Diffuse Reflectance – Theory and Applications

Diffuse Reflectance – Ideal for Powdered Samples and Intractable Solids

Diffuse reflectance is an excellent sampling tool for powdered or crystalline materials in the mid-IR and NIR spectral ranges. It can also be used for analysis of intractable solid samples. As with transmission analysis, samples to be run by diffuse reflectance are generally ground and mixed with an IR transparent salt such as potassium bromide (KBr) prior to sampling. Diffuse reflectance is an excellent sampling technique as it eliminates the time-consuming process of pressing pellets for transmission measurements. Diffuse reflectance can also be used to study the effects of temperature and catalysis by configuring the accessory with a heating chamber.

Perhaps one of the greatest additional benefits of diffuse reflectance sampling is that it is ideally amenable to automation. Methods can be developed with a manual version diffuse reflectance accessory and then moved to automation to increase sample throughput. PIKE Technologies offers several diffuse reflectance accessory configurations – basic, advanced with heat chamber capabilities, upward directed IR beam for easy sampling access, and fully automated for maximum sampling efficiency.

How Diffuse Reflectance Works

Diffuse reflectance relies upon the focused projection of the spectrometer beam into the sample where it is reflected, scattered and transmitted through the sample material (shown on the right). The back reflected, diffusely scattered light (some of which is absorbed by the sample) is then collected by the accessory and directed to the detector optics.

Only the part of the beam that is scattered within a sample and returned to the surface is considered to be diffuse reflection.

Some powders may be analyzed by diffuse reflectance as neat samples (coal samples, soil samples, diffuse coatings on a reflective base). Usually, the sample must be ground and mixed with a non-absorbing matrix such as KBr. The sample to matrix ratio should be between 1 to 5% (by weight). Diluting ensures a deeper penetration of the incident beam into the sample which increases the contribution of the scattered component in the spectrum and minimizes the specular reflection component.

The specular reflectance component in diffuse reflectance spectra causes changes in band shapes, their relative intensity, and, in some cases, it is responsible for complete band inversions (Restrahlen bands). Dilution of the sample with a non-absorbing matrix minimizes these effects (particle size and sample loading mechanics also play an important role).

This is shown below in the spectral data for caffeine, where the upper spectrum is diluted to about 2% by weight in KBr and demonstrates very high quality with sharp, well-defined absorbance bands. The lower spectrum is of undiluted caffeine measured by diffuse reflectance and shows derivative shaped bands in the 1700 cm⁻¹ and 1500 cm⁻¹ region of the data. The upper spectrum of diluted caffeine is clearly of higher spectral quality than that of the undiluted caffeine.

Other factors related to high spectral quality for diffuse reflectance sampling are listed below:

- **Particle Size** – reducing the size of the sample particles reduces the contribution of reflection from the surface. Smaller particles improve the quality of spectra (narrow bandwidths and better relative intensity). The recommended size of the sample/matrix particles is 50 micrometers or less (comparable to the consistency of the finely ground flour). This fine powder is easily achieved by using a ShakIR mixer.

- **Refractive Index** – effects result in specular reflectance contributions (spectra of highly reflecting samples will be more distorted by the specular reflectance component). This effect can be significantly reduced by sample dilution.

- **Homogeneity** – samples prepared for diffuse reflectance measurements should be uniformly and well mixed. Non-homogenous samples will lack reproducibility and will be difficult to quantify. An ideal way to mix samples for diffuse reflectance is by using a ShakIR.

- **Packing** – the required sample depth is governed by the amount of sample scattering. The minimum necessary depth is about 1.5 mm. The sample should be loosely but evenly packed in the cup to maximize IR beam penetration and minimize spectral distortions.
Even with all these sample preparation practices, the raw diffuse reflectance spectra will appear different from its transmission equivalent (stronger than expected absorption from weak IR bands). A Kubelka-Munk conversion can be applied to a diffuse reflectance spectrum to compensate for these differences. This conversion is available in most FTIR software packages.

The Kubelka-Munk equation is expressed as follows:

\[ f(R) = \frac{(1 - R)^2}{2R} = \frac{k}{s} \]

Where:
- \( R \) is the absolute reflectance of the sampled layer,
- \( k \) is the molar absorption coefficient and
- \( s \) is the scattering coefficient.

The spectra shown above demonstrate this spectral conversion for ibuprofen collected by diffuse reflectance. The sample was diluted to about 1% by weight in KBr and mixed using the ShakIR. The Kubelka-Munk converted spectrum for ibuprofen shows excellent comparison with the transmission spectrum and is easily identified using library search of a transmission spectral data base.

The Kubelka-Munk equation creates a linear relationship for spectral intensity relative to sample concentration (it assumes infinite sample dilution in a non-absorbing matrix, a constant scattering coefficient and an “infinitely thick” sample layer). These conditions can be achieved for highly diluted, small particle samples (the scattering coefficient is a function of sample size and packing) and a sample layer of at least 1.5 mm. With proper sample preparation diffuse, reflectance spectroscopy can provide ppm sensitivity and high quality results.

**Plastic Bumpers and Tough Samples**

Sometimes it is necessary to analyze a sample which simply does not fit in a spectrometer’s sample compartment – the analysis of polymer-based automotive components or painted panels are typical examples.

A special diffuse reflectance technique allows quick and simple analysis of such samples in a relatively non-destructive manner. A small amount of the sample can be collected by abrasion on a diamond or silicon carbide (SiC) abrasion disk and analyzed immediately with the help of a diffuse reflectance accessory.

For the analysis of powders the following procedure is recommended;

- Place about 200-400 mg of KBr into the ShakIR vial and shake for 30 seconds
- Fill the background diffuse cup with this KBr
- Remove excess KBr with a flat edge – the KBr should be loosely packed
- Add 1 to 5 mg of the sample to the remaining KBr in the ShakIR vial and shake for 30 seconds
- Fill the sample diffuse cup with this mixed sample/KBr
- Remove excess sample with a flat edge – the sample should be loosely packed
- Place the background and sample diffuse cups into the sample holder
- Slide the sample holder into the accessory
- Position the KBr cup in the beam and collect a background
- Move the holder to the sample position and collect a sample spectrum (the ratio of these two spectra will produce a spectrum of the sample)
- Convert the raw diffuse reflectance spectrum to Kubelka-Munk

Under ideal conditions the transmission of the strongest band in the spectrum should be in the 50% range. If the resulting bands are too intense or distorted, further dilute the sample and make sure that all other measurement affecting factors (particle size, homogeneity and packing) are within required limits.

**Summary**

Diffuse reflectance accessories make the analysis of a wide range of solid samples easier, faster and more efficient. Advanced options for diffuse reflectance provide the ability to heat the sample and monitor a reaction process. Automation versions of diffuse reflectance accessories provide the ability to greatly increase sample throughput.