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A REVIEW OF FT-IR DIFFUSE REFLECTION SAMPLING CONSIDERATIONS

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ABSTRACT

Diffuse reflectance is widely used for examining rough surfaced materials, samples abraded on substrates, powder, and reactions on powders. A variety of sampling methods are used for diffuse reflectance analysis. It is important to understand the theoretical constraints to correctly interpret the data for qualitative or quantitative applications. This article reviews the most commonly used theory of diffuse reflectance and discusses its limitations relative to the various sample handling methods used and the commercially available diffuse reflectance accessories.

I. INTRODUCTION

Diffuse reflectance spectroscopy was originally developed for UV-VIS spectroscopic inspection of materials used in the paper and textiles industries. It was subsequently applied as a general method for infrared analysis of rough surfaced materials and powders. Today, many of those samples are examined by ATR due to more straightforward sample handling and data interpretation. However, diffuse reflectance continues to be used, particularly for studying reactions and samples deposited on rough substrates.

Unlike internal (ATR) or specular reflection, diffuse reflection spectroscopy lacks an exact theoretical description. This is due to the complexity of the problem rather than a lack of understanding the fundamental underlying mechanisms and phenomena. The complexity of the exact description stems from the fact that powders are inhomogeneous on a scale comparable to the wavelength of light. This results in scattering in addition to absorption when the incident radiation interacts with the medium. Scattering alters the effective pathlength of the light through the medium. Thus diffuse reflectance depends not only on the properties that govern the interaction of light with materials but also the scattering characteristics of a particular sample.

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Several models have been developed to describe diffuse reflectance,[1–4] the most widely used model being that put forth by Kubelka and Munk.[5]

This article reviews the Kubelka-Munk theory of diffuse reflectance, touching upon concepts that are important to understanding the imposed design constraints and the experimental results. This provides a foundation for the discussion of accessories and sample handling methods that follows.

II. THEORY

The diffuse reflectance spectroscopic technique has an extremely narrow definition relative to the physical phenomenon of diffuse reflectance. Consider light impinging on a flat, roughened, metallic surface. Each ray reflects from the surface in accordance to the laws of reflection. However, the aggregate effect of the surface texture is to scatter the reflected radiation over a large solid angle. This type of reflection is generally considered front surface reflection or diffused specular reflection since no light penetrates into the material.

For transparent material such as finely ground glass, the light reflects from the surface of the powder and penetrates into the powder (see Fig. 1). Since the powder is internally inhomogeneous, the radiation penetrating into the sample scatters from numerous points. This is the key to the theoretical description of diffuse reflection.

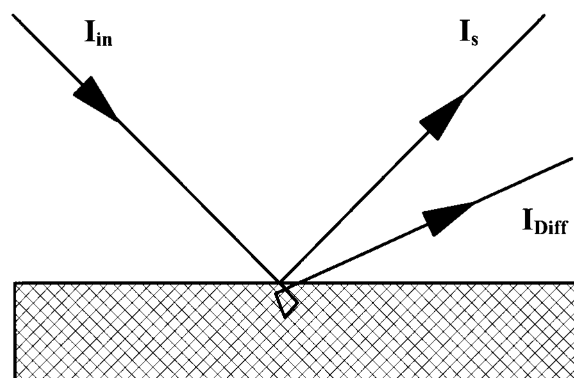

Figure 1. The two components of reflected light in diffuse reflectance: I_s is the front surface or specularly reflected light and I_{Diff} is the diffusely reflected radiation.

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Due to the nature of inhomogeneous materials, only approximate theoretical descriptions of diffuse reflectance exist. Of these, the Kubelka-Munk model is the most widely accepted.

