Fiber Optic Sampling in the Near-infrared Region Utilizing a High-Performance Infrared Spectrometer

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Near-infrared spectroscopy is a popular technique for many analytical applications for two main reasons: the sampling advantages of near-infrared over mid-infrared spectroscopy for certain types of organic materials and the availability of sophisticated chemometric software for composition and property determination. Although near-IR may be a simpler sampling technique for a number of applications, the spectra that are produced are not as easy to interpret as normal infrared spectra. Many of the advances in near-IR chemometric analyses were made because there are seldom unique sharp spectral features that are directly related to the concentrations of a specific component in the sample. Very high precision in the data point location is a key requirement for these chemometric techniques and can be a problem for many dispersive near-IR spectrometers.

Recently several companies have introduced Fourier transform near-infrared (FT-NIR) systems for use in chemical analysis. A major advantage of FT-NIR systems is the wavelength accuracy that results from the use of the HeNe laser as an internal wavelength reference. A number of FT-NIR systems are also capable of high resolution and sophisticated data acquisition techniques that can provide better peak shapes and lower noise in the spectral data.

Near-IR spectroscopy has become even more popular with the availability of low cost optical fibers that transmit light in the spectral region from 1 - 2.5 microns. These fiber optic cables provide high performance over distances of several meters. This makes it quite feasible to perform analyses of samples on-line, in reaction vessels and in dangerous locations.

To implement the advantages of near infrared spectroscopy in different applications, Nicolet has developed a fiber optic accessory for the Magna-IR® spectrometer which is optimized for near-IR sampling. This accessory mounts in the sample compartment and focuses the light from the spectrometer into the fiber optic bundle and from the fiber optic cable to a near-IR detector that has been specially designed for use with the Magna-IR system. With this accessory and the proper spectrometer components, the instrument can be switched from mid-IR to near-IR operation in a matter of minutes.

SYSTEM PERFORMANCE

The following section describes the results of a series of evaluation tests that were performed with a Nicolet Magna-IR spectrometer operating in the near-IR spectral region. All of the data in this section was acquired with a two meter long bifurcated fiber optic bundle. The spectrometer was configured with a white light source, Calcium Fluoride beamsplitter and a Peltier cooled, lead sulfide detector. Most of the data in this report were acquired at 16 cm^{-1} resolution with an acquisition time of one minute.

Figure 1 shows a spectrum of the fiber optic system ratioed to a scaled open beam spectrum. This spectrum shows the features and spectral cut-off that can be attributed to the fiber optic cable and the transfer optics. The units on this spectrum are arbitrary because of the need to aperture down the open beam energy to insure that the signal does not exceed the dynamic range of the digitizer.

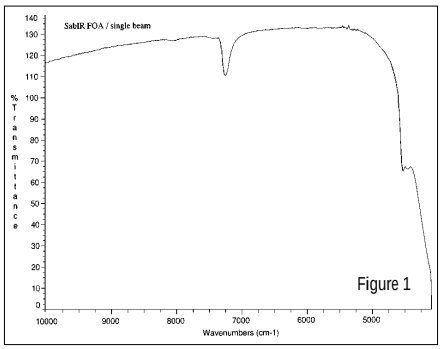


Figure 1

Figure 2 shows a single beam spectrum from a diffuse gold surface. We chose this as our reference material for backgrounds over a polished mirror since much of our evaluation work involved diffuse reflectance measurements. There are no significant spectral features contributed by the gold sample. This spectrum also shows that the useful spectral region cuts off at about 4100 cm^{-1} or slightly above 2.5 microns. This is due mainly to absorptions from this particular optical fiber.

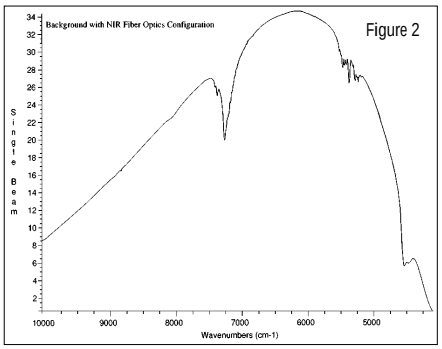


Figure 2

Figure 3 shows a 100% line obtained from two measurements of the diffuse gold surface. This data was acquired at 16 cm^{-1} resolution; one minute measurement time. The signal-to-noise over most of the spectral range is much less than 0.01% T.

