T2 *SpectraTech*

Introduction to Diffuse Reflectance
Infrared Fourier Transform Spectroscopy
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INTRODUCTION

Diffuse reflectance has long been employed as a versatile sample analysis technique for ultraviolet, visible, and infrared spectroscopic analyses. [1,2] Initially, its use was restricted to the ultraviolet/visible or near-infrared regions of the spectrum because of the low energy throughput of many diffuse reflectance sampling devices, restrictions in spectrometer hardware, and acquisition procedures. With the advent of Fourier transform infrared spectrometers and improvements in diffuse reflectance accessory design, the technique became practical for routine use in the mid-infrared region. Currently, Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) offers a number of advantages as a sample analysis technique, including:

- *minimal or no sample preparation*
- *very high sensitivity (down to low ppm levels)*
- *applicability across a wide range of sample concentrations from parts per million to neat*
- *ability to analyze most non-reflective materials, including highly opaque or weakly absorbing materials*
- *ability to analyze irregular surfaces or coatings, such as polymer coatings on glass fibers*
- *suitability for very large, intractable samples through the use of specialized sampling devices*

High sensitivity and broad sample applicability make the technique especially popular. This Technical Note will explore the theory behind this versatile sample analysis technique, and will identify some practical considerations affecting its use in the analytical laboratory.

THEORY

When an infrared beam is focused onto a fine particulate material, the incident beam can interact with the particle in one of several ways. First, radiation can be reflected off the top surface of the particle at an angle of reflection equal to the angle of incidence without penetrating into the particle. This top surface reflection mode represents true specular reflection and is a function of the refractive index and the absorptivity of the material. Second, the light can undergo multiple reflections off particle surfaces, all without penetrating into the particle. After these multiple reflections, the resulting beam emerges from the sample at a random angle relative to the incident beam. This reflection mode, called diffuse

specular reflectance, is once again a function of the complex refractive index of the sample. The third mode of interaction, true diffuse reflectance, results from the penetration of the incident radiation into one or more sample particles and subsequent scatter from the sample matrix. The resulting radiation may emerge at any angle relative to the incident radiation and since it has traveled through the particulates it now contains information about the absorption characteristics of the sample material. However, this diffuse reflection is optically indistinguishable from diffuse specular reflection. These various energy/particle interactions are illustrated in *Figure 1*.
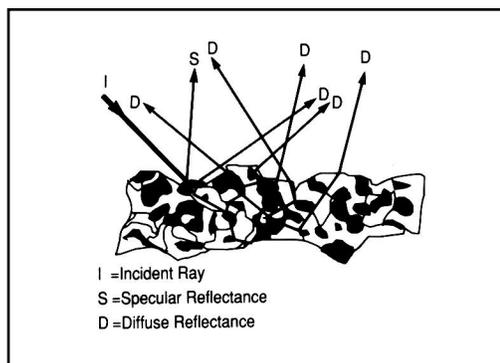

Figure 1: *Comparison of specular and diffuse reflection.*

The mixing of these different spectral contributions can lead to distortions in the final data which reduces the effectiveness of the technique. The following sections will explore some of the important factors controlling the absorption/reflection phenomena which influence diffuse reflectance spectra.

QUANTITATIVE MEASUREMENTS - THE KUBELKA-MUNK EQUATION

The classical description for the theory of diffuse reflectance at scattering surfaces is the Kubelka-Munk theory, developed in 1931.[3] The Kubelka-Munk model relates sample concentration to the intensity of the measured infrared spectrum in a manner analogous to the way Beer's Law (A=ecl, where A = -log T) relates band intensities to concentration for transmission measurements. The Kubelka-Munk equation is generally expressed as:

$$f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K}{S}$$

where R∞ is the absolute reflectance of the layer, k is the molar absorption coefficient, and s is the scattering coefficient.

