

DIFFUSE REFLECTANCE SAMPLING METHODS

INTRODUCTION

Diffuse reflectance is frequently used for quantitative and qualitative infrared analysis of powders and rough surface solids. However, this technique has come to encompass two slightly different methods: true diffuse reflectance and 'in-line diffuse' reflectance. True diffuse reflectance optimizes the collection of the scattered radiation and minimizes the collection of specularly reflected radiation, reducing reststrahlen effects and more closely matching the Kubelka-Munk theoretical requirements. In-line diffuse reflectance, on the other hand, collects much more light, by detecting both the scattered and specular radiation. Although not strictly diffuse reflectance, this technique is frequently used for quickly obtaining spectral information. This paper demonstrates the differences between these two sampling techniques for the common types of samples investigated by diffuse reflectance. These samples include neat solids, solids diluted in a non-absorbing matrix, liquids deposited onto a scattering surface, and solids deposited onto an abrasive.

THEORY

The diffuse reflection spectroscopic technique was developed to facilitate analysis

of materials such as papers and powders in their neat state. The theory of diffuse reflection has been investigated in detail by many authors^{1,2,3}.

When an inhomogeneous material is illuminated, some of the impinging radiation penetrates the sample and some is reflected from the surface (see Fig. 1). The portion that penetrates the sample undergoes scattering at a large number of points in its path. The fraction of this radiation that comes back out of the sample is the diffusely reflected component. This component is theoretically described by the widely-used Kubelka-Munk model⁴. The specularly reflected component is just directionally scrambled reflectance (*i.e.* diffused) and hence is described by the Fresnel equations.

In the low absorption limit, the specular component as a function of the refractive index is mainly determined by the real part of the refractive index. Hence it is essentially independent of wavelength and merely causes an easily removable offset in the measured value.

For a strong absorption index, however, the front surface reflectance is a function of both components of the complex refractive index. So the specular component increases with an increase in absorption index. This increased level of reflected radiation counteracts the

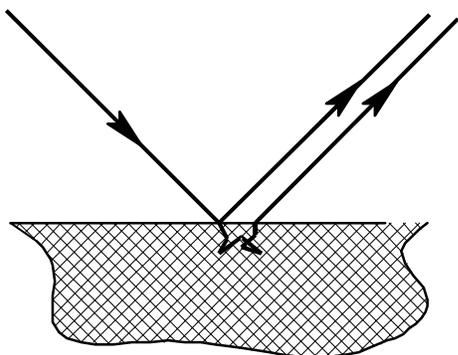


Figure 1. Schematic of the two components of the reflected radiation present in diffuse reflection. Reflected rays are shown in only one direction for clarity.



Figure 2. The Cricket™ Diffuse Reflectance Accessory. Shown here with its TransFlex™ substrates.

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absorption by the sample. Thus as a function of the absorption index, the in-line diffuse reflectance at first decreases and then reverses direction and starts increasing. As a result, strong absorption peaks degenerate into spurious doublets, also known as reststrahlen bands, and the in-line diffuse reflectance becomes un-interpretable.

Experimental methods that avoid or at least suppress the influence of the specular component collect the true diffuse reflectance spectra. Those that collect a combination of the diffuse and specular components are often also referred to as 'diffuse reflectance,' but are perhaps more correctly named in-line diffuse reflectance.

EXPERIMENTAL

The diffuse reflectance spectra were recorded using a Nicolet Nexus 670 set for 8 cm^{-1} resolution and 32 scans. The Nexus was equipped Harrick Scientific's Cricket™, shown in Figure 1. The Cricket™ was used with both of its modes of operation to collect either in-line diffuse reflectance or diffuse reflectance. For comparison, ATR spectra were collected using the Harrick SplitPea™.

The samples were chosen to reflect the variety of samples that can be analyzed by diffuse reflectance. Specifically, these

samples included white paper, spackle (Custom Building Product's Interior Spackling Paste), malachite rock, silicone oil, and a residue.

Several different methods were used to sample these materials, depending on the nature of the sample. The paper was examined neat. The spackle and silicone oil were smeared onto TransFlex™ (roughened aluminum) substrates for analysis. For the residue, a drop of the contaminated toluene was placed on a TransFlex™ substrate and allowed to dry. The malachite rock was abraded by 220-grit silicon carbide sandpaper (Norton Consumer Product's Tukbak Gold T481) and analyzed thereon. The malachite was also pulverized for dilution in ground KBr and for smearing onto a TransFlex™ substrate.