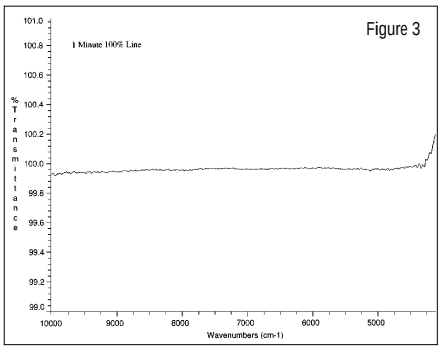
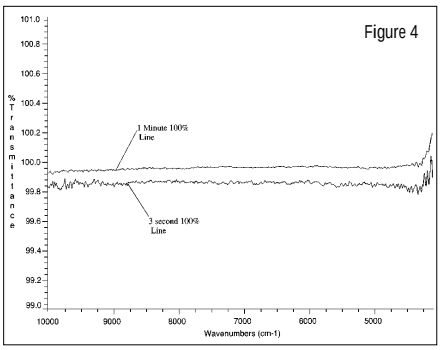


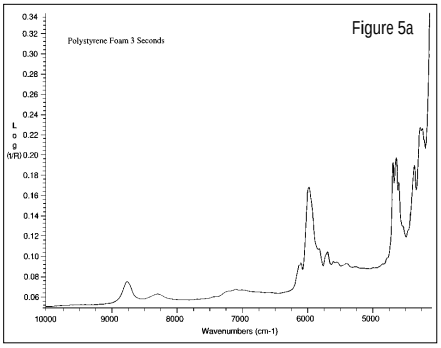
Figure 3

Figure 4 shows a comparison of the one minute measurement and a three second measurement. These results are reported in log (1/R) units and micrometers. These are the units frequently used in near-IR spectroscopy. Log (1/R) has the same scale as absorbance. As expected the noise level for the three second measurement time is much higher than the one minute and corresponds to the square root of signal averaging time. The noise level for the three second measurement corre-



sponds to about 100 micro absorbance units.

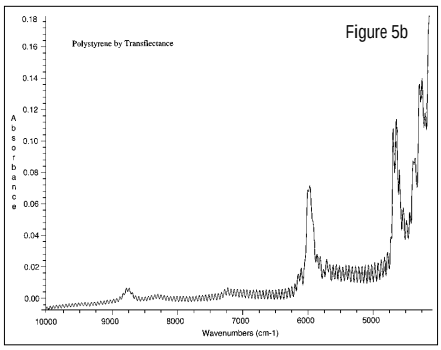
Figure 5a shows the spectrum from a sample of white polystyrene foam ratioed to a spectrum from the diffuse gold reference. This spectrum was acquired in three seconds and clearly demonstrates the quality of spectra that can be obtained by near-IR diffuse reflectance from many white powdered or foam samples.



TRANSFLECTANCE MEASUREMENTS

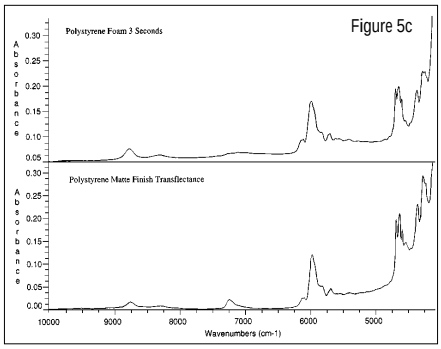
A second measurement technique frequently used in near-IR is called "Transflectance". In this technique, a mirrored surface is positioned a certain distance from the fiber optic cable such that the light is specularly reflected back into the bundle. If a transparent sample is placed between the optic cable and the mirror, a transmittance spectrum of the sample is obtained. In this measurement, the light passes through the sample twice, which can greatly enhance the sensitivity for thin samples.

Figure 5b shows a spectrum obtained from a polystyrene film placed between the mirror and the fiber optic cable. This film shows the fringing commonly observed with samples that have polished flat surfaces. The fringes are caused by light reflecting from surfaces. In some cases the frequency of this fringe pattern can be



used to calculate the thickness of the sample.

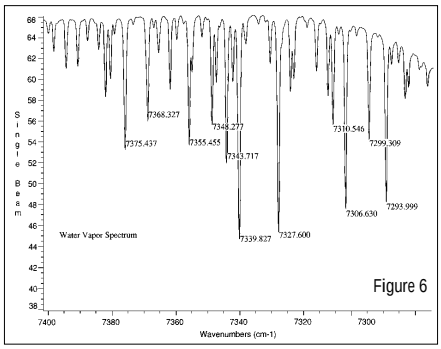
Figure 5c shows a comparison of a transflectance spectrum of a matte finish polystyrene film and the diffuse reflectance spectrum from the white polystyrene foam. The scatter in the spectrum from the matte finish transflectance spectrum is actually lower than the foam sample.



