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Reflectance IR Spectroscopy

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1. Introduction

Infrared spectroscopy is study of the interaction of radiation with molecular vibrations which can be used for a wide range of sample types either in bulk or in microscopic amounts over a wide range of temperatures and physical states. As was discussed in the previous chapters, an infrared spectrum is commonly obtained by passing infrared radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy (the energy at which any peak in an absorption spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule).

Aside from the conventional IR spectroscopy of measuring light transmitted from the sample, the reflection IR spectroscopy was developed using combination of IR spectroscopy with reflection theories. In the reflection spectroscopy techniques, the absorption properties of a sample can be extracted from the reflected light.

Reflectance techniques may be used for samples that are difficult to analyze by the conventional transmittance method. In all, reflectance techniques can be divided into two categories: *internal reflection* and *external reflection*. In internal reflection method, interaction of the electromagnetic radiation on the interface between the sample and a medium with a higher refraction index is studied, while external reflectance techniques arise from the radiation reflected from the sample surface. External reflection covers two different types of reflection: *specular* (regular) reflection and *diffuse* reflection. The former usually associated with reflection from smooth, polished surfaces like mirror, and the latter associated with the reflection from rough surfaces.

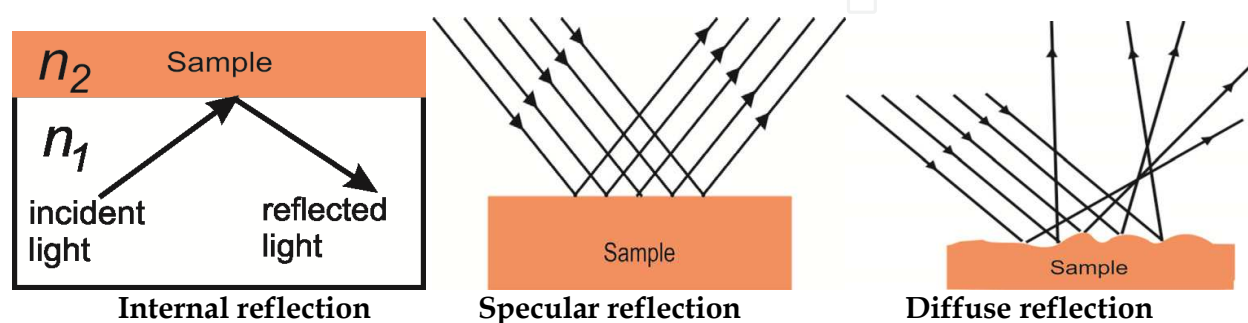


Fig. 1. Illustration of different reflection phenomenon.

2. Reflectance methods

Upon interaction of electromagnetic radiation with a sample surface, depending on the characteristic of the surface and its environment, the light may undergo three types of reflection, *internal reflection*, *specular reflection* and *diffuse reflection*. In practice, all three types of reflections can occur at the same time, although with different contributions. Specular reflection is defined as light reflected from a smooth surface such as a mirror (any irregularities in the surface are small compared to λ) at a definite angle whereas diffuse reflection produced by rough surfaces that tend to reflect light in all directions.

2.1 Internal reflectance spectroscopy (IRS)

Internal reflectance Spectroscopy (IRS) date back to the initial work of Jacques fahrenheit and N.J.Harrick [1, 2] that independently devised the theories of IRS spectroscopy and suggested a wide range of applications. Internal reflection Spectroscopy is often termed as attenuated total reflection (ATR) spectroscopy. ATR became a popular spectroscopic technique in the early 1960s.

Attenuated total reflection spectroscopy utilizes total internal reflection phenomenon[3]. An internal reflection occurs when a beam of radiation enters from a more dense medium (with a higher refractive index, n_1) into a less-dense medium (with a lower refractive index, n_2), the fraction of the incident beam reflected increases as the angle of incidence rises. When the angle of incidence is greater than the critical angle θ_c (where is a function of refractive index of two media), all incident radiations are completely reflected at the interface, results in *total internal reflection* (Figure 2). In ATR spectroscopy a crystal with a high refractive index and excellent IR transmitting properties is used as internal reflection element (IRE, ATR crystal) and is placed in close contact with the sample (Figure 3). The beam of radiation propagating in IRE undergoes total internal reflection at the interface IRE- sample, provided the angle of incidence at the interface exceeds the critical angle θ_c . Total internal reflection of the light at the interface between two media of different refractive index creates an "evanescent wave" that penetrates into the medium of lower refractive index [3].

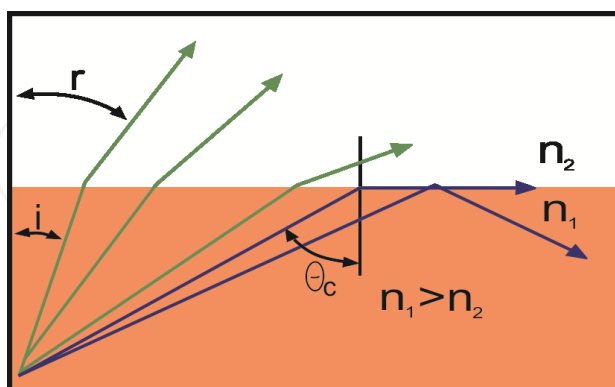


Fig. 2. Illustration of total internal reflection.

The evanescent field is a non-transverse wave along the optical surface, whose intensity decreases with increasing distance into the medium, normal to its surface, therefore, the field exists only the vicinity of the surface. The exponential decay evanescent wave can be expressed by Eq. (1):

$$I_{ev} = I_0 \exp (-Z/P) \quad (1)$$

Where z is the distance normal to the optical interface, dp is the penetration depth (path length), and I_0 is the intensity at $z = 0$.

