent of the angle of incidence.

characterize the scattering and absorbance characteristics of the sample. The most often used theory to describe and analyze diffuse reflectance spectra is the Kubelka-Munk theory. The two-constant Kubelka-Munk theory leads to conclusions that are qualitatively confirmed by experiment and can be used for quantitative work in many cases. Most molecular spectroscopic software can convert spectra to Kubelka-Munk units automatically. The best description of the fundamentals of diffuse reflectance spectroscopy can be found in a book by Kortüm [1].

The first serious diffuse reflectance studies were carried out around 1940 in the visible region at about the same time that precision spectrophotometers became available. Since then diffuse reflectance spectroscopy has been expanded to the near-infrared (NIR) and the mid-infrared regions. Applications of diffuse reflectance spectroscopy, especially in the latter two regions, have truly exploded in the past 10 years. Uses of this technique range from quality control of products on the factory floor to a sophisticated research tool for characterizing catalytic surfaces.

Using diffuse reflectance spectroscopy in the various regions of the electromagnetic spectrum involves different possibilities, trade-offs, and experimental considerations. On the more theoretical side, in the UV-visible and mid-infrared regions, fundamental electronic absorptions and vibrational modes are excited, respectively. The potentially large absorptivities (i.e., the sample can absorb much of the incoming radiation) of samples in these regions can require special sample preparation procedures to avoid spectral artifacts. On the practical side, different optical accessories are used to irradiate the sample and collect the diffusely reflected radiation in the mid-infrared region as compared to the UV-visible and NIR regions.

More detailed discussions of how diffuse reflectance fits into the myriad techniques in modern molecular spectroscopy, the interplay between theoretical and experimental considerations, and selected applications follow. Competitive techniques to diffuse reflectance spectroscopy will be compared and contrasted. A discussion of diffuse reflectance, the assumptions inherent in the widely applied Kubelka-Munk theory, and practical experimental considerations necessary to acquire reliable spectra will then be discussed. Finally, a review of selected applications using diffuse reflectance spectroscopy will be presented.

5.2 ROLE OF DIFFUSE REFLECTANCE IN MOLECULAR SPECTROSCOPY

There are many different sample-handling techniques available to the molecular spectroscopist including diffuse reflectance, external reflectance, internal reflectance, and photoacoustic spectroscopy. Given all these choices, it is easy to lose sight of the fact that these different techniques should

all be compared to the benchmark transmission method. There is one overriding factor that should always be kept in mind: *If it can be done using transmission spectroscopy then do it!* There are a variety of reasons for saying this. First, transmission spectroscopy is experimentally simpler and less expensive than other methods. There are no optical accessories to align, and the theory governing transmission spectroscopy is firmly grounded in the fundamentals. Also in a transmission experiment most of the energy emanating from the source reaches the detector. Thus the signal-to-noise (S/N) ratio of a transmission spectrum will usually be greater than when using competitive techniques if everything else is equal. Since much of the energy emanating from the source does not reach the detector using alternative sampling techniques, these spectra are often detector noise limited. In other words, the sensitivity of the detector limits the S/N ratio of the resulting spectrum. For example, a perfectly aligned diffuse reflectance cell in the mid-infrared containing a nonabsorbing, diffusely reflecting sample will pass only 15–20% of the energy from the source to the detector. That is why high-sensitivity detectors, such as liquid nitrogen cooled MCT (mercury-cadmium-telluride) detectors are used in many applications of diffuse reflectance mid-infrared spectroscopy. If one can get around these inherent limitations by using transmission spectroscopy why not do it?

In many instances, some obvious and some not so obvious, transmission spectroscopy is not viable. Restricting our discussion to solid samples, if a beam of light cannot be passed through the sample using a transmission method like the KBr pellet technique, then one has no choice but to consider alternate means of spectral acquisition. Just because a transmission spectrum can be obtained does not necessarily mean it is advisable. The high pressures required to press a KBr pellet for transmission spectroscopy can alter the sample [2] or even cause unwanted reactions to occur [3]. For these and other reasons, alternate methods of spectral acquisition have been developed.

The pertinent sampling techniques for our discussion (other than transmission and diffuse reflectance spectroscopy) have been previously listed as external reflectance, internal reflectance, and photoacoustic spectroscopy. If the sample has a smooth, polished surface then external reflectance should be considered (Chapter 3). Internal reflectance (or attenuated total reflectance, ATR) is also a possibility if the sample can be placed in intimate contact with the internal reflection element (Chapter 4). Samples that exist as powders, or can be conveniently converted to powder form, are ideal candidates for either diffuse reflectance or photoacoustic spectroscopy. In other words, diffuse reflectance spectroscopy is not competitive with either internal reflectance or external reflectance spectroscopy. Diffuse reflectance and photoacoustic spectroscopy are often applied to the same types of samples and are therefore competitive.

Since photoacoustic and diffuse reflectance spectroscopy are competitive techniques, Childers et al. have compared these two methods in the

UV-visible and NIR [4] and in the mid-infrared [5] under precisely controlled conditions. These authors' conclusions were similar whatever the spectral region considered. Diffuse reflectance spectroscopy exhibits a superior S/N ratio and is therefore more sensitive. It is also superior for samples that are not intensely absorbing. If sample particle size is $> 100 \mu\text{m}$ and is not amenable to grinding and/or dispersion in a nonabsorbing matrix, photoacoustic spectroscopy exhibits certain advantages. Often it is also possible to perform depth-profiling studies using photoacoustic spectroscopy. The diffuse reflectance method has thus far exhibited a limited capacity to perform such studies.

Despite these comparisons, photoacoustic spectroscopy has not been nearly as widely applied as has diffuse reflectance. Although similar information can often be obtained using either technique, as a practical matter diffuse reflectance has proved more generally useful. At one level, due to the way in which a photoacoustic signal is generated, spectral acquisition times are generally greater than when using the diffuse reflectance technique. Perhaps even more important, mechanical vibrations play havoc on a photoacoustic signal. The best photoacoustic spectra are often obtained in the middle of the night when the laboratory is deserted and external vibrations are at a minimum. Given the trend of molecular spectroscopy being applied more frequently in nonlaboratory environments, such as the factory floor, it is not surprising that diffuse reflectance has received more attention. The vast majority of diffuse reflectance near infrared spectroscopic work has been and will continue to be aimed at these types of process environments.

In summary, if one has an application in which a sample that scatters radiation must be analyzed, and the sample cannot be conveniently made to contact with an internal reflection element, diffuse reflectance and photoacoustic spectroscopy are the two choices. This of course assumes that transmission spectroscopy, for whatever reason, has been ruled out. Unless it is a specialized case, diffuse reflectance spectroscopy is a more practical alternative as compared to photoacoustic spectroscopy for reasons that have been previously described.

Before discussing the specific nuts and bolts of obtaining a diffuse reflectance spectrum, the first part of the next section will describe in more detail the theory of diffuse reflectance spectroscopy.

5.3 DIFFUSE REFLECTANCE THEORY AND PRACTICE

Fresnel and Kubelka-Munk Reflectance

The concepts of specular and diffuse reflectance have been previously discussed. The optical phenomena resulting in diffuse reflectance are many and complex; far from a comprehensive treatment will be given here.

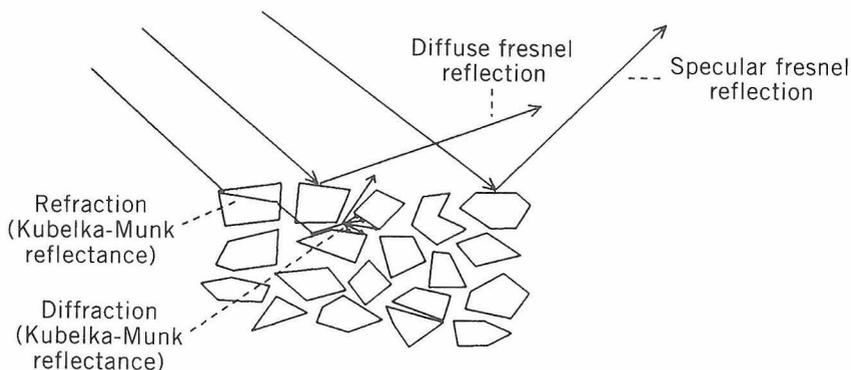


Fig. 5.2 Optical phenomena resulting in diffuse reflectance.

However, it is important that a requisite level of understanding be attained. The way in which samples are prepared and analyzed are inextricably related to diffuse reflectance theory. When diffuse reflectance spectra are obtained without considering the assumed optical phenomena, misleading and spurious results can be obtained. In this section only the theory that has direct, practical implications to the collection and interpretation of diffuse reflectance spectra will be discussed. The relationship between theory and experiment will be made as explicit as possible.

Figure 5.2 schematically shows some optical phenomena involved in a diffuse reflectance experiment. Consider the sample as a randomly distributed powder. The incoming radiation can undergo specular reflection from the individual particles. The first theoretical treatment to explain the phenomenon of diffuse reflectance was given by Bouguer. It was assumed that diffuse reflection occurs from specular reflection from elementary mirrors of the sample surfaces with planes statistically distributed at all angles. Specular reflection can thus be further differentiated into diffuse Fresnel reflection and specular Fresnel reflection. Since the individual sample particle surfaces are randomly distributed, the surface of the particle is not necessarily parallel with the macroscopic sample surface. So although the radiation reflected from such a surface undergoes specular reflection (angle of incidence = angle of reflection), the reflected radiation appears diffuse with respect to the macroscopic sample surface. Therefore, we have the term diffuse Fresnel reflection. If the surface of the particle is parallel with the macroscopic sample surface, and specular reflection occurs, this is specular Fresnel reflection. Since both diffuse and specular Fresnel reflection result from the same phenomenon, spectroscopically the same information content is contained in each. The beam of light in Fresnel reflection interacts only once with the sample surface. If the source beam interacts more intimately with the sample, say, by undergoing multiple reflections, it

stands to reason that more absorption by the sample will occur. This is the case when the phenomenon known as diffuse reflectance occurs.