RESOLUTION AND WAVELENGTH ACCURACY

The Magna-IR spectrometer is a high performance laboratory spectrometer with a great deal of flexibility. One of the major advantages of using FT-IR for near-IR applications is the inherent wavelength accuracy obtained with the HeNe reference laser. An FT-IR system is routinely capable of wavelength precision better than 0.1 cm^{-1}.

This corresponds to a value of 0.01 nanometers at a wavelength of 1000



nanometers. Figure 6 shows a portion of a single beam spectrum taken with the fiber optic accessory in a Magna-IR spectrometer at a resolution of 0.5 cm^{-1}. The system was not purged, so the sharp peaks correspond to water vapor in the optical bench.

The use of the automatic peak finder routine in the software can be used to certify the precision of the spectrometer wavelength registration. Under normal operation; wavelength drift should be much less than 0.1 cm^{-1} or 0.01 nanometers.

Figure 7 shows an expansion of the water vapor spectrum displayed in microns. The peak width at half height for the peak near 1.3622 micrometers is 0.00007 microns. While this quality of spectrum is rarely needed in most near-IR applications, it clearly demonstrates the excellent precision of this system. Most samples that are analyzed by NIR have very broad peaks, but resolution must still be considered.

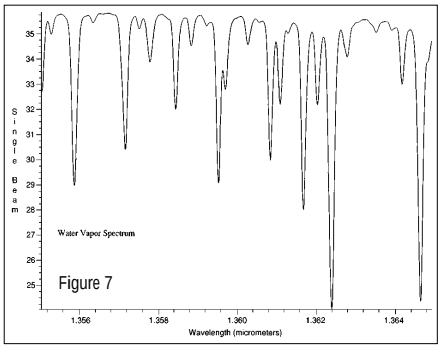
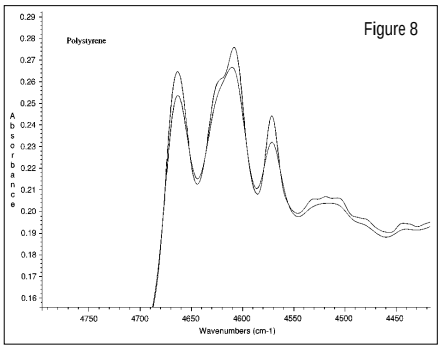


Figure 8 shows two spectra of polystyrene acquired at 16 cm^{-1} and 8 cm^{-1} resolution. This spectrum shows that a number of the peaks and shoulders in the polystyrene spectrum are better resolved at 8 cm^{-1} resolution. However, for the same measurement time the noise in the 8 cm^{-1} resolution will be higher than in the 16 cm^{-1}



spectrum. This is an example where the flexibility of the Magna-IR spectrometer allows the user to optimize the data acquisition for a specific application. In cases where signal-to-noise is critical, lower resolution may provide better quantitative results. In situations where precise component identification is important, higher resolution may provide more information.

SPECTRAL ANALYSIS

Nicolet has over 15 years of experience in developing software for spectral manipulation and analysis, including the OMNIC® Windows™ compatible spectroscopy analysis software package. Much of the OMNIC software package is directly applicable to problems in near-IR spectroscopy with important functions like baseline correction, spectral subtraction, derivative spectra, spectral smoothing and zero filling. The following section provides examples of some of the potential applications of this software to near-IR spectroscopy.

Figure 9 shows a diffuse reflectance spectrum obtained from a tablet containing 325 milligrams of aspirin. The first and second derivative spectra are also shown in this figure. Depending on the application, it may be useful to use either the first or second derivative spectrum. OMNIC software can be configured to automatically process the spectra to the appropriate final format.

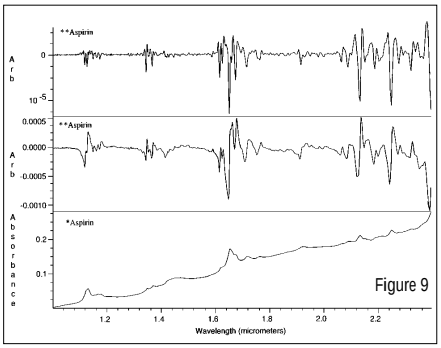


Figure 9

Because of scattering effects, many near-IR diffuse reflectance spectra have a significantly sloping baseline. Figure 10 shows a spectrum of Penicillin-G taken through a glass bottle by diffuse reflectance. Because of the very sharp peaks in this spectrum a resolution of 8 cm^{-1} and two levels of zero filling were used in this example. Zero filling is a method of improving the peak shapes by actually performing a Fourier transform that is much larger than the number of data points. The effect of this process is to provide interpolation points in the spectrum, providing a better representation of the peak shapes.