The depth of penetration, dp , is defined as the distance from the IRE- sample boundary where the intensity of the evanescent wave decays to $1/e$ (37%) of its original value), is given by Eq. (2):

$$dp = \lambda / \{ 2\pi n_1 [\sin^2 \theta - (n_2/n_1)^2]^{1/2} \} \quad (2)$$

Where λ is the wavelength of the radiation, n_1 is the refractive index of the IRE (ATR crystal), and n_2 refractive index of the sample, and θ is the angle of incidence. Figure 3 illustrates the evanescent wave formed at the internal reflection element- sample interface.

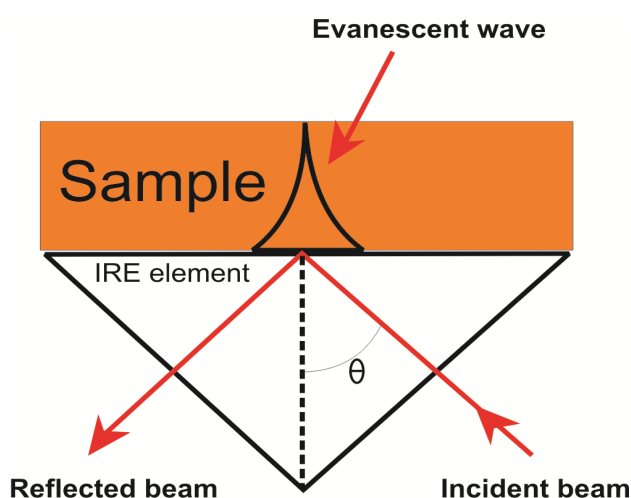


Fig. 3. Penetration of evanescent wave into the sample.

An ATR spectrum can be obtained by measuring the interaction of the evanescent wave with the sample. If an absorbing material is placed in contact with ATR crystal, the evanescent wave will be absorbed by the sample and its intensity is reduced (attenuated) in regions of the IR spectrum where the sample absorbs, thus, less intensity can be reflected (attenuated total reflection). The resultant attenuated radiation as a function of wavelength produces an ATR spectrum which is similar to the conventional absorption spectrum except for the band intensities at longer wavelengths (Figure 4). This difference is due to the dependency of the penetration depth (dp) on wavelength: at longer wavelength, the evanescent wave penetrates deeper into the sample, thus, the absorption bands at longer wavelengths are relatively more intense than those shorter wavelengths. This results in greater absorption on the longer wavelength side of an absorption band, contributing to band distortion and band broadening.

Additionally, compared to the transmission spectrum, small differences may be seen in an ATR spectrum which arises from dispersion effects (variation of refractive index of a material with change of wavelength). An anomalous dispersion causes the refractive index and the penetration depth changes through an absorption band. For instance the effect of dispersion on penetration depth for cocaine is demonstrated in Figure 5. As can be seen, penetration depth changes strongly at wavelength in which the dispersion is the highest.

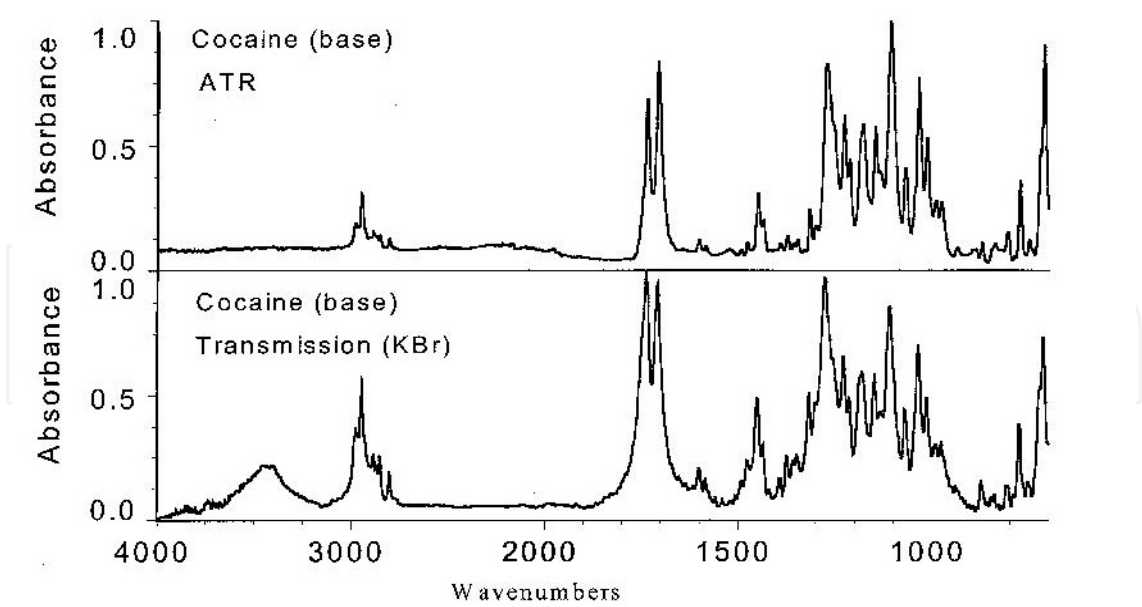


Fig. 4. Representation of ATR and Transmittance IR spectrum of Cocaine [4].