The Bouguer elementary mirror hypothesis discussed above did not allow for the possibility of refraction. Due to refraction the incoming beam will also penetrate inside the particle and, if not absorbed, will exit from the surface after many reflections and diffractions. This radiation can be termed Kubelka-Munk reflectance. A competitive theory to that proposed by Bouguer assumed that Kubelka-Munk reflectance is solely responsible for diffuse reflectance. (At the time this theory was proposed, Kubelka and Munk were not yet born. The term Kubelka-Munk reflectance was adopted later.) After much experimental work early in the visible region [1], and more recently in the mid-infrared region [6–8], it has been found that both Fresnel and Kubelka-Munk reflectance nearly always occur simultaneously to greater or lesser extents, based on the nature of the sample and sample preparation methods.

To understand why there is usually a combination of Fresnel and Kubelka-Munk reflectance, one needs to understand what governs Fresnel reflectance. The Fresnel equations for specular reflectance show that as absorptivity (the likelihood that light will be absorbed by the sample) increases, so does specular reflectance. Under the simplest conditions, the Fresnel reflectance can be described as follows:

$$R_F = (\eta - 1)^2 + \frac{\eta^2 \kappa^2}{(\eta + 1)^2} + \eta^2 \kappa^2, \quad (5.1)$$

where R_F is the Fresnel reflectance, η is the sample's refractive index, and κ is proportional to the absorptivity. As κ increases, which will happen near an absorption band, there is an increase in Fresnel reflectance. Only nonabsorbing materials, which are uninteresting spectroscopically, can even in principle be ideal Kubelka-Munk reflectors. Thus, when radiation is reflected from a dull or mat surface, diffuse and Fresnel fractions are superimposed. This is a real problem in diffuse reflectance spectroscopy for a variety of reasons. First, Fresnel reflection contains less spectroscopic information than the diffusely reflected component because the latter interacts more with the sample increasing the likelihood of absorption. Second, a large Fresnel component means spectral distortion in diffuse reflectance spectroscopy.

Many seeming anomalies of diffuse reflectance spectra arise from the almost inevitable phenomenon of specular reflectance. However, the Kubelka-Munk theory to quantitatively describe diffuse reflectance spectroscopy assumes no specular reflection component. Since very complex processes are involved in diffuse reflectance spectroscopy, other simplifying assumptions are also inherent in the Kubelka-Munk theory.

Before plunging into the Kubelka-Munk theory, a cautionary note is warranted. Although the Kubelka-Munk theory is the most widely applied theory to describe diffuse reflectance, and can be thought of as analogous to Beer's law for transmission spectroscopy, there are important differences. Beer's law is a rigorously proven theory soundly based in the fundamentals of spectroscopy. The Kubelka-Munk theory is little more than an empirical model of diffuse reflectance that often works if care is taken to fulfill the assumptions of the model. Other empirical models exist to describe diffuse reflectance, but a discussion of these models is beyond the scope of this chapter.

Kubelka-Munk Theory

In this section Kubelka-Munk theory is described in terms of how it is used to analyze diffuse reflectance spectra. Many assumptions, both explicit and implicit, will be discussed as they relate to practical experimental considerations. First, definitions and analogies to transmission spectroscopy are provided. This is followed by the form of the Kubelka-Munk function. Important experimental procedures to enhance the validity of the Kubelka-Munk function are then considered. Finally, a few examples are given to illustrate what can happen if caution is not exercised when using diffuse reflectance spectroscopy.

In transmission spectroscopy, where a beam of light is passed through a sample, the transmittance is the ratio of intensities of transmitted to incident light:

$$T = \frac{I}{I_0}, \quad (5.2)$$

where T is the transmittance (1 for a completely transparent sample), I is the intensity of transmitted light, I_0 the intensity of the incident beam. In an analogous fashion the remittance of a diffusely reflecting sample is the ratio of intensities of reflected to incident light:

$$R_\infty = \frac{J}{I_0}, \quad (5.3)$$

where R_∞ is the absolute remittance, J is the intensity of the reflected radiation, and I_0 is again the intensity of the incident beam. (The ∞ subscript denotes that the sample is "infinitely thick"; in other words, none of the light irradiating the sample penetrates to the bottom of the sample holder. This is usually the case when the sample thickness is approximately 5 mm or more). A perfect diffusely reflecting substance, practically never attained, would have $R_\infty = 1$.

Since it is not practical to measure R_∞ , the absolute remittance, the measured quantity is usually the relative remittance, R'_∞ :

$$R'_\infty = \frac{R_{\infty \text{ sample}}}{R_{\infty \text{ standard}}} \quad (5.4)$$

Notice that if $R_{\infty \text{ standard}} = 1$, then the absolute and relative remittances must be equal.

The relative remittance is analogous to transmittance in transmission spectroscopy. In transmission spectroscopy it is often convenient to present data in absorbance units, A , where $A = \log(1/T)$. This is because Beer's law says that absorbance is linearly related to the concentration of absorbing species. In an analogous fashion, it is possible to plot $\log(1/R'_\infty)$ against wavelength or frequency. This is called apparent absorbance units. This does not imply, however, that Beer's law is valid for diffuse reflectance spectroscopy.

Ideally one would like a function, like Beer's law in transmission spectroscopy, to linearly relate analyte concentration with the reflectance characteristics of a diffusely reflecting sample. The function must used is that derived by Kubelka and Munk:

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K}{S} = \frac{2.303\epsilon C}{S} \quad (5.5)$$

where K is the absorption coefficient (twice the Beer's law absorption coefficient), S is twice the scattering coefficient of the sample, ϵ is the absorptivity, and C is the analyte concentration. One can see why the Kubelka-Munk theory is a two-constant theory: the reflectance characteristics are related to the ratio of the absorption to scattering coefficients which are the two constants.

Table 5.1 gives a better feel for the behavior of the Kubelka-Munk function. The first column, % reflectance, is analogous to % transmittance in transmission spectroscopy. The second column, apparent absorbance, is calculated from the % reflectance as one would using Beer's law from transmission spectroscopy. The third column is the corresponding value in Kubelka-Munk units corresponding to the % reflectance data in the first column. It can be seen from these data that the Kubelka-Munk function slights the weak bands (high reflectance) and enhances the strong bands (low reflectance) as compared to a classical absorption spectrum.

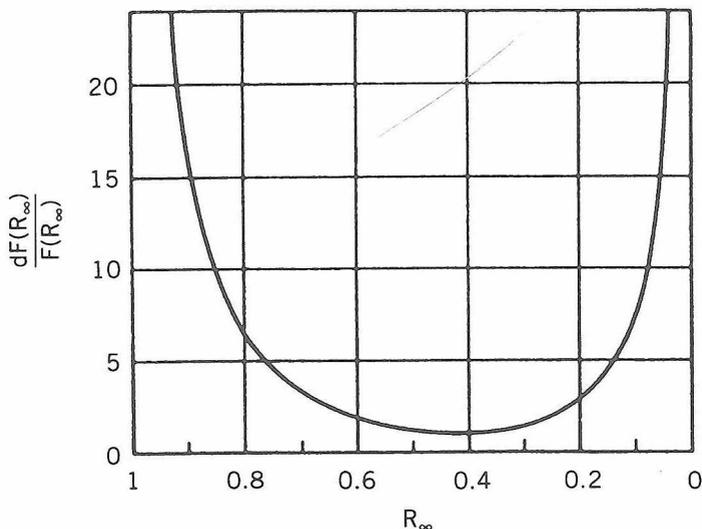
Let us take a small detour. If the accuracy of measurements depends only on the intensity difference of the diffusely reflected radiation (no instrumental error), the relative error in the Kubelka-Munk function can be

TABLE 5.1 Comparison of Absorbance and Kubelka-Munk Units at Various % Reflectance Values

% Reflectance	Apparent Absorbance ($\log 1/R_\infty$)	Kubelka-Munk Units [$(1 - R_\infty)^2/2R_\infty$]
100	0	0
90	0.046	0.0056
80	0.097	0.025
70	0.15	0.064
60	0.22	0.13
50	0.30	0.25
40	0.40	0.45
30	0.52	0.82
20	0.70	1.6
10	1.0	4.0
1	2.0	49

obtained. Results of this mathematical analysis are shown in Fig. 5.3. From these results the most favorable range for measurement lies between $0.2 < R_\infty < 0.7$. In other words, best results are obtained between 20 and 70% reflectance (remittance). As seen from Fig. 5.3, the error at larger and smaller reflectances increases very rapidly.

It is apparent from equation (5.5) that the Kubelka-Munk function linearly relates analyte concentration with band intensity provided that S

Fig. 5.3 Inherent error in the Kubelka-Munk function versus R_∞ .

remains constant and the assumptions made in deriving the Kubelka-Munk equation are valid. To obtain diffuse reflectance spectra that have the best chance of obeying the Kubelka-Munk equation with quantitative validity, the question becomes what are the relevant assumptions made in deriving and using the Kubelka-Munk equation?