RESULTS AND DISCUSSION

Figures 3 and 4 demonstrate the fundamental difference between diffuse and in-line diffuse reflectance. Figure 3 shows the reflectance of paper, recorded by both diffuse reflectance techniques and by ATR. As seen in the ATR spectrum, paper is highly absorbing around 1040- cm^{-1} . This results in reststrahlen bands in the in-line diffuse reflection spectrum that are

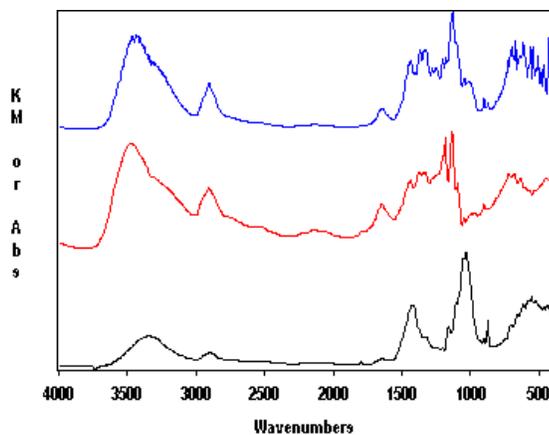


Figure 3. The Reflectance Spectra of Paper Measured by Diffuse Reflectance (top), In-Line Diffuse Reflectance (middle), and ATR (bottom).

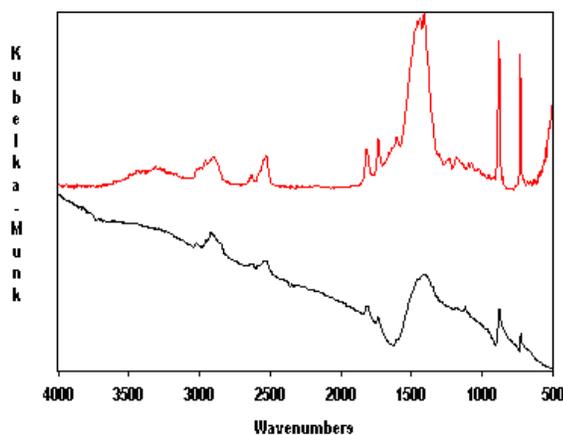


Figure 4. The Reflectance Spectra of Spackle Measured by Diffuse Reflectance (top) and In-Line Diffuse Reflectance (bottom).



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absent in the diffuse reflection spectrum.

Figure 4 shows the reflectance of spackle on a TransFlex™ substrate. Here, the in-line diffuse reflection spectrum shows dispersion effects through band inversions and a sloping baseline. These effects are not apparent in the diffuse reflection spectra, although the noise level is higher due to the lower signal levels. This clearly indicates that diffuse reflectance sampling is a better method for strongly absorbing materials, like paper and spackle, than in-line diffuse reflectance.

Figure 5 shows spectra from powdered malachite diluted in KBr. By diluting this sample, it has been made into a weak absorber. Theory predicts that, under these conditions, the diffuse reflection spectrum and the in-line diffuse reflection spectrum will be similar. This is indeed the case. The spectra show only minor differences, particularly in the C-H region.

Figure 6 shows the diffuse reflectance spectra from malachite sampled in three different ways. Dilution in KBr is the traditional method of choice for analysis of solids and powders, despite the fact that it is labor-intensive. The top curve shows the excellent quality of spectra achieved by this method. An alternate approach is to abrade the sample with silicon

carbide sandpaper. This is a quick and easy method to use. However, since the sandpaper itself is a poor reflector, this can produce noisy spectra with poorly resolved bands, as shown in the lower spectrum. The result of another quick and easy method is shown in the middle spectrum, where the powdered sample was smeared across the TransFlex™ substrate. Because of the higher total reflectivity of the substrate, better quality spectra are obtained than with the sandpaper.

Figures 7 and 8 demonstrate that these reflectance methods can also be used to examine liquids. Figure 7 shows the spectra of the residue from contaminated toluene evaporated on a TransFlex™ substrate. Here, the diffuse reflection spectrum more clearly resolves the O-H stretch, even though the spectrum is noisier. The comparable band in the in-line diffuse reflection spectrum is obscured by the sloping baseline and other distortions. The contaminant here is, most likely, a type of wax.

Figure 8 is the spectrum of silicone oil smeared on a TransFlex™ substrate, recorded in the diffuse reflectance mode of the Cricket™. As can be seen from the spectrum, this technique, also known as transfectance, can be used effectively to obtain spectral information on liquids.