A. Overview of the Kubelka-Munk Model

The Kubelka-Munk model assumes that the scattering process can be described in a similar manner to the absorption process. The scattering process is a direct result of the grain boundaries. Assuming that the powder is randomly inhomogeneous, the phases of the scattered waves add randomly giving zero time average in the product. Thus instead of describing diffuse reflectance using the amplitude of the radiation, it can be described by the intensity of the light propagating through the randomly inhomogeneous medium. The amount of radiation scattered, I_s, along the infinitesimal path, dx, is proportional to the radiation intensity, I, and the scattering coefficient, s:

$$\frac{dI_s(x)}{dx} = -I(x) \tag{1}$$

Eq. (1) is the direct analog to the absorption law:

$$\frac{dI_{\text{abs}}(x)}{dx} = -I(x) \tag{2}$$

Essentially, the difference between Eqs. (1) and (2) is that the radiation is absorbed by the medium in the latter, while, for the former, the light is scattered by the medium but remains inside. Thus scattering causes the radiation to propagate in various directions through the medium, preserving the overall radiation intensity. By scattering in various directions, the effective pathlength through the medium increases.

If a semi-infinite sample is illuminated from above, two components of light can be distinguished within the sample. One component, $I_+(x)$, travels generally downward and the other, $I_-(x)$, travels generally upward. According to Eqs. (1) and (2), the change in intensity of the two components can be expressed as:

$$\begin{aligned} \frac{dI_+(x)}{dz} &= -(k+s)I_+(x) + sI_-(x) \\ \frac{dI_-(x)}{dx} &= -(k+s)I_-(x) - sI_+(x) \end{aligned} \tag{3}$$

The first term of Eq. (3) represents the decrease in radiation intensity due to scattering and absorption. The second term is the positive contribution to the intensity that comes from the scattered component traveling in the

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opposite direction. The reversal of the sign in Eq. (3) is a consequence of the opposite direction of travel of $I_{-}(x)$ with respect to x-axis. Equation (3) can be rewritten as:

$$\frac{d}{dz}\begin{pmatrix} I_{+} \\ I_{-} \end{pmatrix} = \begin{pmatrix} -(k+s) & s \\ -s & (k+s) \end{pmatrix}\begin{pmatrix} I_{+} \\ I_{-} \end{pmatrix} = \mathbf{A}\begin{pmatrix} I_{+} \\ I_{-} \end{pmatrix} \tag{4}$$

Equation (4) formally looks like a single first order differential equation with a constant "coefficient" $\mathbf{A}$. The solution is:

$$I(x) = e^{\mathbf{A}x} I(0) \tag{5}$$

In order to calculate $e^{\mathbf{A}x}$, first define matrices σ_1 and σ_2 as:

$$\begin{aligned} \sigma_1 &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \\ \sigma_2 &= \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \end{aligned} \tag{6}$$

Note that:

$$\sigma_1\sigma_2 + \sigma_2\sigma_1 = 0 \tag{7}$$

Using Eq. (11) we can write $\mathbf{A}x$ as:

$$\mathbf{A}x = \alpha_1\sigma_1 + \alpha_2\sigma_2 \tag{8}$$

where $\alpha_1 = -(k+s)x$ and $\alpha_2 = sx$. Thus:

$$e^{\mathbf{A}x} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \tag{9}$$

where:

$$\begin{aligned} a_{11} &= \cosh\sqrt{\frac{k}{s}\left(\frac{k}{s}+2\right)}sx - \frac{k/s+1}{\sqrt{\frac{k}{s}\left(\frac{k}{s}+2\right)}}\sinh\sqrt{\frac{k}{s}\left(\frac{k}{s}+2\right)}sx \\ a_{12} &= \frac{1}{\sqrt{\frac{k}{s}\left(\frac{k}{s}+2\right)}}\sinh\sqrt{\frac{k}{s}\left(\frac{k}{s}+2\right)}sx \\ a_{21} &= -\frac{1}{\sqrt{\frac{k}{s}\left(\frac{k}{s}+2\right)}}\sinh\sqrt{\frac{k}{s}\left(\frac{k}{s}+2\right)}sx \\ a_{22} &= \cosh\sqrt{\frac{k}{s}\left(\frac{k}{s}+2\right)}sx + \frac{k/s+1}{\sqrt{\frac{k}{s}\left(\frac{k}{s}+2\right)}}\sinh\sqrt{\frac{k}{s}\left(\frac{k}{s}+2\right)}sx \end{aligned} \tag{10}$$

For the sample of thickness t one can rewrite Eq. (5) as:

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$$\begin{pmatrix} I_r \\ 0 \end{pmatrix} = \mathbf{A} \begin{pmatrix} I_{\mathrm{IN}} \\ I_R \end{pmatrix} \tag{11}$$

where $I^-(t) = 0$ because there is no light entering sample from the back side, $I^+(t) = I_T$, $I^+(0) = I_{\mathrm{IN}}$, and $I^-(0) = I_R$. Rewriting Eq. (11) explicitly yields:

$$\begin{aligned} I_T &= a_{11} I_{\mathrm{IN}} + a_{12} I_R \\ 0 &= a_{21} I_{\mathrm{IN}} + a_{22} I_R \end{aligned} \tag{12}$$

Since $R = I_R/I_{\mathrm{IN}}$, the second equation in Eq. (12) becomes $R = -a_{21}/a_{22}$. Also, since $T = I_T/I_{\mathrm{IN}}$, it follows from the first equation in Eq. (12) that $T = a_{11} - a_{12}a_{21}/a_{22}$.

For a semi-infinite sample thickness, $t \to \infty$, the reflectance is:

$$R_\infty = \frac{1}{1 + \frac{k}{s} + \sqrt{\frac{k}{s}\left(\frac{k}{s} + 2\right)}} = 1 + \frac{k}{s} - \sqrt{\frac{k}{s}\left(\frac{k}{s} + 2\right)} \tag{13}$$

This, of course, is just the Kubelka-Munk result. In the same limit, $t \to \infty$, the solutions for the components become:

$$I_\pm(x) = I_\pm(0) e^{-\sqrt{k(k+2s)}x} \tag{14}$$

Thus the solution simplifies to exponentially decaying functions.

Note that as k/s approaches zero, the reflectance, R, nears one. The reflectivity decreases infinitely sharply as k/s increases from zero. This implies the extreme sensitivity of diffuse reflectance to weak absorptions.

To obtain an absorption-like spectrum from diffuse reflectance, k/s needs to be expressed in terms of R. Rearranging Eq. (13) gives:

$$\frac{k}{s} = \frac{(1 - R)^2}{2R} \tag{15}$$

Eq. (15) is the well-known Kubelka-Munk transform. The Kubelka-Munk formula describes reflectance of semi-infinite sample with negligible front surface reflectance.

Expression (15) is the analog of the absorbance transformation in transmission spectroscopy. Due to it simplicity, the Kubelka-Munk method has been widely incorporated as the diffuse reflectance transform in the standard infrared spectroscopy software of all commercial FTIR spectrometers.

Note that as $k \to 0$, $R_\infty \to 1$, i.e., all the incident light is eventually reflected, and the solutions become:

$$I_\pm(x) = I_\pm(0) \tag{16}$$

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Finally, let's examine the solutions for a finite sample thickness for non-absorbing but strongly scattering samples (i.e., $k = 0$ and $s \neq 0$). In that case, the equations in Eq. (10) reduce to:

$$\begin{aligned} a_{11} &= 1 - sx \\ a_{12} &= sx \\ a_{21} &= -sx \\ a_{22} &= 1 + sx \end{aligned} \tag{17}$$

If the matrix elements (Eq. (17)) are inserted into the expression for reflectance, we find:

$$R = \frac{1}{1 + (1/st)} \tag{18}$$

and similarly for transmittance:

$$T = 1 - st + \frac{st}{1 + (1/st)} \tag{19}$$

where t is sample thickness. Note that, since there is no absorption, energy conservation requires that:

$$R + T = 1 \tag{20}$$

This can be verified by explicit calculation from Eqs. (18) and (19). Finally, the solutions within the sample for the sample of final thickness t are:

$$\begin{aligned} I_{+}(x) &= \frac{1 + s(t - x)}{1 + st} I_{\mathrm{IN}} \\ I_{-}(x) &= \frac{s(t - x)}{1 + st} I_{\mathrm{IN}} \end{aligned} \tag{21}$$

We see that in the limit $t \to \infty$ the above solutions become constants (I_{IN} and I_{R}) as already determined in Eq. (16) and fully consistent with infinite penetration depth.