Kubelka-Munk theory predicts a linear relationship between spectral data and sample concentration under conditions of a constant scattering coefficient and infinite sample dilution in a non-absorbing matrix. Hence, the relationship can only be applied to highly diluted samples in a non-absorbing matrix such as KBr. In addition, the scattering coefficient is a function of particle size, so samples must be prepared to a uniform, fine size if quantitatively valid measurements are desired. Finally, the equation only applies to an "infinitely thick" sample layer, which in infrared spectroscopy occurs at a sample thickness of approximately 3mm.

These restrictions reduce the number of spectra presentable in Kubelka-Munk units, but do not restrict "non-ideal" samples from quantitative diffuse reflectance analysis. Typically, quantitative diffuse reflectance measurements are presented in log [1/R] units, analogous to absorbance log [1/T] units for transmission measurements. In this presentation, bands increase logarithmically with changes in the reflectance values. By comparison, bands in spectra displayed in Kubelka-Munk units vary as a function of the square of reflectance. This difference emphasizes strong absorbance bands relative to weaker bands. *Figure 2* compares the spectra of methyl orange plotted in either log [1/R] (a), and Kubelka-Munk units (b).
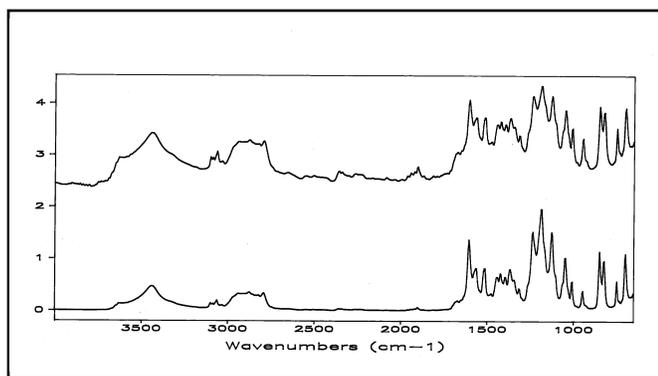

Figure 2: Spectra of methyl orange (1% in KBr) plotted in log 1/R (a) and Kubelka-Munk units (b).

FACTORS AFFECTING SPECTRAL DATA

Several factors determine band shape and relative/absolute intensity in diffuse reflectance spectroscopy through their effect on the reflection/absorbance phenomena specific to the sample. These include:

- Refractive index of the sample
- Particle size considerations
- Sample homogeneity
- Concentration

REFRACTIVE INDEX OF THE SAMPLE

As mentioned previously, refractive index effects result in specular reflectance contributions to diffuse reflectance spectra. With organic samples, the spectra display pronounced changes in band shape and relative peak intensities, resulting in non-linearity in the relationship between band intensity and sample concentration. For some inorganic samples, strong specular reflection contributions can even result in complete band inversions (reststrahlen bands).

This overlay of diffuse reflectance and specular reflectance spectra, and the resulting spectral distortions, can be minimized by dilution of the sample in a non-absorbing matrix. In addition, accessory design can help reduce specular reflectance contributions. As shown in *Figure 3*, the Spectra-Tech Collector® employs a device called the Blocker ®, a knife edge divider placed on the sample at a point bisecting the sample cup . By this method, the Blocker® prevents true specular radiation from reaching the detector.
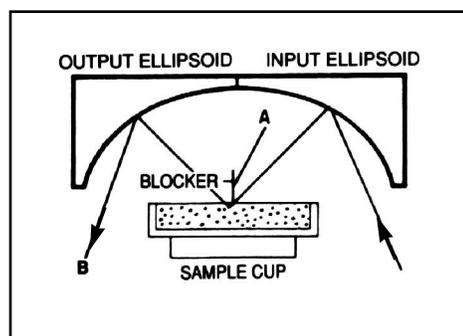

Figure 3: Representation of a diffuse reflectance accessory showing how the Blocker ® (A) eliminates the specular component of light (B).