The assumptions in deriving and using the Kubelka-Munk equation are many. Those assumptions with practical implications will now be discussed. (1) All Fresnel reflection is ignored. This is the single most important consideration when obtaining any diffuse reflectance spectrum [9]. As has been previously discussed, Fresnel reflection increases with absorptivity. When collecting diffuse reflectance spectra of samples with high absorptivity, take care to reduce Fresnel reflectance. (2) The particles in the sample are much smaller than the thickness of the entire sample. (3) The sample thickness should be greater than the beam penetration depth to meet the "infinitely thick" criterion. (4) The sample diameter should be much greater than the focus of the incident beam to avoid optical effects that are not due to the sample. Also the sample area detected should be smaller than the area illuminated.

For qualitative diffuse reflectance work, the only real concern is to reduce Fresnel reflection to avoid spectral artifacts. An artifact known as anomalous dispersion is caused by an increase in Fresnel reflectance near strong absorption bands (5.1). This can be detected by either derivative shaped features or a shift in the peak maximum to higher frequency or lower wavelength. For bands of very high absorptivity, the increase in Fresnel reflectance around the absorption actually increases the reflectance in this region. The resulting large reflectance maximum results in a reststrahlen band. These types of spectral artifacts only occur in regions of high absorptivity. In the mid-IR region, where fundamental vibrational modes predominate, very high absorptivities are not uncommon. These artifacts can be eliminated by diluting the sample with a nonabsorbing matrix. In mid-IR diffuse reflectance spectroscopy, this is commonly done by diluting the sample in a solid mixture of KCl. The mid-IR spectrum of pure silica powder is compared to that of a 5% mixture of silica in KCl in Fig. 5.4. Since 95% of the sample is nonabsorbing in the 5% mixture (Fig. 5.4*b*), the decrease in the sample's absorptivity results in a decrease in Fresnel reflection. The reststrahlen band is thus eliminated.

Due to the very high absorptivities, if care is not taken to reduce Fresnel reflectance, these types of artifacts will be common in the mid-IR. In the NIR vibrational overtone and combination bands that have orders of magnitude lower absorptivities. These spectral artifacts are therefore not a problem in the NIR. In the UV-visible region, fundamental electronic absorptions predominate. High absorptivities are again common, though these highly distorted spectral features are not nearly as common in the UV-visible region as compared to the mid-IR.

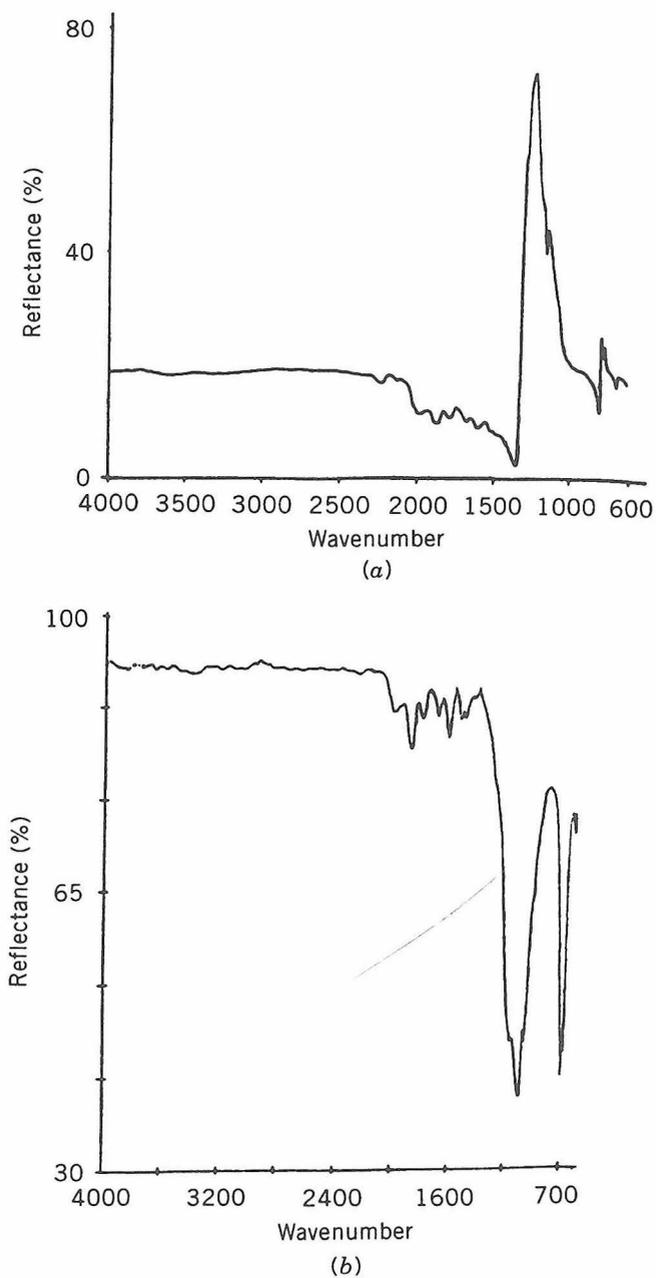


Fig. 5.4 (a) Diffuse reflectance spectrum of pure silica illustrates the *reststrahlen* band at 1100cm^{-1} from an increase in Fresnel reflectance. (b) Dilution of the silica sample in KCl eliminates the spectral artifact.

When using diffuse reflectance spectroscopy for quantitative purposes, beyond the above considerations, precise methods of sample preparation are necessary. The scattering coefficient must be kept constant from sample to sample to perform quantitative diffuse reflectance work. To achieve this, two important parameters must remain constant from sample to sample: particle size and sample packing. Particle size can be controlled by sieving, or more quickly and practically by a ball and mill grinder to powder the sample (provided that grinding time is kept constant). Depending on the nature of the sample, adequate sample packing reproducibility can be attained by gentle tapping of the sample in the sample cup, or more precisely by applying a known amount of pressure to the sample for a specified time. High pressures should be avoided, however, since resulting surface gloss is an indication of Fresnel reflection.

Changes in the scattering coefficient impact quantitative work in unforeseen ways. Take, for instance, crystals of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, which have a fairly strong blue color. Grind these crystals to smaller particle size, and the material becomes a pale blue. At very small particle sizes, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ appears practically white. In other words, the sample absorbs less light, in the visible region, with decreasing particle size. Since the absorptivity in fact increases with decreasing particle size [10], which should result in a *more* colored material, the scattering properties of the sample must be changing. As particle size increases scattering decreases. The radiation can thus penetrate deeper into the sample, resulting in more Kubelka-Munk reflectance with corresponding increased absorbance and more intense color. This is a strikingly visual example of how the scattering properties of the sample affect reflectance spectra.

In contrast to the previous example, strongly absorbing materials such as KMnO_4 in the visible region, exhibit an increase in apparent absorbance (KMnO_4 is more colored) as particle size is decreased. This can be explained by the fact that the reflection characteristics of strongly absorbing materials contain a large contribution from specular reflectance. As particle size increases, so does specular reflectance. Thus, by decreasing particle size, the specular reflectance component decreases, resulting in an increase in apparent absorbance. Again the sample's scattering constant changes as a function of particle size, but now the opposite effect is obtained. Another anomaly from specular reflectance.

An additional characteristic of diffuse reflectance spectra of strongly absorbing species is that when such samples are diluted with a nonabsorbing matrix, reflectance characteristics are largely unchanged over a broad concentration range. A plot of band intensity in Kubelka-Munk units versus analyte concentration exhibits negative deviations from linearity at high analyte concentration. (This is often also the case in Beer's law calibration curves, but for different reasons). Since the Kubelka-Munk theory attempts

to describe the reflectance behavior of weakly absorbing samples, the implicit assumption is that the beam penetration depth does not change as analyte concentration increases. In effect it is assumed that the pathlength (as it is called in transmission spectroscopy) is constant. With strongly absorbing samples at high analyte concentrations, the beam penetration depth decreases with increasing analyte concentration. At high analyte concentration therefore, the intensity of strong absorption bands does not linearly vary with concentration, simply because of the reduction in beam penetration depth or pathlength. Dilution of the sample in a nonabsorbing matrix cures this problem.

The scattering properties and reflectance characteristics of the sample must remain constant for quantitative diffuse reflectance work in any spectral region. For qualitative work the requirements are less stringent, but for strongly absorbing samples spectral artifacts are still a possibility.

The Practice of Diffuse Reflectance Spectroscopy

The instrumental requirements for UV-visible, NIR, and mid-IR spectroscopy vary. For our discussion, probably the most important difference between doing spectroscopy in the various regions is detector technology. UV-visible spectrometers use photomultiplier tubes that are highly sensitive devices. Lead sulfide (and other) detectors are also very sensitive in the NIR. Mid-infrared detectors are, however, much less sensitive. Consequently the collection of diffuse reflectance spectra in the UV-visible–NIR spectral regions is done differently than in the mid-infrared region. This section will thus be divided into two parts: UV-visible–NIR diffuse reflectance spectroscopy and mid-infrared diffuse reflectance spectroscopy.

UV-Visible–NIR Diffuse Reflectance Spectroscopy

Most diffuse reflectance spectra collected in these regions are done with an optical accessory called an integrating sphere. The integrating sphere is a hollow enclosure with walls constructed of a diffusely reflecting material that reflects all wavelengths of interest with a high reflecting power. Traditionally freshly prepared MgO was used to coat the inner sphere surface. There are many practical problems with this material, however. The surface is difficult to prepare, fragile, and relatively unstable. Fortunately, modern integrating spheres come with their own durable coatings already applied. A thermoplastic resin with a trade-name of Spectralon^R (Labsphere, Sutton, NH) exhibits an absolute reflectance of >95% from 250–2500 nm (UV → NIR range). This material is used to coat many integrating spheres for diffuse reflectance spectroscopy in these spectral regions.