B. Penetration Depth for Diffuse Reflectance

The penetration depth is defined as the value of x at which the function decays to $1/e$ of the initial value. Thus the penetration depth is, from Eq. (14):

$$d_p = \frac{1}{\sqrt{k(k + 2s)}} \tag{22}$$

Thus stronger scattering and absorption coefficients result in shorter penetration depths. If the absorption coefficient vanishes, the penetration

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becomes infinite. If the absorption is infinitely strong, the penetration depth vanishes. This relationship between the penetration depth and the absorption coefficient is responsible for the extremely high sensitivity of diffuse reflectance to weak absorbers. Since absorption depends on the product of absorption coefficient and the path traveled, and since the path traveled is proportional to the penetration depth, the product:

$$kd_p = \frac{1}{\sqrt{1 + (2s/k)}} \tag{23}$$

becomes infinitely sensitive to small changes in k around $k = 0$.

C. Scattering Coefficient Model

The coefficient, s, introduced in Eq. (1), is a semi-empirical parameter that accounts for the internal scattering processes. Kubelka-Munk theory considers the scattering coefficient essentially constant, so it offers few indications as to its functional dependence on the sample parameters. A simple model can be constructed to learn more about this scattering coefficient.

For the randomly shaped grains of a typical powder, the grain size and the space between the gains are on the same order of magnitude.

A diffusely reflecting material can be described as a series of parallel plates (see Fig. 2). Since a typical powder consists of randomly shaped grains where the grain size and the space between them are on the same

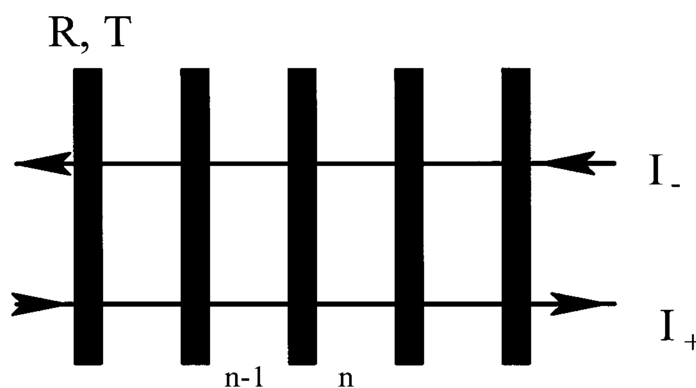

Figure 2. The layer model.

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order of magnitude, both the thickness of the plates and the distance between them can be represented by a single parameter, d.

In traveling through the medium, the light reflects at each plate and is absorbed in the space between the plates. As the reflected and transmitted components travel through the space between the plates, they pick up the standard transmission factor e^{-kd} with a sign that depends on the direction of propagation. At the plate between $(n-1)$th and nth layer, the components traveling in the $(n-1)$th layer are:

$$I_{n-1}^{\pm}(d) = I_{n-1}^{\pm}(0)e^{-kd} \tag{24}$$

where $I_{n-1}(d)$ indicates the value of the component at the end of the $(n-1)$th layer and $I_{n-1}(0)$ is the value of that component at the beginning of this layer. At the plate separating $(n-1)$th and nth layer, the following equations hold:

$$\begin{aligned} I_n^{+}(0) &= TI_{n-1}^{+}(d) + RI_n^{-}(0) \\ I_{n-1}^{-}(0) &= TI_n^{-}(0) + RI_{n-1}^{+}(d) \end{aligned} \tag{25}$$

assuming that the plates are non-absorptive (Eq. (20)).

Using Eqs. (24) and (20) to rearrange Eq. (25) gives:

$$\begin{aligned} I_n^{+} &= \frac{1}{T}\left[(1-2R)e^{-kd}I_{n-1}^{+} + e^{kd}RI_{n-1}^{-}\right] \\ I_n^{-} &= \frac{1}{T}\left[e^{kd}I_{n-1}^{-} - e^{-kd}RI_{n-1}^{+}\right] \end{aligned} \tag{26}$$

where I's refer to $I(0)$. The system (26) describes the propagation of the two components through the medium and can be used to evaluate the components in the next layer from their values in the previous layer. The calculation can precede recursively until one finds an expression connecting the incident reflected and transmitted light.