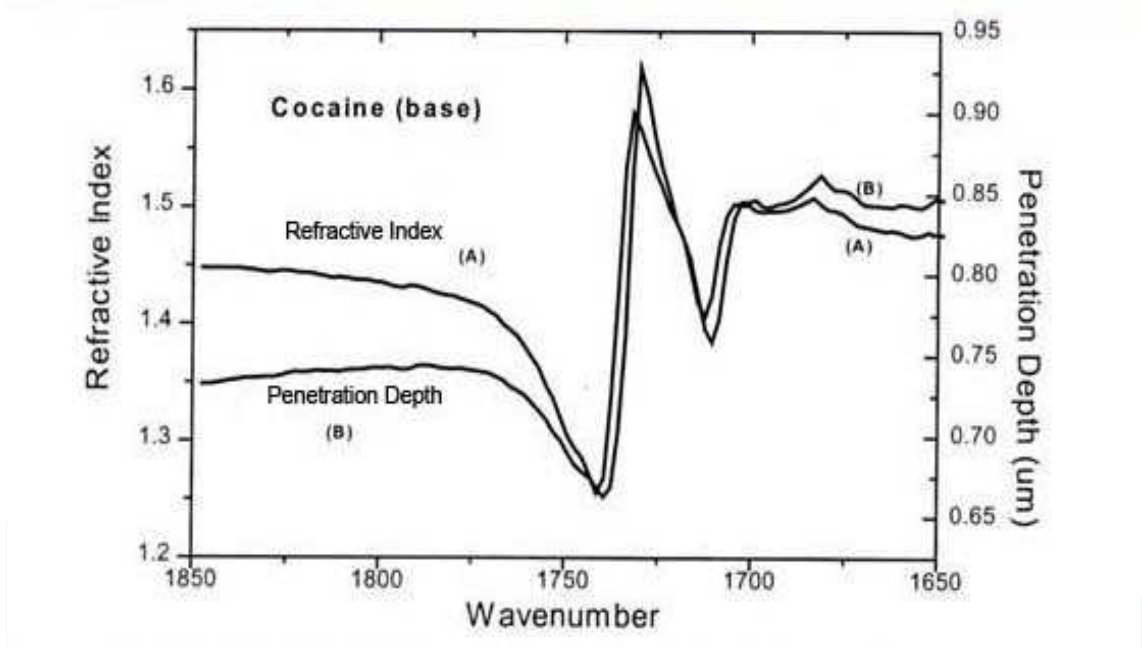


Fig. 5. Penetration depth and refractive index for cocaine at carbonyl absorbance band [4].

Sometimes an empirical so-called ATR correction is applied to compensate across the spectrum for linear wavelength increase, which is termed as Eq.(3):

$$R_{\text{corr}} \sim R / \lambda$$

(3)

Other differences may occur due to the surface effects between the sample and internal reflection element (IRE crystal). For instance, the degree of physical contact between IRE and the sample influences the sensitivity of an ATR spectrum. Since the evanescent wave only propagates 2-15 μm beyond the surface of the crystal, thus, an intimate contact of the IRE with the sample is essential.

Two configurations of ATR accessory are available. In a single bounce-ATR, a single internal reflection occurs using a prism whereas Multi-Bounce ATR, undergoes multiple internal reflections (up to 25) using special prisms, as shown in Figure 6. In a multiple internal reflection cell, the effective path length of the sampling surface is the product of the number of reflections at measurement surface and penetration depth. In practice, multiple internal reflections (in Multi-Bounce ATR technique) produce more intensive spectra by multiple reflections and, hence it is useful for weak absorbers, while the single bounce-ATR is suitable for strong absorbers.

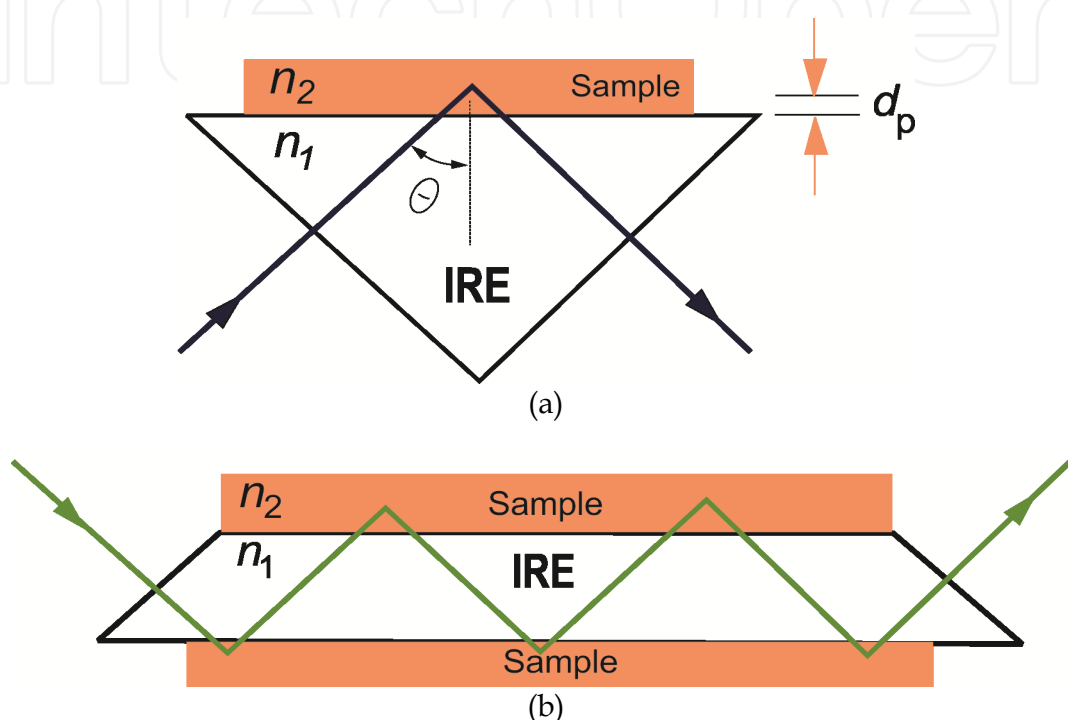


Fig. 6. Schematic representation of total internal reflection with (a) Single reflection, and (b) Multiple reflections.