However, because diffuse specular components are randomly directed, the Blocker® is not able to completely eliminate specular contributions in spectra. Consequently, in samples with a high refractive index, the analyst must assume that some specular contribution does occur, thereby reducing quantitative accuracy.

PARTICLE SIZE CONSIDERATIONS

Particle size is a major consideration when performing diffuse reflectance measurements of solids. *Figure 4* shows the effect of particle size on the diffuse reflectance spectra of a pure organic compound - neat (undiluted) azobenzene. The band widths decrease and relative intensities are dramatically altered as particle size decreases. These effects are even more pronounced in spectra of highly absorbing inorganic materials with high refractive indices. For these samples, specular contributions can dominate the final spectra if the particle size is too large.

To acquire a true diffuse reflectance spectrum, it is necessary to uniformly grind the sample and dilute it in a fine, non-absorbing matrix. Similar preparation must be applied to the non-absorbing matrix material, in order to provide an "ideal" diffuse reflector for background analyzes and as a supporting matrix for the sample.

Sample Homogeneity

The Kubelka-Munk model for diffuse reflectance is derived for a homogeneous sample of infinite depth. However, some sample analysis methods, especially those designed for liquid samples (e.g. deposition of sample onto a powdered supporting matrix), can result in a higher concentration of sample near the analysis surface. In these circumstances, variations in relative peak intensities may be noticed. In particular, weaker absorbing wavelengths tend to be attenuated at higher sample concentrations as shown by the labeled band in *Figure 4*[5]. To avoid these peak intensity variations, it is necessary to distribute the analyte as uniformly as possible within the non-absorbing background matrix.
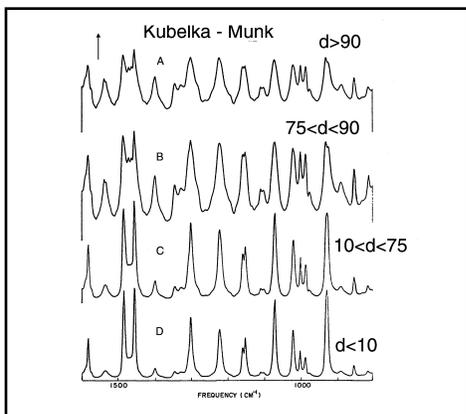

Figure 4: Spectra of Azobenzene at varying particle sizes.

Concentration

One particularly important advantage of diffuse reflectance spectroscopy, especially in comparison to transmittance measurements, is its extremely broad sample analyzing range. While it is theoretically possible to acquire usable diffuse reflectance spectra on samples ranging from highly dilute to neat, practical considerations often complicate the analysis process.

With high concentration samples, especially those with a high refractive index, you can expect a dramatic increase in the specular contribution to the spectral data. As a result, some sample data may be uninterpretable without adequate sample dilution. Even when samples can be measured satisfactorily at high concentration, it is advisable to grind the sample to a very uniform and fine particle size to minimize both specular reflectance and sample scattering effects which adversely affect quantitative precision.

Sampling Methods and Considerations

Diffuse reflectance spectroscopy offers exceptional versatility in sample analysis. This versatility results from both its sensitivity and optical characteristics.

Classically, diffuse reflectance has been used to analyze powdered solids in a non-absorbing matrix of an alkali halide, such as KBr or KCl. The sample is typically analyzed at low concentration, permitting quantitative presentation of the data in Kubelka-Munk units. A typical spectrum,