Note, however, that $I_{n-1}^{\pm}(0)$ really represents the value of component I at a distance $(n-1)d$ from the surface of the first plate. Assuming that d is small, $kd \ll 1$. This means that $e^{\pm kd} \approx 1 \pm kd$, so Eq. (26) can be rewritten as follows:

$$\begin{aligned} I^{+}(x+d) &= \left[1 - \left(\frac{R}{d} + k\right)d\right]I^{+}(x) + \frac{R}{d}dI^{-}(x) \\ I^{-}(x+d) &= \left[1 + \left(\frac{R}{d} + k\right)d\right]I^{-}(x) - \frac{R}{d}dI^{+}(x) \end{aligned} \tag{27}$$

Comparison with system (3) yields the result $s = R/d$.

The above result for the scattering coefficient has a compelling intuitive base, but it predicts apparently incorrect behavior for the scattering

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coefficient in the limit where $d \to 0$. As d approaches zero, the boundaries disappear and the material becomes perfectly homogeneous. Hence this implies that the reflectance, R, must also be a function of d.

Consider the reflectance of a thin free-standing film of refractive index n and thickness d. The expression for reflectance has been derived[6] to be:

$$R = \frac{|r|^2 4 \sin^2(nkd)}{1 + |r|^4 - 2|r|^2 \cos(2nkd)} \tag{28}$$

where the notation of Ref. [5] has been followed. Neglecting the $|r|^4$ and higher terms, Eq. (28) simplifies to:

$$R = 4|r|^2 \sin^2(nkd) \tag{29}$$

If $\lambda = (2\pi/k) \gg d$, then $ndk \ll 1$ and $\sin^2(nkd) \to (nkd)^2$. Thus for a grain size much smaller than the wavelength, the scattering coefficient is:

$$s = \frac{R}{d} = 4|r|^2 n^2 k^2 d \tag{30}$$

Hence when the "grain size" approaches zero, the scattering coefficient also nears zero, as expected. Note that Eq. (30) gives a definite prediction for the dependence of the scattering coefficient on wavelength, which differs significantly from Rayleigh's λ^4 law.

In the case of wavelengths that are short relative to the particle size, the reflectance of a grain involves a term, $\sin^2(nkd)$, which oscillates rapidly as the wavelength changes. Since there is a spread in the particle size, d, around some average value and since the average value of $\sin^2(nkd) = 1/2$, Eq. (30) can be rewritten as:

$$s = \frac{2|r|^2}{d} \tag{31}$$

Thus this intuitive picture of the scattering coefficient leads to a reasonable description of its dependence on the particle size.

The scattering coefficient is dominated by particle size and by the refractive index of the sample. It is a weak function of the wavelength[7] and the absorption coefficient. In addition, the scattering coefficient changes significantly with packing density.[8]

D. Front Surface Reflectance

The Kubelka-Munk model ignores the effects of front surface or specular reflectance. Front surface reflectance causes spectral anomalies,

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ranging from simple offsets in the measured values to severely distorted bands depending on the strength of the absorption index.

This effect can be understood by examining the Fresnel equations at normal incidence:

$$R = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2} \tag{32}$$

So the front surface reflectance varies with the absorption index. Note that in transmission, diffuse reflection and ATR the opposite effect occurs, i.e., an increased absorption index results in increased absorption by the sample, reducing the amount of light reaching the detector. In diffuse reflectance, only the light that was not specularly reflected from the sample can enter the sample and hence be absorbed. So an increased level of specularly reflected radiation counteracts absorption by the sample. Since the detector integrates both reflected components, the total reflectance at first decreases and then starts increasing as a function of the absorption index. This causes strong absorption bands to appear as spurious doublets, making the results inconclusive. Therefore, it becomes imperative to avoid or suppress the specular component.

III. SAMPLING CONSIDERATIONS

The Kubelka-Munk model incorporates several requirements regarding the sample. These assumptions are that the scattering coefficient is essentially constant throughout the sample, the front surface reflectance is minimized, the sample is infinity thick, and the illumination of the sample is isotropic. To apply this theory to the experimental measurements, these assumptions must be fulfilled as closely as possible.