There are different designs of ATR cell including traditional ATR, horizontal ATR and cylindrical ATR for solids and liquids samples. In the traditional ATR, a thin sample is clamped against the vertical face of the crystal. This design has been replaced by more modern designs, horizontal and cylindrical designs. In horizontal ATR (HATR), the crystal is a parallel-side plate (typically 5 cm by 1 cm) with the upper surface exposed (Figure 6 (b)). The number of reflections at each surface of the crystal depends on length and thickness crystal as well as the angle of incidence (usually between five and ten).

The traditional design is used for continuous surface such as sheets and horizontal ATR (HATR) cells are suitable for liquids and pastes as well as soft powder and sheets films. Application of cylindrical ATR (Figure 7) cell is limited to mobile fluids.

2.1.1 ATR crystals

The ATR crystals are made from materials that have a very high refractive index and low solubility in water. Table 1 summarizes some of the commonly materials used in ATR crystals. Amongst these materials, diamond, zinc selenide (ZnSe) and germanium (Ge) are

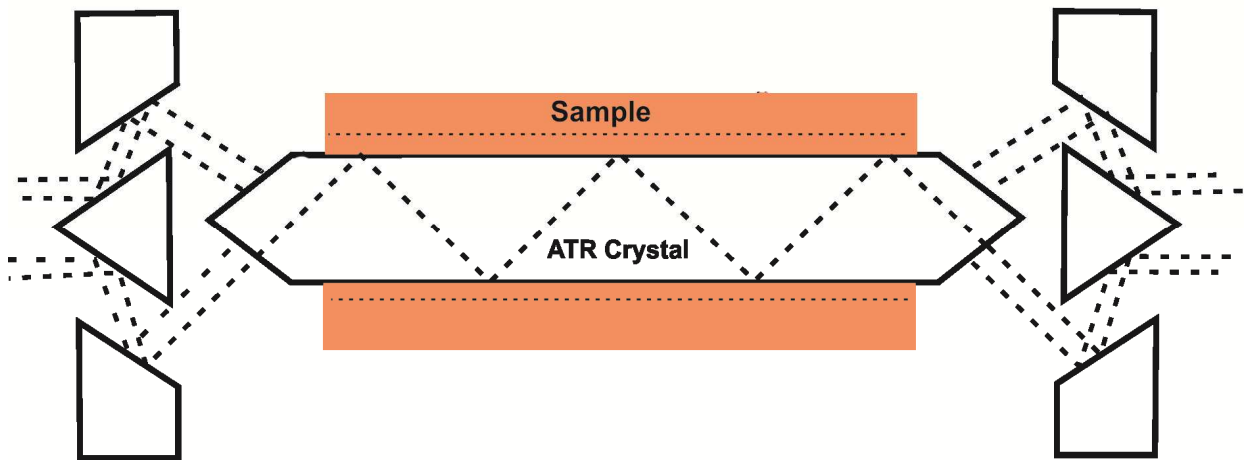


Fig. 7. Schematic representation cylindrical ATR cell.

| Material | Wave range (cm ⁻¹) | Refractive index (at 1000 cm ⁻¹) |
|--|--------------------------------|--|
| Zinc Sulfide (ZnS) | 17,000 - 950 | 2.2 |
| Zinc Selenide (ZnSe) | 20,000- 650 | 2.41 |
| Diamond | 45000-2500; 1800 -< 200 | 2.4 |
| Germanium (Ge) | 5,5 00 -870 | 4.0 |
| Cd telluride (CdTe) | 10,000-450 | 2.65 |
| Saphire (Al ₂ O ₃) | 25,000-1800 | 1.74 |
| Cubic Zirconia (ZrO ₂) | 25,000-1800 | 2.15 |
| KRS-5 (TlI ₂ /TlBr ₂) | 20,000-350 | 2.37 |
| AMTIR (As/Ge/Se glass) | 11,000-750 | 2.5 |

Table 1. Materials used as ATR crystals

the most common materials used ATR crystals. Diamond can be used for a wide range of samples, because it is resistant to scratching and abrasion and can tolerate a wide pH range as well as strong oxidants and reductants. Also, due to its ideal properties, it often used as a protective film for ATR crystals such as zinc sulfide (ZnS). However, high cost of diamond causes that its application is limited. Ge with a higher refractive index is suitable for analyzing of samples with high refractive index. However, ZnSe preferred for all routine applications, but because of its low resistivity towards surface etching, reactivity with complexing agents such as ammonia, and damaging with strong acids and alkalis, its application is limited. AMTIR with similar refractive is a good alternative for ZnSe crystal, when involve strong acids.

2.1.2 Application of ATR spectroscopy

ATR technique is used commonly in the near -infrared for obtaining absorption spectra of thin films and opaque materials. However, ATR spectra can be obtained using dispersive IR instruments, but the higher-quality spectra are obtained using FTIR spectrometers.

ATR is one of the most versatile sampling techniques that requires little or no sample preparation for most samples. It only requires that the sample is placed in intimate contact with the IRE crystal, which achieved by pressing the solid onto the crystal with a high pressure

clamp. Powders and soft pliable films can be used without any additional preparation and highly crystalline solids should be ground before application. It is an ideal method for liquids and oils, because the contact between the crystal and a liquid is inherently close and hence without requiring the high pressure clamp, liquids are applied directly onto the crystal.