There are many experimental arrangements used for diffuse reflectance spectroscopy with an integrating sphere. Most of these arrangements can be

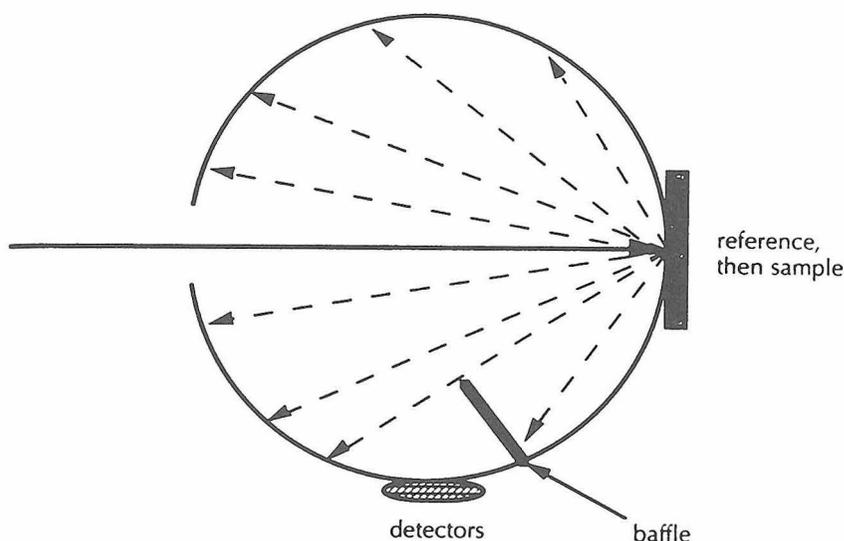


Fig. 5.5 Integrating sphere used to obtain a diffuse reflectance spectrum by the substitution method. Reprinted with permission from [16].

classified as either a substitution or a comparison method. The way to obtain a diffuse reflectance spectrum using the substitution method with a dispersive single beam spectrophotometer is illustrated in Fig. 5.5. Monochromatic radiation enters the sphere from an external source through the aperture. First a highly reflective reference material, such as Spectralon^R which should be provided with the sphere, is illuminated. The radiation intensity is measured by a detector mounted on the sphere wall. The standard is then replaced by the sample and the measurement repeated. The relative reflectance values of sample/standard thus provide the raw data for the sample's spectrum. A single port is provided in the integrating sphere for measurements made using the substitution method. So-called sphere error occurs in this method due to the sample becoming part of the sphere wall. When the sample and reference exhibit different reflectance values, which is inevitable for a spectroscopically interesting sample, the ratio of sphere wall radiances is not directly equal to the ratio of reflectances. In effect the blank and sample scans are measured as if they were done in two separate integrating spheres. The sphere or substitution error is small (roughly 5%) in cases where the sample and standard are approximately equal in reflectivity. If the sample and standard have very different reflectivities, substitution error can be significant.

Substitution error can be dealt with in many ways. First, it can be reduced by making the sample and reference areas small with respect to the

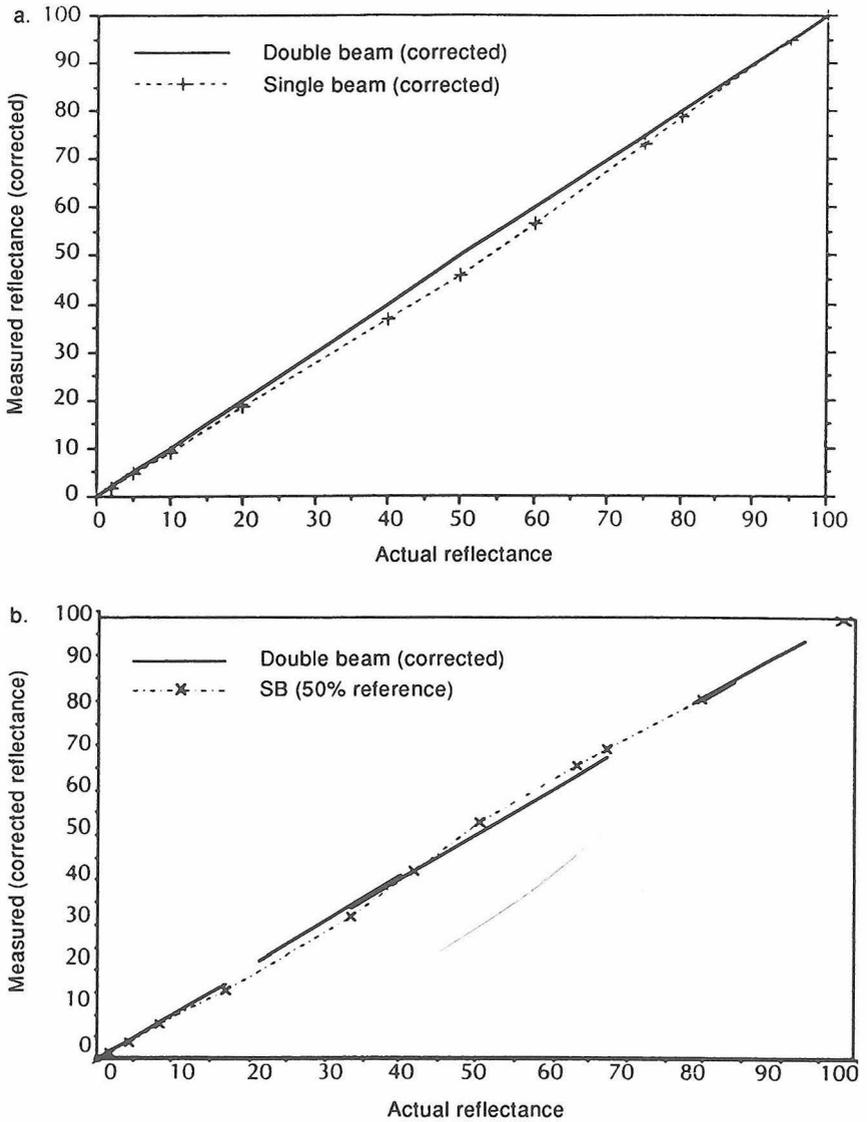


Fig. 5.6 (a) Single-beam substitution error with a 100% reflector as a reference. Deviation from the solid line is maximum at 50% reflectance. (b) Single-beam substitution error with a 50% reflector as a reference. Reprinted with permission from [16].

total surface. In other words, use a larger sphere. This can only be taken so far, however. There is a loss in sensitivity as sphere size is increased. Thus a compromise must be reached in which one trades off sphere error for sensitivity (spectral S/N). Another way to reduce substitution error is to use a reference that is very close in reflectance to the sample. Figure 5.6*a* illustrates a single-beam substitution error with a 100% reflector as a reference. Deviation from the actual reflectance is maximum as the sample approaches 50%. Figure 5.6*b* illustrates single beam substitution error with a 50% reflector as a reference. Comparison of Figs. 5.6*a* and 5.6*b* shows less substitution error using the 50% reflectance material. Thus, by matching the reflectance of the reference and sample, an accurate measurement of reflectance using the substitution method can be developed. Calibrated standards also exist that can be used to calibrate the sphere for substitution error. Sets of reflectance standards can be obtained [11] that have been measured on a sphere without substitution error. A table of measured versus actual readings can then be generated and used to correct for substitution error.

When should you be concerned with substitution error? If you are doing strictly qualitative work, identifying the location of peaks, substitution error should be of no concern. If you are trying to extract quantitative data from your spectra, however, substitution error is something well worth considering.

The second method for obtaining diffuse reflectance UV-vis–NIR spectra is the comparison method. Now both the sample and the standard make up a part of the sphere wall throughout the measurements. Two sphere ports are provided for simultaneous mounting of sample and reference. First the sample to be measured is placed in a “dummy” port, and the calibrated standard in the sample port. After obtaining the blank scan, the sample is substituted for the standard, and the reflectance spectrum is obtained. The comparison method eliminates substitution or sphere error because the geometry of the sphere is identical in measuring both the blank and the sample. The comparison method is more time-consuming than the substitution method, however, since the blank must be rescanned with each new sample.