A. Scattering Coefficient

The Kubelka-Munk model for a semi-infinite sample assumes that the absorption and scattering coefficients are uniform throughout the sample. From an experimental standpoint, this means that the sample must be thoroughly mixed and be as consistent as possible in grain size and packing density. Several devices for packing samples reproducibly have been described.[9,10]

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B. Front Surface Reflectance

To fulfill the Kubelka-Munk theoretical requirements, the collection of the front surface reflectance must be minimized. This is accomplished by a two-fold approach, involving both accessory design and sample preparation.

For most diffusely reflecting samples, the specularly reflected component is not isotropic. There is always a sizable component reflected as though the sample were a mirror. Two different accessory designs have been developed to avoid collecting this component. One method[11] employed simply avoids collecting radiation from that direction, as illustrated in Fig. 3. The other method[12] physically blocks the specular component, as shown in Fig. 4.

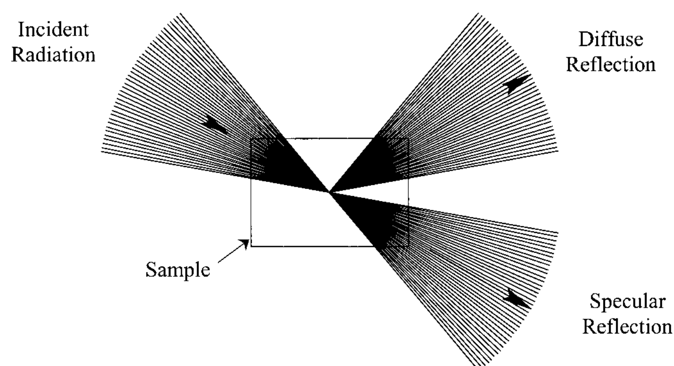

Figure 3. The geometric discrimination against collecting the specularly reflected radiation shown from above the sample.

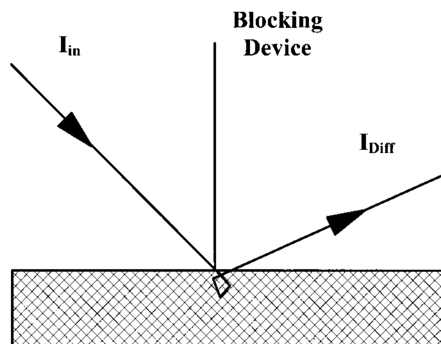

Figure 4. Physically blocking the specular component.

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An opaque shield is inserted at the focus of the accessory, touching the sample and thereby blocking all the specularly reflected radiation. The radiation passing through the sample under the blocking device is collected. This method is highly effective but also masks a large portion of the desired, diffusely scattered radiation. Even though both methods minimize the collection of the specularly reflected light, it is imperative to remember that specular reflection still occurred. Hence the Kubelka-Munk theory must be applied with care.

The specular component can also be suppressed by diluting the sample in a non-absorbing matrix. Samples are typically diluted to 5% in KBr. KBr powder is ideal since it is non-absorbing in the mid-infrared, soft, and hence easily ground with the sample. Since KBr adsorbs water, care must be taken to minimize interference from water. By diluting the sample in a non-absorbing matrix, the absorption index of the mixture is diluted, while the refractive index is not since KBr and the sample have similar refractive indices. This makes the specular reflectance essentially constant and total reflectance becomes interpretable through the Kubelka-Munk model.

C. Sample Thickness

The sample must be semi-infinitely thick to legitimately apply the Kubelka-Munk model. Thus, it is important to determine the minimum thickness for a sample to comply with this assumption. This can be deduced from the penetration depth, d_p, described in Eq. (22).