As a conclusion, ATR is a non-destructive technique for a variety of materials including soft solid materials, liquids, powders, gels, pastes, surface layers, polymer films, samples solutions after evaporation of the solvent. It is an ideal technique for thick and dark colored materials which often absorb too much energy to be measured by IR transmission. Despite of these advantages, lack of a good contact between the sample and IRE can lead to non-accurate results. Also, there are a few IRE crystals to be compatible with the samples properties, especially from pH point of view.

2.2 Specular reflectance spectroscopy

The incident radiation focused onto the sample may be directly reflected by the sample surface, giving rise to specular reflection, and it may also undergo multiple reflections at the sample, resulting in diffuse reflection. In external reflectance techniques, the radiation reflected from a surface is evaluated (Figure 8).

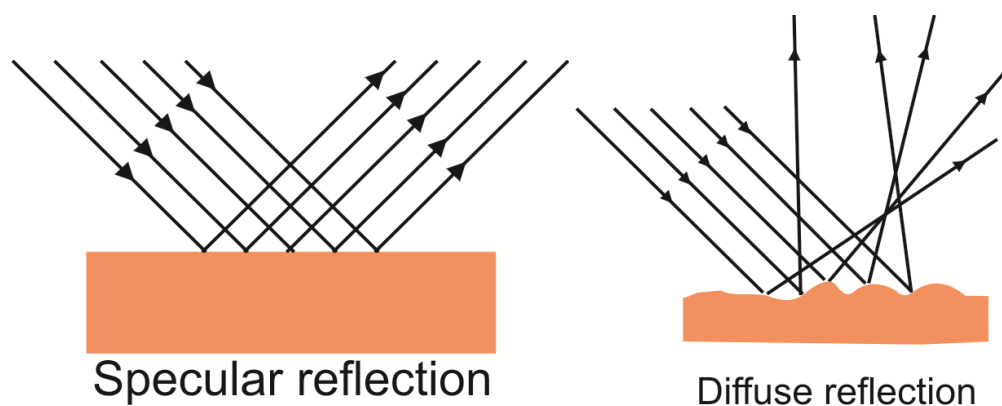


Fig. 8. Illustration of external reflection.

Specular reflectance techniques basically involve a mirror-like reflection from the sample surface that occurs when the reflection angle equals the angle of incident radiation. It is used for samples that are reflective (smooth surface) or attached to a reflective backing. Thus, specular techniques provide a reflectance measurement for reflective materials, and a *reflection-absorption (transflectance)* measurement for the surface films deposited on, or pressed against reflective surfaces (Figure 9).

The reflectance spectra differ from those recorded in transmission, they appear as "derivative-like" bands. These spectra can be converted into absorption one by using of Kramers-Kronig transformation (K-K transformation) that is available in most spectrometer software package. Figure 10 depicts specular reflectance spectrum of oil on surface of machined steel cylinder.

In absorption-reflection measurement, one fraction of the radiation is reflected on the upper interface and contributes towards the spectrum via specular reflection. Another part of the radiation penetrates the surface film and is reflected by the reflective surface, thus, the light

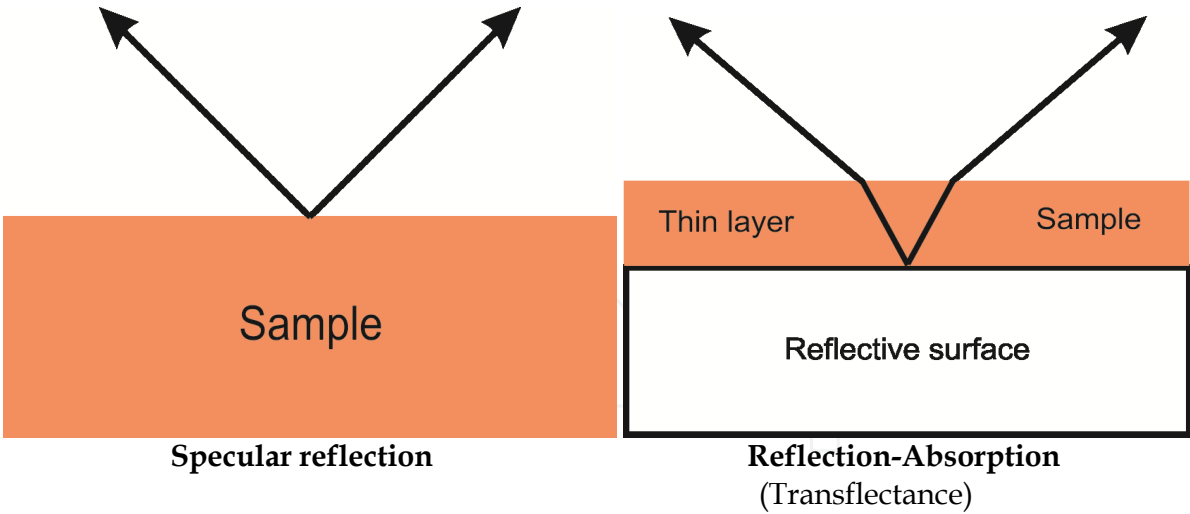


Fig. 9. Illustration of specular reflectance.