Unlike FT-IR instruments which all collect spectra in fundamentally the same way, UV-vis–NIR instruments can work in very different ways. The discussion so far has been concerned with single-beam instruments. Most UV-vis–NIR spectrometers are now double-beam, dual-beam, or diode array instruments. An integrating sphere accessory for a double-beam spectrophotometer is shown in Fig. 5.7. The chopped signal from the source is separated into sample and reference beams. The sample and reference are measured concurrently, thus allowing for a comparison measurement without sacrificing analysis time. An integrating sphere accessory for a dual beam spectrophotometer requires a substitution measurement. Instead of a

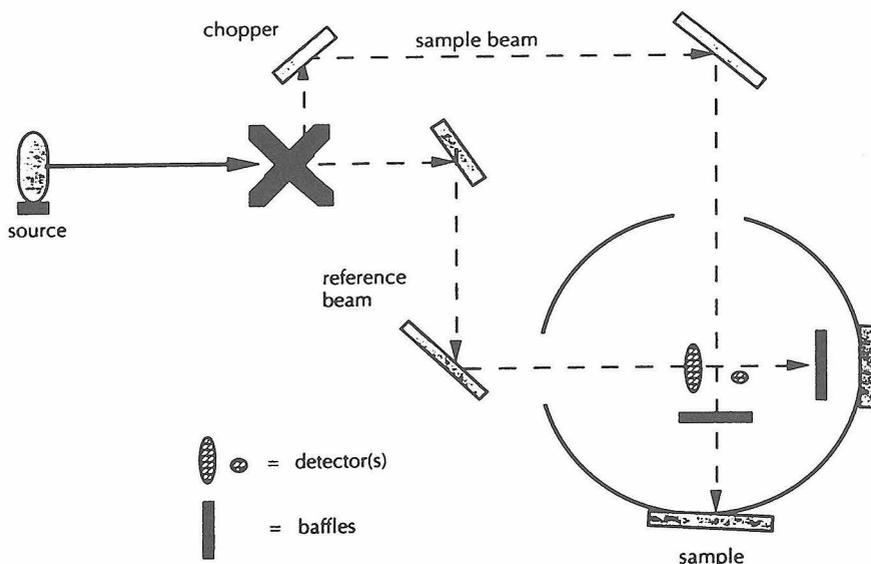


Fig. 5.7 Interesting sphere for a double-beam spectrophotometer. Reprinted with permission from [16].

mechanical chopper the beam is split using a beam splitter. Half the beam is sent toward the original instrument detector, while the other half is sent to the integrating sphere set up for a substitution measurement. Diode array spectrometers have become increasingly popular because of the speed in which a spectrum can be taken. A reflectance spectrum using a diode array spectrometer contains the source inside the sphere to produce polychromatic illumination (Fig. 5.8). Collection of a diffuse reflectance spectrum using a diode array instrument, like a dual-beam instrument, requires a substitution measurement.

The analysis of powdered samples using the diffuse reflectance technique is easiest. Sample holders are usually either a Teflon or aluminum block at least 5 mm deep to meet the “infinitely thick” criterion discussed in the theory section. A quartz window can be used for UV \rightarrow NIR measurements, although a less-expensive glass window is fine if UV measurements need not be done.

The collection of diffuse reflectance spectra for qualitative information, such as color matching by visible spectrometry, is straightforward. Place the powder in the sample holder and collect the spectrum using either the substitution or comparison method, whichever is appropriate for the instru-

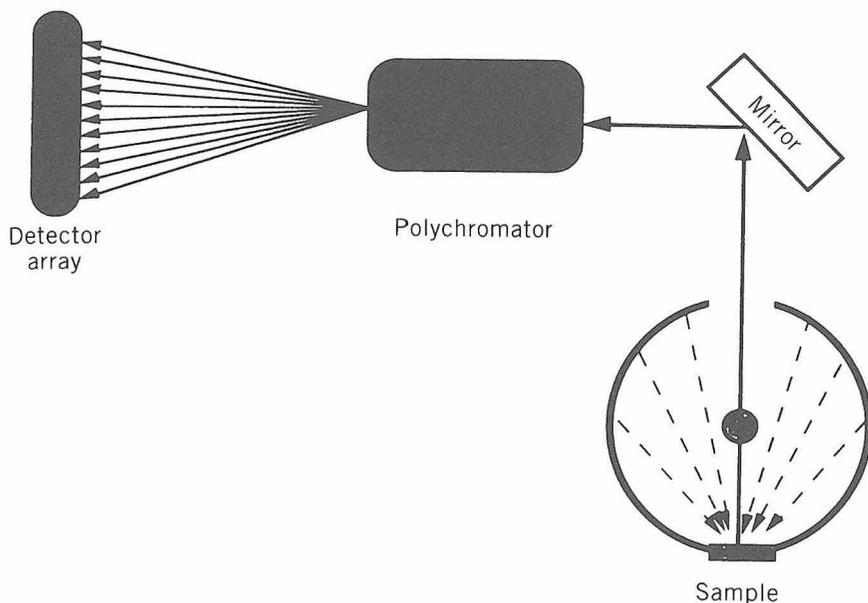


Fig. 5.8 Integrating sphere for a diode array spectrometer. The source inside the sphere results in diffuse illumination of the sample. Reprinted with permission from [16].

ment type. The only concern should be the possibility of spectral artifacts for intensely absorbing samples, as was discussed in the previous section. Dilution of the powdered sample in a nonabsorbing matrix such as MgO or BaSO_4 may be necessary in extreme cases. Loosely packed powders can also be measured in a cuvette, but the reference should be measured in a matched cuvette. Another alternative is to press the powder into a pellet, but take care to avoid a glossy surface appearance which suggests specular reflectance.

Using integrating spheres to obtain quantitatively valid diffuse reflectance spectra requires more care. Substitution error is only one source of error associated with the use of integrating spheres. There are further factors to discuss, and for a full consideration, see Clarke and Compton [12].

From the theory section, it can be surmised that since the packing density affects the scattering coefficient, a constant packing density must be attained. The nature of the particle surface also has an effect on the reflectance spectrum. If possible, the surface should be smooth and even but free of gloss. Particle size is also very important since this parameter also affects the scattering coefficient. A grinding device such as a Wig-L-Bug should be used to grind the sample. Very fine particles agglomerate, so a stationary state is

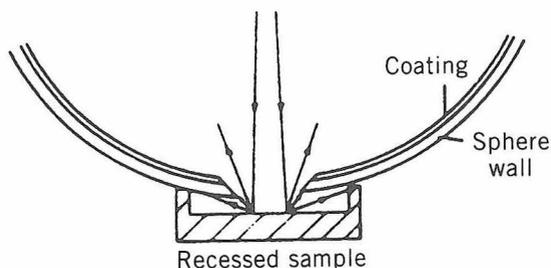


Fig. 5.9 Sample recess error. Some diffusely reflected radiation from the sample does not reenter the sphere if the sample is not flush with the sphere.

reached in the $0.2 \rightarrow 2 \mu\text{m}$ range. Sample recess error is less obvious. Different distances of the sample surface from the sphere wall causes difference in reflectance. Some diffusely reflected radiation will not enter the sphere if the sample is set back from the sphere wall (Fig 5.9). If the sample and reference are recessed by the same amount, the resulting error will be much smaller. Sample preparation, sphere geometry, sphere alignment, and sample alignment all have an effect on diffuse reflectance spectra. Quantitative diffuse reflectance work using integrating spheres in the UV-vis-NIR, or biconical devices in the mid-infrared (to be discussed), should not be done in a cavalier fashion. Despite these concerns, quantitative work has and will continue to be done. Quantitative diffuse reflectance work in the NIR abounds, as will be discussed.

Diffuse reflectance spectra of samples other than powders can also be obtained. Spectra of solid, nonglossy materials can be easily obtained by placing the sample flush with the sample port. Spectra of samples that are smaller than the sample port should be collected using a masking technique. The masked sample, and an identically masked reference, should fill the sample port. The usually black mask is fabricated such that stray light does not enter the sphere from the outside, and reflectance from the mask within the sphere does not add to the reflectance of the sample. An effective mask can be easily prepared from a manila file folder painted with flat black paint cut such that it is large enough to fill the sample port. A hole is cut out of the mask so that the sample and reference can be mounted behind the mask for spectral acquisition.

Spectra of nontraditional samples such as fabrics can also be obtained. The fabric sample is stretched to introduce a flat, nonwrinkled surface to the sphere port. The sample must be backed by a light trap (similar in function to a mask) to ensure that external light does not enter the sphere to affect the spectrum. Since spectral acquisition of so many different sample types can be obtained, procedures are commonly devised as they are needed.

Mid-Infrared Diffuse Reflectance Spectroscopy

Although an integrating sphere is the most commonly used device to collect diffuse reflectance spectra in the UV-visible–NIR regions, the integrating sphere presents several problems for mid-infrared work. First, coatings for the integrating sphere suitable to mid-infrared spectroscopy cannot be made with the same high reflectance characteristics as in the UV-visible region. Second, infrared detectors are orders of magnitude less sensitive than photomultiplier tubes used in UV-visible spectroscopy. Given these two reasons, and the fact that integrating spheres are intrinsically inefficient, the S/N ratio of mid-infrared diffuse reflectance spectra will be low. This is not to say that integrating spheres cannot be used in modern FT-IR spectrometers, but thus far their application has been limited. The fact remains that if an absolute reflectance measurement must be made, an integrating sphere is the accessory to use.

With the advent and widespread availability of Fourier transform infrared (FT-IR) spectrometers and high-sensitivity infrared (liquid nitrogen cooled mercury-cadmium-telluride or MCT) detectors, Fuller and Griffiths [13] show the feasibility of collecting practical mid-infrared diffuse reflectance spectra. The optical configuration that they have devised is no longer used in commercially available accessories, but their work has paved the way for this technique which is now almost commonplace. Diffuse reflectance accessories now available for the mid-infrared use ellipsoidal mirrors to focus and collect the infrared energy. Optical configurations for the two main types of commercially available accessories, typified by Spectra-Tech's Collector and Harrick's Praying Mantis are shown in Fig. 5.10. The main difference between these two types of accessories involves the reduction of specular reflection. The Spectra-Tech accessory has no reasonable way to reduce the specular component, which can be a problem with highly absorbing samples, as has been discussed. The Harrick-type design is superior in this respect. With these accessories, sample position or height with respect to the ellipsoidal mirrors is crucial for obtaining reliable spectra with high S/N ratio. In this regard the Spectra-Tech accessory is superior. If one is to obtain routine diffuse reflectance spectra, either type of accessory will afford the opportunity to obtain quality spectra.