From Eq. (22), it is apparent that, for diffuse reflection, light penetration into the sample is influenced by the absorption coefficient of the sample. The results (14) and (22) indicate that, as a rule of thumb, the sample thickness should be at least three times the penetration depth. At that depth into the sample, the radiation intensities (Eq. (14)) diminish to 5% of their surface value. The problem with this requirement is that the penetration depth becomes infinite for a non-absorbing sample ($k = 0$). In practice, this is overcome by placing a sample onto a reflective surface. Diffuse reflection accessories are virtually always equipped with a powder sample cup made from metal that are typically more than 3 mm deep, providing ample sample thickness for a semi-infinite sample.[13]

An alternate sampling method recently become popular, even though it does not meet the Kubelka-Munk criterion for a semi-infinite sample. Diamond or SiC abrasives[14] are used as substrates for the sample. The background spectrum is measured with the clean abrasive and then the abrasive is rubbed against the sample for the sample spectrum. Since the sample is spread on the surface of the abrasive, this process is not even diffuse reflectance. However, this technique is convenient and quick.

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D. Isotropic Sample Illumination

Implicit in the Kubelka-Munk formulation is the assumption that the sample is subject only to diffuse irradiation. Uniform and isotropic illumination of the sample is clearly unattainable, since the solid angle above the sample must be used for both sample illumination and reflectance collection. An effort must be made to comply with this constraint as closely as possible.

This, however, is not the only limitation placed on sample illumination. Mid-infrared diffuse reflectance measurements are almost exclusively performed with commercial spectrometers, due to their high signal-to-noise ratios and excellent computational capabilities. The sample must be diffusely irradiated within the constraints imposed by the optical and mechanical design of these spectrometers. Typical FT-IR spectrometers have their infrared beam focused and this beam must be reimaged appropriately onto the sample.

The approach adopted for diffuse reflection accessories involves the use of a beam condenser with two symmetrically disposed ellipsoids to reimage and minify the beam. The strong minification used and the resulting large solid angle of the illuminating radiation provides isotropic illumination of the sample. The poor imaging quality of the ellipsoids helps scramble the image, making the radiation density fairly uniform across the sample. The use of a second ellipsoid, symmetrically positioned with respect to the sample, allows collection of the diffusely reflected radiation only from the illuminated portion of the sample.

By using this arrangement, flat mirrors can be integrated into the accessory design to direct the beam from the source image through the beam condensing ellipsoids to the spectrometer detector in a manner that is acceptable for the detection optics of the spectrometer. To further optimize the signal to noise ratio, the amount of the reflected radiation collected should be maximized. All of the spectrometer's radiation can be used to irradiate the sample, but only a portion of the reflected radiation is collected and sent to the detector. Some of the radiation is reflected away from the collecting mirror and is never measured by the detector.

Typically, only 5–10% of the incident radiation is collected. This is readily handled by most FTIR spectrometers.

IV. ACCESSORIES FOR DIFFUSE REFLECTANCE SPECTROSCOPY

There are two basic categories of diffuse reflection accessories available: basic and research grade. The research grade accessories minimize the

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specular component and accept reaction or environmental chambers, while the basic accessories are lower cost and most simply ignore the specular component.

One example of a research grade accessory is Harrick Scientific's Praying Mantis, the first commercially available accessory for diffuse reflectance. The Praying Mantis, shown in Fig. 5, pioneered geometrically discriminating against the collection of the specular component. This is accomplished by collecting the diffusely scattered radiation 60° away from the specular direction. The Praying Mantis has no restrictions on the sample size, since the incoming and outgoing rays from the sample are entirely contained either above or below the sampling plane. The Praying Mantis is