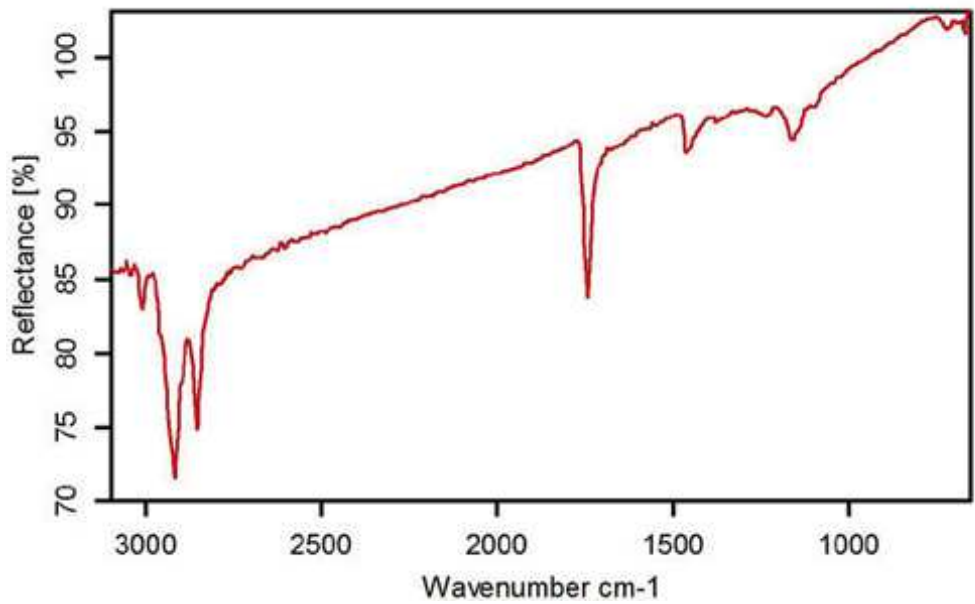


Fig. 10. Specular reflectance spectrum of oil on surface of machined steel cylinder.

passes through the surface layer twice-to and from the reflective surface, leading to increase the intensity of the reflectance spectrum as compared to the normal transmission. The effective path length depends on the angle of incidence, therefore, for thin films, a grazing angle of incidence as high as 80°- 85° from normal incidence should be used, and for thick films an angle close to normal incidence is applied.

The most common applications of this technique are evaluation of surfaces such as: coating, thin films, contaminated metal surface.

2.3 Diffuse Reflectance Spectroscopy (DRS)

In diffuse reflectance spectroscopy, the electromagnetic radiation reflected by roughened surfaces is collected and analyzed. When this technique is applied in (FT) IR region, it is termed as diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). It is also

known "*Kubelka-Munk*" reflection, because they developed a theory on the radiation transport in scattering media [5].

Light incident onto a solid sample may be partly reflected regularly (specular reflection) by the sample surface, partly scattered diffusely, and partly penetrates into the sample. The latter part may be absorbed within the particles or be diffracted at grain boundaries, giving rise to diffusely scattered light in all directions. Diffuse reflectance spectroscopy associated with the reflected lights which are produced by diffuse scattering (Figure 11). Since regular reflection distorts the DRS spectra, thus, the regular reflection component should be eliminated in diffuse reflectance measurement. The DRIFTS accessory is designed to eliminate the specularly reflected radiation.

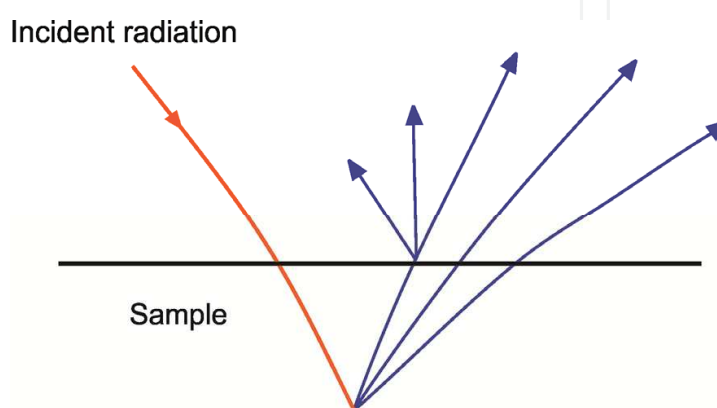


Fig. 11. Representation of diffuse reflectance.

In diffuse reflectance spectroscopy, there is no linear relation between the reflected light intensity (band intensity) and concentration, in contrast to traditional transmission spectroscopy in which the band intensity is directly proportional to concentration. Therefore, quantitative analyzes by DRIFTS are rather complicated. The empirical Kubelka - Munk equation relates the intensity of the reflected radiation to the concentration that can be used for quantitative evaluation. The Kubelka-Munk equation is defined as:

$$f(R_{\infty}) = (1 - R_{\infty})^2 / 2R_{\infty} = c/k = K/s \quad (4)$$

where $f(R_{\infty})$ is Kubelka-Munk function, R_{∞} is the absolute reflectance of layer (the ratio of the sample diffuse reflectance spectrum and a non-absorbing reference (normally KBr or KCl)), both measured at indefinite depth. K is the absorption coefficient, s is the diffusion (scattering) coefficient which is proportional to the fraction of diffused light, k is molar absorption coefficient (proportional to the fractional of transmitted light) and c is sample concentration. The reflectance, R_{∞} , indicates the sample is thick enough that no radiation reaches the back surface (indefinite thickness). Applying Kubelka-Munk function on the reflectance spectrum produces a spectrum (corrected spectrum) that resembling the transmission spectrum (Figure 12). Also the corrected spectrum demonstrates a linear relationship between band intensity and the sample concentration.