Whatever the accessory you choose, proper alignment of the accessory in the FT-IR spectrometer is the single most critical factor. Follow the instructions that come with the accessory, but do not think it will be easy. Alignment is a painstaking process, nevertheless, it is absolutely necessary that it should be done properly. Many accessories collect dust inside cabinets because they are deemed useless as a result of improper alignment. The idea is to obtain the maximum amount of signal by maximizing the

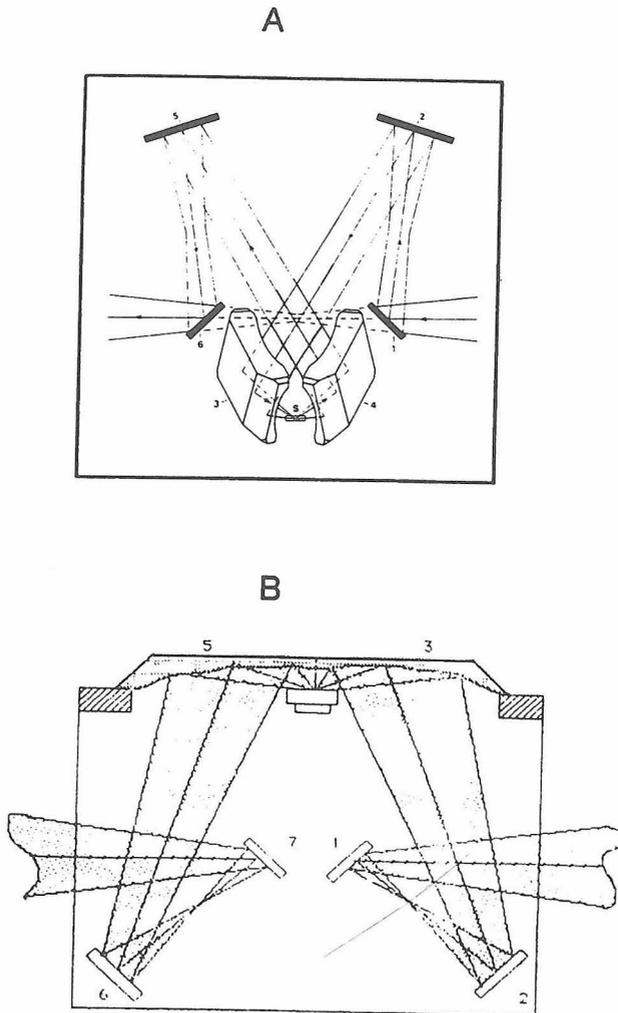


Fig. 5.10 Ray diagrams of two types of commercially available FT-IR diffuse reflectance accessories. (a) The accessory from Harrick uses an off-line optical geometry to eliminate specular Fresnel reflectance. (b) The accessory from Spectra-Tech uses an on-line optical geometry that collects the specular Fresnel component.

interferogram centerburst. This is usually done by monitoring the signal reaching the detector in the spectrometer's alignment mode while aligning the accessory. Be sure that any apertures present in the FT-IR spectrometer are fully open and that the detector gain is increased when beginning alignment procedures to enhance any potential signal.

Since most of the signal will, in any event, not reach the detector in diffuse reflectance spectroscopy, for best results it is important to have an FT-IR spectrometer that is properly configured. There are two primary considerations. First, the spectrometer should be equipped with a high-energy infrared source. Second, and probably more important, the spectrometer should be equipped with a high-sensitivity detector. Although a room temperature DTGS (deuterated triglycine sulfate) detector can be used, a liquid nitrogen cooled MCT detector is highly recommended.

It is not always necessary, but most diffuse reflectance mid-infrared work is performed by diluting the sample in a nonabsorbing matrix. It is a prudent practice to avoid spectral artifacts. This matrix is usually either powdered KBr or KCl. The particle size should be less than about 40 μm . Such small particles cannot be easily obtained by grinding in a mortar and pestle. The KCl should be first ground by hand in a mortar and pestle, followed by two minutes in a Wig-L-Bug grinder. This gives a particle size of about 5–10 μm . The KCl should then be dried in an oven for a few days and stored in a desiccator for use. Adsorbed water can have significant adverse effects on diffuse reflectance spectra.

Once the FT-IR is properly configured, the diffuse reflectance optical accessory is properly aligned, and the nonabsorbing matrix is prepared and dry, a background spectrum of the pure nonabsorbing matrix can be obtained. The sample cup should be filled with KCl and leveled off. For quantitative results if the KCl is to be packed, the sample spectrum must also be packed with the same force and duration. The sample height is then adjusted to maximize the signal at the detector, and the spectrum is ready to be obtained. Sample height is very important; changes in sample height of 0.1 mm or less from the optimum can cause significant distortions in the spectra [14].

Now that the background spectrum has been collected, it is time to collect the sample spectrum. Usually anywhere from a 2–15% by weight dispersion of the sample in KCl is adequate. The sample is mixed with KCl in a Wig-L-Bug for about one minute to provide a good dispersion. If grinding the sample is to be avoided, use the Wig-L-Bug without the grinding ball. The sample cup is then filled and leveled, the sample height is optimized as with the KCl background, and the spectrum is obtained. If qualitative or functional group information is all that is required, there is no need to convert the spectrum to Kubelka-Munk units. Simply analyze the spectrum as percent reflectance (analogous to percent transmittance) as a function of wavenumber.

To maintain quality spectra over time, one should realign the optical accessory weekly. This assumes the accessory has not been moved and no significant adjustments to the FT-IR have been made. New background spectra should be obtained daily in order to obtain the best possible spectra.

The aforementioned procedures represent what is deemed to be the best way to obtain diffuse reflectance mid-infrared spectra. This is not to preclude a hurried analyst from simply taking a powdered sample, placing it in the sample cup, optimizing sample height, and obtaining a spectrum (ratioed to pure KCl). If, however, the spectrum exhibits broad peaks, appears undifferentiated and/or distorted, diluting the sample in KCl and decreasing the sample's particle size will almost certainly improve the quality of the resulting spectrum.

5.4 APPLICATIONS OF DIFFUSE REFLECTANCE SPECTROSCOPY

Diffuse Reflectance UV-Visible Spectroscopy

Diffuse reflectance UV-visible spectroscopy is mostly used in the applied sciences for the analysis of dyestuffs, printing inks, paints and pigments, paper, ceramics, and so on. For color matching/analysis, visible diffuse reflectance spectroscopy is used for denture materials, tiles, cosmetics, and medicinal tablets, to name a few applications. Most of these applications do not reach the traditional chemical or spectroscopic literature for a variety of reasons. Much of this work is proprietary, and even if it is not proprietary it is industrially driven, so the desire or need to publish is not present. Also much of this work is not considered cutting edge research, since these applications have been around for many years. Even when the work is of excellent quality, it may be hard to publish. An excellent but older review of UV-visible diffuse reflectance applications is given by Wendlandt and Hecht [15]. A more recent general review of applications does not exist. However companies such as Labsphere, which are in the business, put out, useful literature [16] and are happy to offer assistance to someone with an interest in the technique. Although some capabilities and methods have changed, many applications have not. A few applications worth mentioning specifically follow.

Schmidt and Heitner [17] review the use of UV-visible diffuse reflectance spectroscopy for chromophore research on wood fibers. These workers investigated the chemistry of light-induced yellowing and reduction. UV-visible diffuse reflectance spectroscopy is also useful in applications where transition metal oxidation state is important, such as studies of metal oxidation and heterogeneous catalysis. One recent catalysis study [18] involved an *in situ* UV diffuse reflectance study of silica supported noble metal catalysts. The stainless steel cell, with gas inlet and outlet ports, is capable of temperatures as high as 500°C. The integrating sphere is externally interfaced with the spectrometer through fiber optic cables, so the

measurement is made remote to the spectrometer. The integrating sphere is directly attached to the quartz window of the reactor. The use of fiber optics for remote measurements in the UV-visible regions is now a practical option. For applications in which it is not feasible or wise to place the spectrometer where the sample is, fiber optics allows these measurements to be performed remotely.

Diffuse Reflectance Near-Infrared Spectroscopy

To say that NIR spectroscopic applications have in the past 10 years exploded is almost an understatement. A review article on NIR reflectance analysis (really diffuse reflectance, although not usually named as such in NIR parlance) in 1983 [19] called it a "Sleeper among Spectroscopic Techniques." Approximately 10 years later, an updated review article on NIR spectroscopy [20] proclaimed that "The Giant Is Running Strong." NIR reflectance spectroscopy has become an accepted tool for monitoring many industrial processes because it is fast, involves little sample preparation, is nondestructive, and can perform multicomponent analyses.

Absorption of radiation in the near-infrared region results predominantly from vibrations of light atoms with strong bonds. Primarily N-H, O-H, and C-H bonds are probed by NIR spectroscopy. This limits the chemical structures observed to mostly organic compounds. Since near-infrared absorption consists of overtones and combinations of fundamental (mid-infrared) absorptions, unique functional group type structural information is obscured. This fact makes it impossible to visually observe a spectrum to distinguish structural features. This has not deterred NIR spectroscopists because statistical methods allow one to perform quantitative analyses of extraordinarily complex samples with astounding success.