1% sugar in KBr, is shown in *Figure 5.* This technique yields spectra which are qualitatively similar to those produced by conventional transmittance or pellet methods. However, they exhibit higher sensitivity for quantitation, and are less subject to the scattering effects which cause sloping baselines in pellet measurements. The spectrum in *Figure 6* offers an example of the sensitivity achievable with a high performance diffuse reflectance accessory in a commercial FT-IR spectrometer.
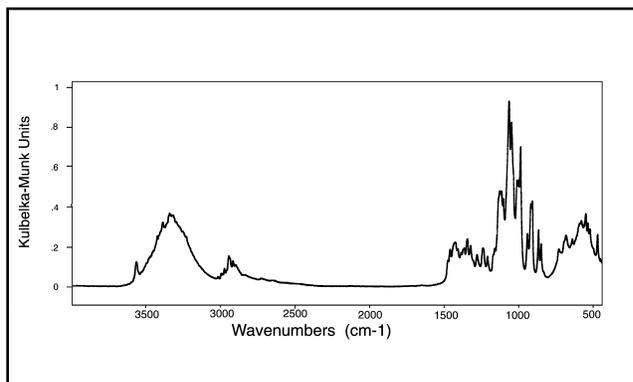

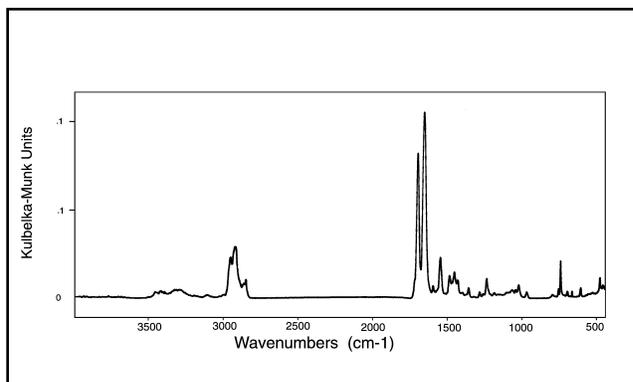*Figure 5:* Spectrum of 1% sugar in KBr

Figure 6: Spectrum of 800 nanograms of caffeine in methylene chloride deposited on KBr.

Alternate methods of sample analysis in diffuse reflectance include:

- evaporation of volatile solutions of a solid in the presence of a non-absorbing supporting matrix,

- deposition of a liquid sample or dissolved solid onto the surface of a non-absorbing supporting matrix, as in analysis of liquid chromatography eluent,

- direct analysis of certain solid samples. The direct analysis technique has been successfully employed on a broad array of sample types, including starch, wool cloth, paper, plant leaves, pharmaceutical tablets, and cedar wood siding. [4,5]

In addition, diffuse reflectance is not limited to powders, small solid samples, or liquids. Through the use of a Si-Carb™ Sampler, diffuse reflectance can be extended to analysis of large, intractable samples, such as rigid polymer sheets. The Si-Carb™ Sampler available from Spectra-Tech uses a small disk of silicon carbide paper to abrade the surface of a sample, transferring a small amount of the sample onto the paper. An infrared spectrum of the paper is acquired and ratioed against a spectrum of clean silicon carbide paper. This yields a high resolution spectrum of the sample material. *Figure 7* shows an example of this technique for Polymethylmethacrylate, a hard polymer. For very hard materials, diamond paper is also available.
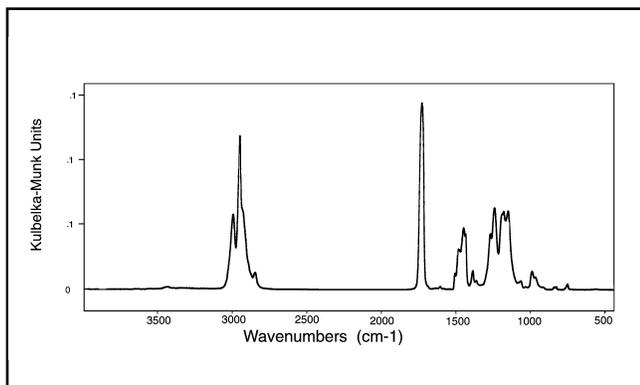

Figure 7: *Spectrum of Polymethylmethacrylate abraded with the Si-Carb™Sampler.*

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The COLLECTOR holds U.S. Patent number 4,661,706