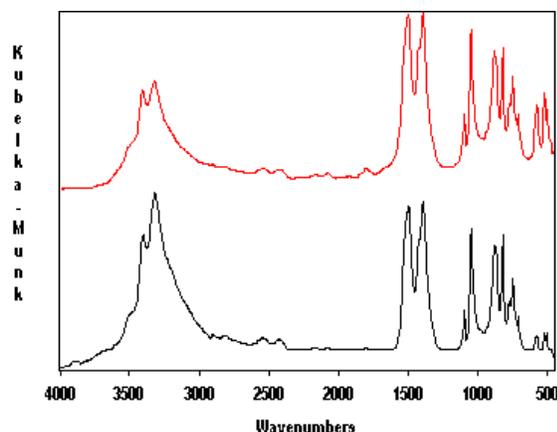


Figure 5. The Reflectance Spectra of Ground Malachite in KBr Measured by Diffuse Reflectance (top) and In-Line Diffuse Reflectance (bottom).

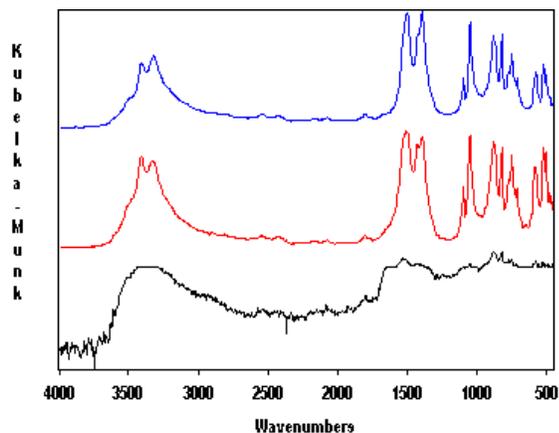


Figure 6. The Reflectance Spectra of Malachite Powder Diluted in KBr (top), Powder Smeared on a TransFlex™ substrate (middle), and Abraded with Silicon Carbide Sandpaper (bottom).

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CONCLUSION

The diffuse reflectance technique has come to encompass two slightly different methods: diffuse reflectance and in-line diffuse reflectance. This paper demonstrates that diffuse reflectance is superior for obtaining spectra that are free from distortions than the quick in-line diffuse reflectance sampling methods in use today.

Of the different sample preparation methods available for these types of measurements, examining the samples neat or smeared on a TransFlex™ substrate will give the best spectra in the least amount of time. Dilution in KBr, however, remains the best choice for strict applications of the Kubelka-Munk theory.

Furthermore, diffuse reflectance techniques are not just for solids anymore. With the appropriate hardware, information on liquids and pastes can be readily obtained.

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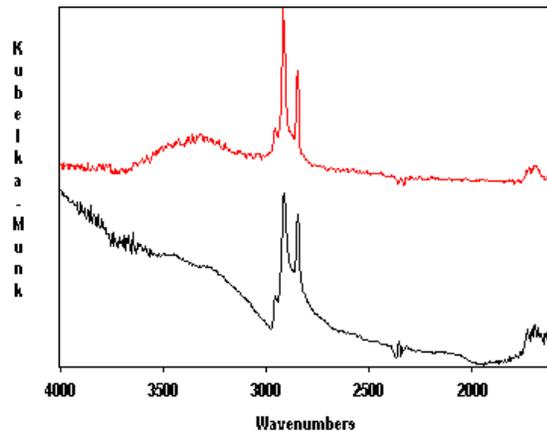


Figure 7. The Reflectance Spectra of the Residue from Evaporated Contaminated Toluene Measured by Diffuse Reflectance (top) and In-Line Diffuse Reflectance (bottom).

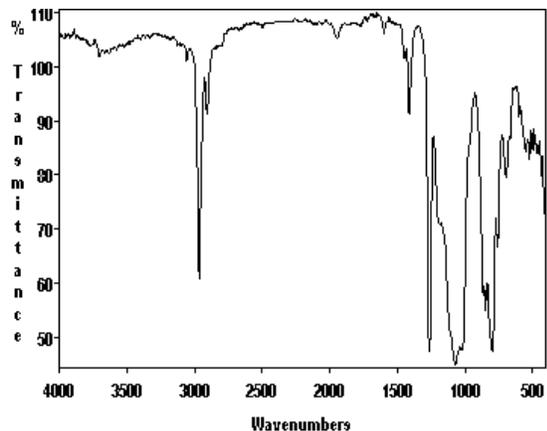


Figure 8. The Transmittance Spectrum of Silicon Oil on a TransFlex™ Substrate.



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