The NIR literature abounds with various statistical analyses of data sets such as partial least squares, principal components analysis, multiple linear regression, and neural networks. A sampling of a very small portion of this literature is provided [21-23]. The presumed problem with NIR reflectance analysis is that it relies so heavily on chemometrics. A spectroscopist cannot directly interpret an NIR reflectance spectrum. The quantitative data generated (which is pretty much what NIR spectroscopy is used for) comes from an algorithm that to most is a black box. This can lead to a feeling of a lack of control over the analysis, but it works! It should be noted that the ultimate success of a quantitative NIR reflectance analysis is dependent on intricate calibration procedures involving a training sample set that must be chosen and analyzed very carefully. The data generated are limited by the quality of the calibration. The interpretation of NIR spectra has advanced recently because of yet another sophisticated statistical correlation method described by Barton et al. [24].

A primary reason for the applicability of NIR reflectance spectroscopy is that since overtone and combination bands have extremely low absorptivities, this is the ideal region for diffuse reflectance applications. Recall from (5.1) that as absorptivity increases so does Fresnel or specular reflectance, the bane of diffuse reflectance spectroscopy. In the mid-IR, and to a lesser extent in the UV-visible, specular reflectance is reduced by dilution of the sample in a nonabsorbing matrix. Due to the low absorptivities in the NIR, specular reflectance is not a problem. This simplifies sample preparation requirements considerably. On the negative side, however, low absorptivities make NIR diffuse reflectance analysis a poor tool for trace analysis. If components are present in a sample at levels below 1%, NIR becomes a less than ideal tool.

NIR spectroscopy is dominated by necessarily pragmatic industrial scientists. Therefore the practice of NIR diffuse reflectance spectroscopy is for the most part dissimilar to work in the other spectral regions. For instance, since the seminal work of Norris [25], quantitative diffuse reflectance measurements in the NIR has become routine for major components in agricultural commodities. Almost all NIR diffuse reflectance spectra are converted to $\log 1/R$ (apparent absorbance) before statistical analysis for quantitative data extraction. This implies that Beer's law is valid for NIR diffuse reflectance spectroscopy. Since Beer's law assumes that reflectance and scattering of radiation by the sample is insignificant, this is surprising. Surely many practitioners of quantitative NIR diffuse reflectance spectroscopy recognize this contradiction, but the use of $\log 1/R$ values for quantitative data interpretation works. Olinger and Griffiths [26], a full 20 years after the widespread use of this technique, attempt to explain this apparent contradiction.

Although the fact that apparent absorbance works in this application is of academic interest, it does not address the real reason for using $\log 1/R$ values. The application of NIR for quantitative work, as has been discussed, requires the use of a complicated chemometric model to extract spectroscopic information. The generation of a statistical model is difficult, costly, and time-consuming. For NIR reflectance spectroscopy to be of practical use, recalibration of the instrument should be rarely, if ever, required. The mathematical model should be as robust as possible. The use of the $\log 1/R$ function minimizes the effect of most of the inevitable changes in the instrument over time on the chemometric model.

Another significant difference between NIR diffuse reflectance spectroscopy and the technique in other spectral regions is how the scattered radiation is collected. Traditional laboratory researchers in NIR reflectance spectroscopy, as has been previously discussed, often use integrating spheres to collect spectra. Since this is a highly applied field, however, ease of sample analysis is very important. In the purchase of an NIR reflectance spec-

trometer for a typical quantitative application, there is no integrating sphere to be found. A holder is provided that you simply fill with sample. The sample scatters the radiation, and the detector collects the scattered radiation at some set of angles determined by the geometry of the spectrometer. Many NIR diffuse reflectance fiber optics applications work on the same principle.

The sheer number and variety of NIR applications published each year is astounding. More than 500 articles a year are now published ranging from agricultural to pharmaceutical to imaging applications. This is not even counting all of the proprietary work that never gets published. Although not all of these involve diffuse reflectance, many NIR applications use this phenomenon. Just a few such applications will be discussed.

One source containing a wealth of recent work in NIR spectroscopy is a book edited by Murray and Cowe [27]. One can find instrumental advances in fiber optics, studies on recent statistical approaches to analyze data sets and NIR reflectance studies of plants, agricultural commodities, polymers, textiles, and so on.

An interesting example of NIR reflectance spectroscopy, described by Lodder et al. [28], involves the direct analysis of single pharmaceutical tablets. A specially designed sample holder was described to enable rapid and convenient measurements of capsules. The sample holder fits into the sample compartment of a commercial NIR spectrometer.

A couple of interesting biomedical applications have been recently published. Tamura [29] used fiber optic bundles to measure absorption changes of rat brains *in vitro*. Marbach and Heise [30] describe a diffuse reflectance accessory for *in vivo* measurements of human skin tissue. These workers demonstrated the ability to perform noninvasive measurements of blood glucose level. Another accessory, not necessarily for biomedical work, is described by Hogue [31]. This accessory allows samples to be mounted horizontally rather than vertically as in an integrating sphere, which is useful for certain applications.

Sample preparation for NIR diffuse reflectance spectroscopy involves just a couple of considerations. Sample particle size and packing density should remain constant. This is because both parameters affect the scattering properties of the sample. One way to keep particle size constant is to grind the sample in a Wig-L-Bug grinder. Many samples, such as agricultural commodities like wheats, should be ground for this reason. Another good reason to grind complex samples such as these is for homogenization. Many complex samples are inherently heterogeneous, so depending on where the sample beam hits the specimen, one may obtain different spectra. For quantitative analysis this state of affairs is not recommended. A relatively new field that has begun to find its way to NIR reflectance spectroscopy is spectral imaging. Imaging spectroscopy determines the distribution of

constituents in a heterogeneous sample. Robert et al. [32] describe an NIR reflectance spectral imaging system to determine the components of wheat. NIR reflectance spectroscopy is a broad and currently very active field.

Diffuse Reflectance Mid-Infrared Spectroscopy

General Considerations

It took a few years, but the work in 1978 by Fuller and Griffiths [13] has resulted in an explosion of applications in diffuse reflectance mid-infrared spectroscopy, many of which were predicted in their original publication. The acronym for this technique, coined by Griffiths, is *Diffuse Reflectance Infrared Fourier Transform Spectroscopy*, or DRIFTS. While this is arguably an unfortunate acronym, the technique has proved to be widely applicable. The wealth of direct spectroscopic information inherent in a mid-infrared spectrum, which results mainly from fundamental vibrational modes, made the promise of extending this already proven technique to mid-infrared spectroscopy highly promising. The technique has come to fulfill many of these expectations, and in this section a smattering of applications of DRIFTS will be discussed.

Undoubtedly the most widely used application of DRIFTS, not to be found in the literature, is the rapid identification of powders with little or no sample preparation. If a lot of sample is available, the option exists to simply fill the sample cup and obtain the spectrum. This is not recommended, however; it is worth taking the extra two minutes to make a dispersion in KCl to collect the spectrum properly. If only a small amount of sample is available, it is necessary to prepare the sample as a dispersion in KCl. An important but little recognized fact is that very little sample is required to obtain a spectrum of high S/N ratio. Most samples will yield a quality spectrum with just 0.1 mg of sample, and detection limits of less than 10 ng of sample dispersed in KCl have been observed [33].

These astonishingly low detection limits, even compared to transmission spectroscopy, are observed because of the phenomena that govern transmission and diffuse reflectance spectroscopy. In transmission spectroscopy the S/N ratio of a spectrum is directly proportional to sample concentration, which can be shown as a consequence of Beer's law. In diffuse reflectance spectroscopy the S/N ratio is proportional to the square root of the sample concentration. So if the FT-IR and accessory are configured such that an adequate signal is reaching the detector, which is easily attainable, DRIFTS is actually a much more sensitive technique than transmission spectroscopy.

DRIFTS as a Chromatographic Detector

Although it is advantageous to dilute a sample in KCl before obtaining a DRIFT spectrum, in some cases this may not be desirable. One such

example is the use of DRIFTS as a detector for species separated by thin-layer chromatography (TLC-IR). While this approach has met with some success as demonstrated by a review article on the subject [34], the strong absorption bands from silica below $\sim 1500\text{ cm}^{-1}$ results in considerable spectral distortion. Many methods have been tried to eliminate the strong absorbance from silica. Most of these methods involve analyte transfer from the TLC plate [35, 36] which, of course, requires significant sample preparation. Danielson et al. [37] have gone so far as to perform TLC on a zirconium oxide stationary phase. These authors' reasoning is that since zirconium oxide does not exhibit intense absorptions until $\sim 1100\text{ cm}^{-1}$, the useful spectroscopic range could be extended without the need for sample transfer. It is probably safe to predict that work will continue in this area before DRIFTS detection of separated species on TLC plates is widely applicable.

DRIFTS in Surface Science and Heterogeneous Catalysis

For a variety of reasons, DRIFTS is becoming the single most important technique for studying the surface chemistry of high surface area powders. A diffuse reflectance spectrum is much more sensitive to surface species than the bulk because the beam is reflected off the surface of particles. This is unlike transmission spectroscopy where a beam passes through the entire sample. Because a scattering sample is mandatory, spectra show no energy loss at high wavenumbers characteristic of transmittance spectra of samples like silica or alumina. Pressing pellets of pure silica or alumina can be very difficult, along with some drawbacks inherent in pellet pressing of these types of samples [2, 3]. Also, in catalytic studies, making a KBr pellet can inhibit adsorption of reactants onto catalyst active sites.

Figure 5.11 illustrates the surface selectivity afforded by DRIFTS as compared to transmission spectroscopy. These spectra are of organosilane-modified Cab-O-Sil[®] fumed silica. The transmission spectrum yields no useful spectroscopic information below $\sim 1400\text{ cm}^{-1}$, whereas the DRIFTS spectrum exhibits peaks to 400 cm^{-1} which is the detector cutoff. The surface selectivity of the DRIFTS technique has allowed the investigation of surface reactions on silica in the 1000 cm^{-1} region underneath the strong silica matrix absorption using spectral subtraction [38]. Many applications of DRIFTS to study surface reactions and interactions both qualitatively [39, 40] and quantitatively [41] have been reported.