In the case of $R_{\infty} < 0.01$, the simpler function $\log 1/R_{\infty}$ is often used for measuring the diffuse reflectance. Since such small R_{∞} value is usually found in the near-IR region, therefore, an alternative relationship between concentration and reflected intensity in near-IR is defined as:

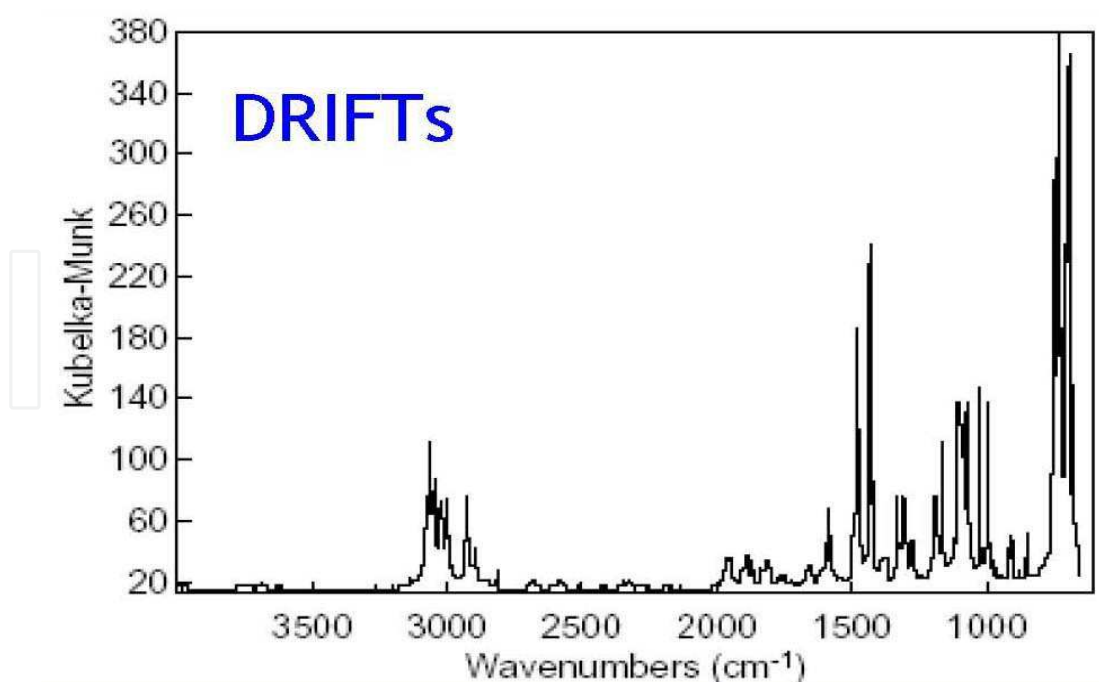


Fig. 12. DRIFT spectrum of 1,2-bis (diphenyl phosphino) ethane, pure powder [6].

$$\log (1/R_{\infty}) = k'c \quad (5)$$

where k' is a constant.

In Kubelka-Munk equation it is assumed that s is independent of wavelength and the sample is weakly absorbing. The former condition is achieved by proper sample preparation and the latter by dilution of strong absorbing samples with non-absorbing substrate powder (such as KBr or KCl). Therefore, to obtain reproducible results, particle size, sample packing and dilution should be carefully controlled, especially for quantitative analysis.

2.3.1 Application of diffuse reflectance spectroscopy

Diffuse reflectance technique is used for powders and solid samples having rough surface such as paper, cloth. In diffuse reflectance technique, particles size, homogeneity, and packing density of powdered samples play important role on the quality of spectrum. A sample with smaller particle size having narrow size distribution is preferred. Thus, in order to obtain a qualified spectrum, the sample should be ground into smaller size.

In this method, the sample can be analyzed either directly in bulk form or as dispersions in IR transparent matrices such as KBr and KCl. Sometimes, a thin film of KBr powder placed on the sample surface to improve the quality of the spectrum. Dilution of analyte in a non-absorbing matrix increases the proportion of diffuse reflectance in the reflected light. Typically, the solid sample is diluted homogeneously to 5 to 10% by weight in KBr. The spectra of diluted samples are similar to those obtained from pellets when plotted in units such as $\log 1/R$ (R is the reflectance) or Kubelka-Munk units.

Diffuse reflectance measurement in near-IR is more common than in mid-IR. Because non-absorbing scattering substrates are rare in mid-IR, and also more efficient scattering occurs at shorter wavelengths (near-IR). Additionally, due to lower efficiency of the scattering in

mid-IR, diffuse reflectance is very weak in this region, as a consequent, in mid-IR, diffuse reflectance could only be measured by FT-IR spectrometer (DRIFTS).

In diffuse reflectance spectroscopy, diffusely scattered light can be directly, collected from material in a sampling cup or, alternatively, collected by using an abrasive sampling pad. In mid-IR, the diffusely reflected light from sample is generally collected by large ellipsoidal mirrors, which cover as much area above the sample as possible. In near-IR, diffuse reflectance spectra are usually measured by an integrating sphere, described by Ulbrich, (Figure 14). The inner surface of "Ulbrich sphere" is coated by strongly scattering, non-absorbing powder. After repeated reflection, all radiations reach the detector. Thus, with Ulbrich sphere the entire radiation reflected by the sample is integrated.

In mid-IR region, the inner surface of diffuse scattering sphere is treated with gold vapor to guarantee a high degree of reflection, while in near- IR region, Ulbrich sphere consists of spectralon (a thermostatic resin) which is applied as white standard due to its high degree of reflection.

DRIFTS is a versatile technique for analyzing nontransparent samples, powders, roughened surfaces and coating. It offers the advantages of easy sample preparation and applicability to analyze samples at elevated temperature and pressure [6]. Consideration spectrum obtained for an organic material by transmission IR using KBr pellet and DRIFTS reveals the capacity of DRIFTS compared to transmission (Figure 12,13). Both spectra show similar spectrum that corresponds to absorption bands of the sample, but in the spectrum recorded in transmission mode an intensive band appeared at 3500 cm^{-1} which is related to the water present in the KBr pellet. This example, demonstrates DRIFTS combines the advantages of easy sample preparation with the absence of water band in the spectrum.