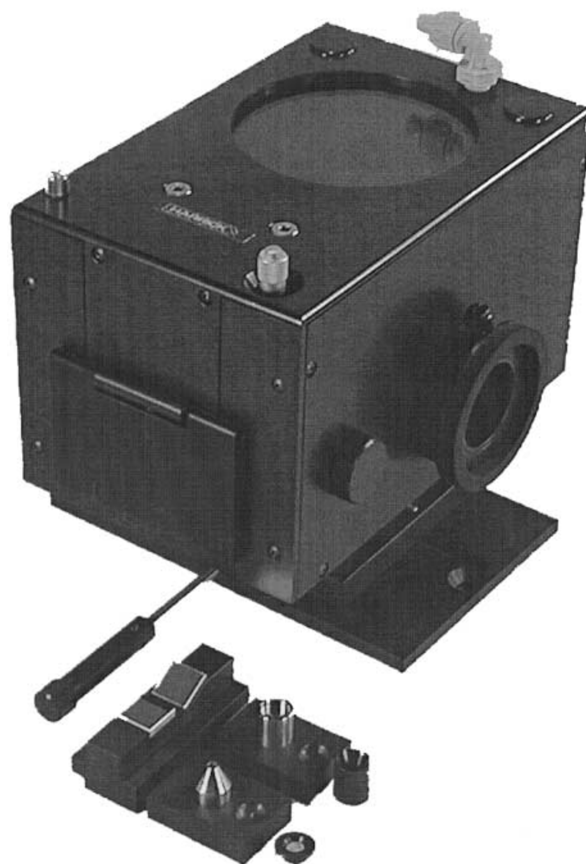

Figure 5. Praying Mantis diffuse reflectance accessory.

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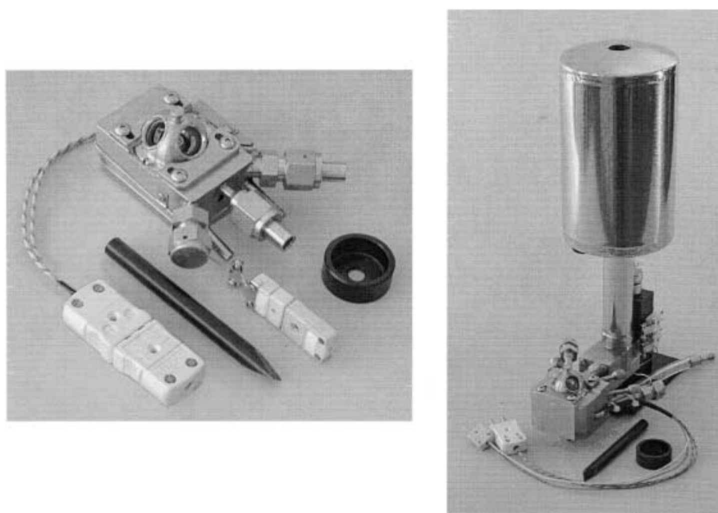

Figure 6. Reaction chambers for Praying Mantis accessory. High temperature chamber shown to the left. Low temperature, low pressure chamber shown to the right.

available in two configurations: a downward-looking model for routine analysis of powders and an upward-looking model for convenient analysis of cohesive solid samples. The downward-looking Praying Mantis accommodates reaction chambers for in-situ reaction and catalytic studies under controlled environmental conditions. These chambers, shown in Fig. 6, allow the sample temperature to be varied from -150°C to in excess of 600°C under vacuum. The sample can be exposed to inert or reacting gases under flow or static conditions and at pressures ranging from ultra-high vacuum to 500 psi.

All the features offered by the research grade diffuse reflectance accessories unfortunately make them complex and costly. As diffuse reflectance became more widely used for routine and QC measurements, the need arouse for simple, inexpensive accessories that are reasonably competent in executing diffuse reflection measurements. These accessories are primarily intended to verify that a sample is within an allowed deviation. One such accessory is Harrick's Cricket, shown in Fig. 7. The Cricket has two modes of operation: diffuse reflectance with optical discrimination against specular reflectance and in-line diffuse reflectance for collection of both the diffuse and specular components. This permits analysis of both diffusely and specularly reflecting materials. For sampling convenience, the Cricket is offered in both upward and downward looking configurations.

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Figure 7. Cricket diffuse reflectance accessory.

V. CONCLUSION

Diffuse reflectance measurements are typically carried out using commercial accessories installed in FT-IR spectrometers with the samples that are neat, diluted, or abraded onto a substrate. The selection of accessory and sampling method hinges on the type of information required. For quantitative results or reaction monitoring where the exact interpretation of the results is important, the Kubelka-Munk theoretical requirements must be satisfied as closely as possible. These limitations can be relaxed for quality control and other applications where quick measurements are important and the data will simply be compared to a standard.

Diffuse reflectance spectroscopy is an invaluable method for studying powders, rough-surfaced solids, and the reactions thereon.

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