The idea that DRIFTS is a highly sensitive technique has been shown to be true in surface analysis as well as in conventional microsampling. Van Every et al. [42] investigated the detection limit of CO adsorbed on a heterogeneous catalyst. These workers showed that adsorbed CO on a 3% Rh/Al₂O₃ catalyst can be detected at 10^{-6} of a monolayer. This detection limit is comparable to that of some ultrahigh vacuum (UHV) methods often

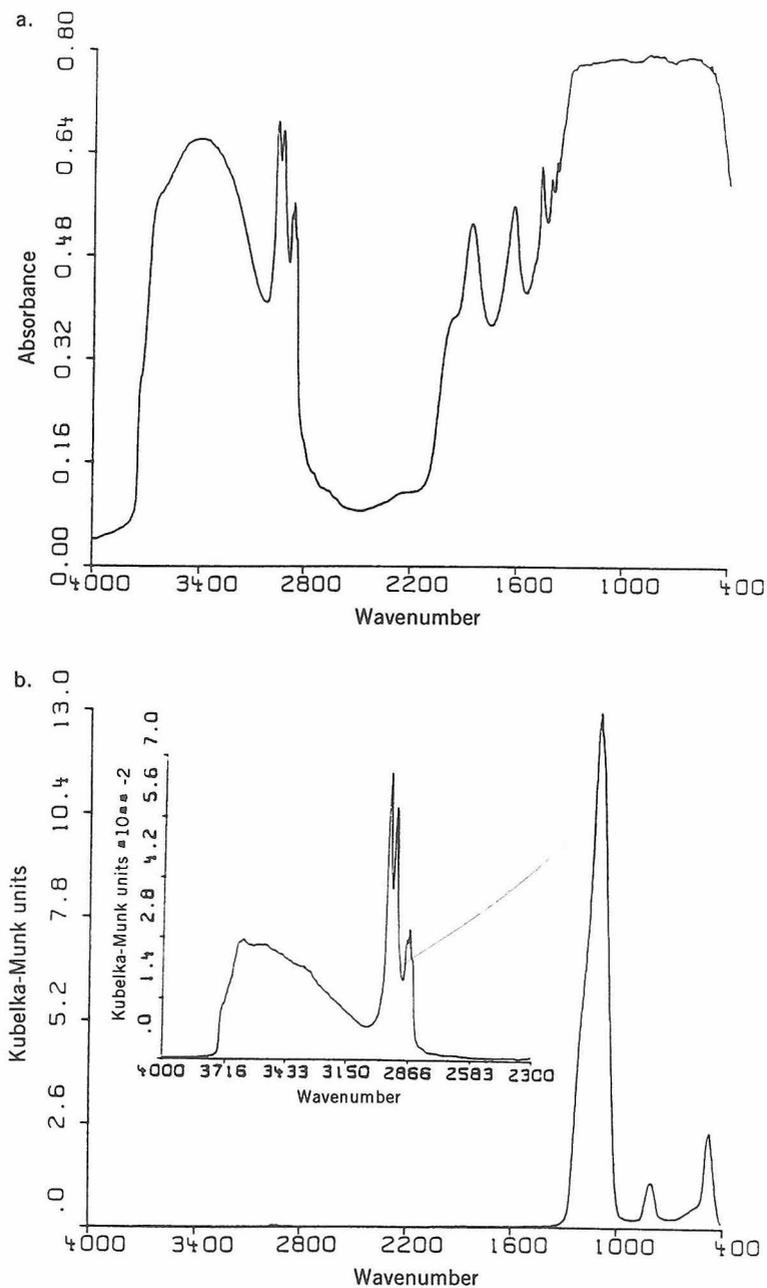


Fig. 5.11 Infrared spectra of a modified silica. (a) Transmission spectrum, and (b) diffuse reflectance spectrum.

used in heterogeneous catalyst characterization without the UHV constraints.

When using DRIFTS for catalytic or degradation studies, it is necessary to perform variable temperature/controlled atmosphere work. These studies require special cells for this work, and extra precautions must be taken to avoid spectral artifacts. These variable temperature/controlled atmosphere cells can be obtained commercially from the same vendors who sell the optical accessories. Since vendors' accessories differ, variable temperature cells are generally not transferrable between different companies' optical accessories.

Murthy et al. [14] were the first to report the fact that sample position varies as a function of temperature in variable temperature DRIFTS work. These workers found that thermal expansion of the sample post as temperature is raised causes significant spectral changes. Thus precise control of sample height is a necessity in performing careful variable temperature DRIFTS work. Venter and Vannice [43] subsequently provided some excellent suggestions for modifying DRIFTS accessories for variable temperature/controlled atmosphere work.

At least one additional factor must be considered when performing variable temperature DRIFTS work. At high temperatures the sample itself becomes an infrared emitter [44] which can saturate the signal reaching the detector. MCT detectors (unfortunately but not surprisingly) are more susceptible to this effect than DTGS detectors [45]. The result of this is that when one performs variable temperature work, it is important that the background spectrum be obtained under identical conditions to the sample spectrum. The spectra should be collected when the sample is at the optimum sample position and at the same temperature to avoid potentially severe spectral artifacts.

In performing catalytic or degradation studies using variable temperature DRIFTS, some workers have found that interfacing the DRIFTS accessory to a mass spectrometer can be very useful. This allows one to simultaneously monitor reactions occurring at the surface of the particle and desorption reaction products. One such apparatus is detailed by White [46] to study polymer degradation. Augustine et al. [47] used DRIFTS/MS to study surface reactions and kinetics of a heterogeneous catalyst for vinyl acetate synthesis. An excellent DRIFTS/MS system for catalyst research has also been described by Highfield and coworkers [48]. One DRIFTS/MS apparatus is schematically shown in Fig. 5.12.

Miscellaneous Applications of DRIFTS

The literature is too diverse to provide a comprehensive review of DRIFTS applications. In this final section a few more applications will be briefly discussed, and the reader can refer to the references provided herein.

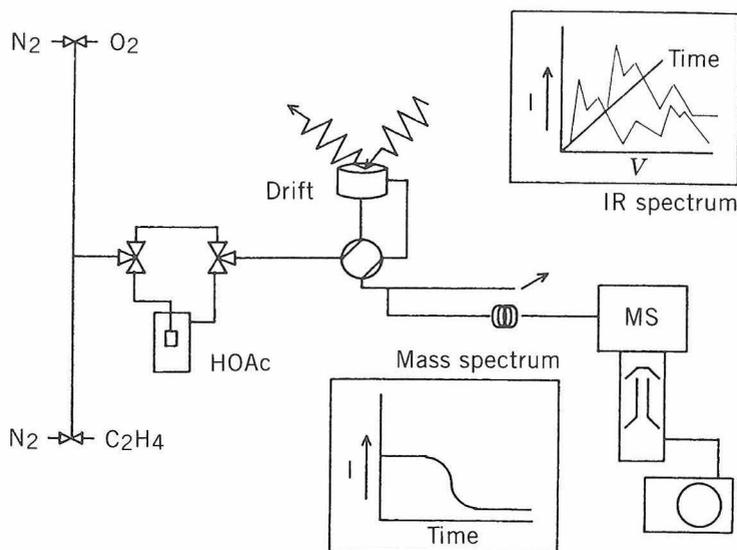


Fig. 5.12 Schematic of an FTIR diffuse reflectance accessory interfaced to a mass spectrometer. The DRIFTS cell, filled with catalyst, is used as a reactor, while the mass spectrometer detects vapor phase reaction products. Reprinted with permission from *Appl. Spectrosc.* 45(1991): 1746.

Polymer studies (powder, composites, foams, fibers) have been particularly amenable to DRIFTS studies. Recently Mitchell published an excellent review on this subject [49] which is highly recommended for anyone new to the field of DRIFTS. Nguyen et al. [50] published a fairly comprehensive treatise on the use of DRIFTS in soil studies. These workers discuss both advantages and disadvantages of the DRIFTS technique for characterizing a range of soil samples. They found that DRIFTS is most useful for the determination of clay mineralogy and organic matter. Suzuki et al. have published a series of papers concerning the application of DRIFTS to forensic science. Their first paper [51] discusses the nuts and bolts of applying DRIFTS to these types of samples. Recently Gilber et al. [52] discuss the application of DRIFTS and chemometrics to distinguish different cellulosic fabric types and the effects of sequential stages of the textile process.

5.5 CONCLUSIONS

Diffuse reflectance spectroscopy is a technique that is widely applied from the UV to the mid-infrared spectral regions. Whereas diffuse reflectance spectroscopy is most readily applicable to powders, any sample that scatters

radiation can be characterized using this technique. To obtain reliable results, one should have some understanding of the fundamentals. The need to dilute samples to minimize specular reflectance, especially in the mid-infrared, should be understood. Each spectral region contains inherent information and also different considerations in performing diffuse reflectance work. The UV-visible and NIR regions primarily utilize integrating spheres to collect diffuse reflectance spectra. In the mid-infrared, biconical optical devices are used. The mid-infrared region contains the most specific chemical information, but in many ways it is also the most demanding region to perform diffuse reflectance work. Many applied studies have been carried out in all of the spectral regions, with the NIR and mid-IR exhibiting the most growth in the past 10 years.

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