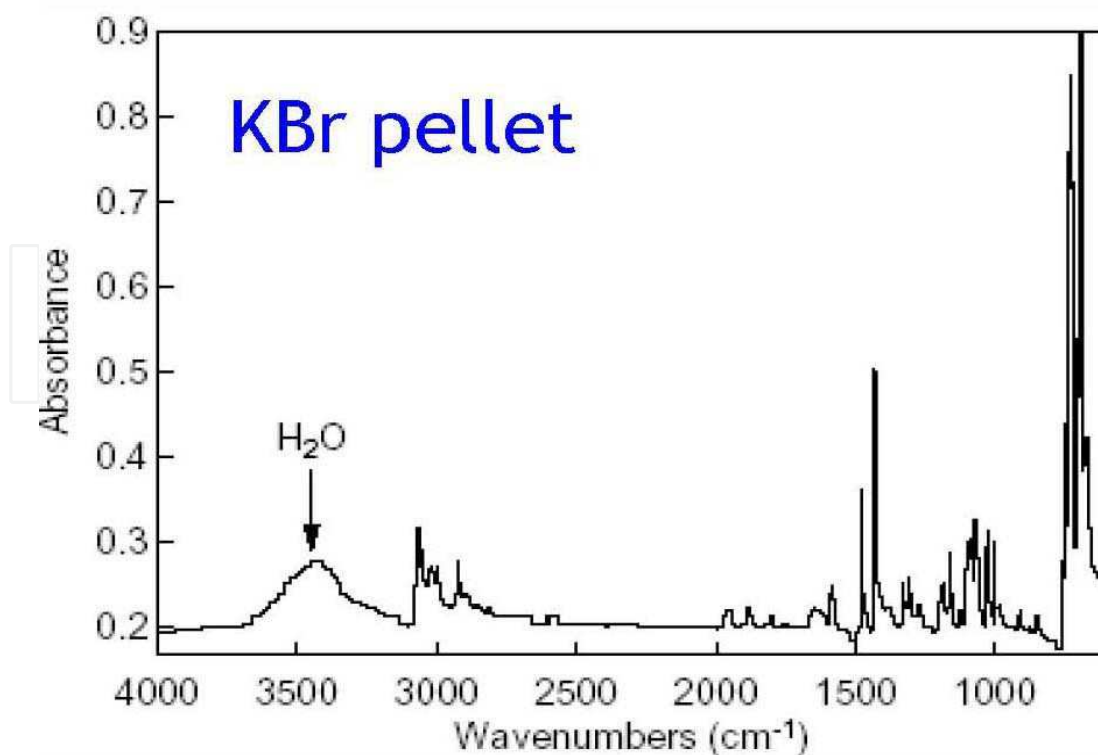


Fig. 13. Transmission spectrum of 1,2-bis (diphenyl phosphino) ethane, KBr pellet [6].

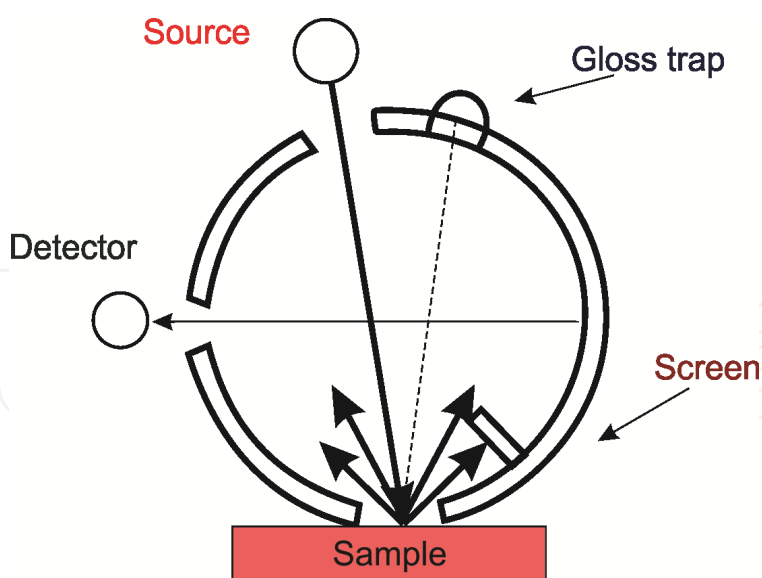
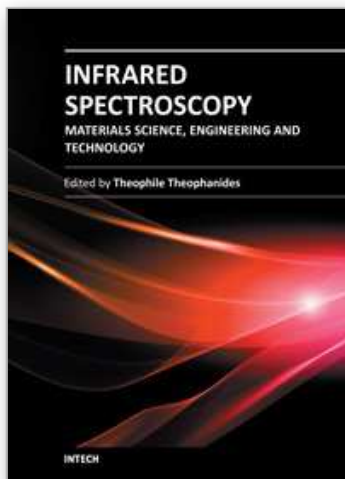


Fig. 14. Integrating Sphere.

The most disadvantage of this technique is difficulty of quantitative analyses. Since the diffusion coefficient strongly depends on sample preparation, thus the reflectance intensity is influenced by the sample preparation. A same sample may produce different spectra in different experiments.

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The present book is a definitive review in the field of Infrared (IR) and Near Infrared (NIR) Spectroscopies, which are powerful, non invasive imaging techniques. This book brings together multidisciplinary chapters written by leading authorities in the area. The book provides a thorough overview of progress in the field of applications of IR and NIR spectroscopy in Materials Science, Engineering and Technology. Through a presentation of diverse applications, this book aims at bridging various disciplines and provides a platform for collaborations among scientists.

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