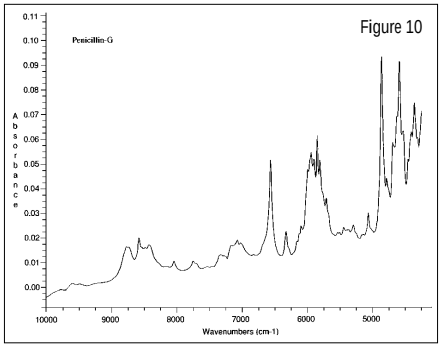


Figure 10

Figure 11 shows the effect of applying the baseline correction software to the spectrum of penicillin. In many cases, this can be used to remove the effects of sampling variance on the sample. However, this procedure should be used with care. In many cases, the scatter background in the spectrum is an important part of the spectral signature for a compound.

Another powerful OMNIC software tool is spectral subtraction. This provides a method of eliminating the spectral features of one compound from a mixture spectrum.

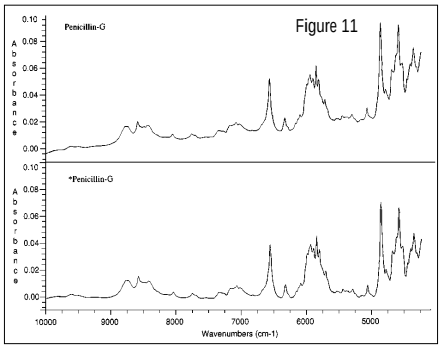


Figure 11

Figure 12 shows an overlay spectrum from a polyethylene film and a spectrum from a polystyrene film and a polyethylene

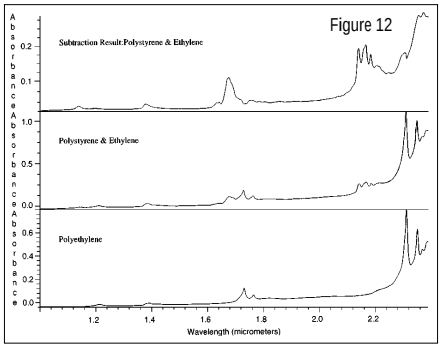


Figure 12

film. The third spectrum in the figure is the spectrum resulting from mathematical subtracting the polyethylene spectrum from the spectrum of the two polymers.

Figure 13 shows a comparison of this subtraction results with a spectrum from the polystyrene polymer. Although there are a few differences, it is clear that the two spectra are from the same material.

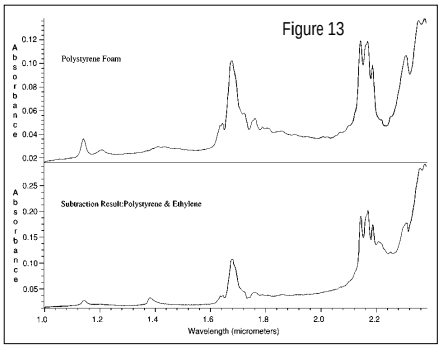


Figure 13

SAMPLING CONSIDERATIONS

One of the advantages of near-IR is the ability to work with glass components. While this is particularly important for the optical fibers, it also makes sampling much easier.

Figure 14 shows a diffuse reflectance spectrum of powdered sugar taken directly from the sample, a spectrum taken through the side of a round bottle (curved surface) and a spectrum taken through the bottom of the bottle (flat surface). Overall, the spectra are very similar but there are slight differences in the slope of the baseline for the spectra. These examples shows that high quality spectra can be obtained directly from samples in clear glass bottles or vials. For many compound identification applications these small differences in spectra should not effect the outcome.

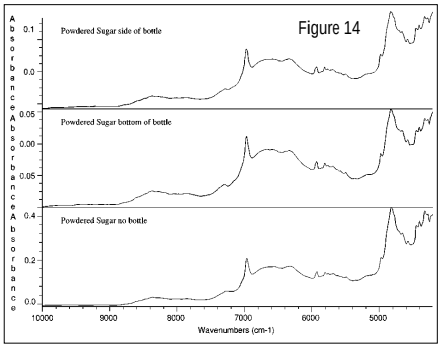


Figure 14

Figure 15 shows two spectra taken from liquid samples in an aluminum weighing dish by transflectance spectroscopy. A

background spectrum was obtained from the empty dish. The first spectrum was obtained after a small amount of acetone was poured into the dish. The second spectrum was obtained after water was added to the sample. This example demonstrates the level of performance that can be expected with flow cells and other liquid sampling accessories.

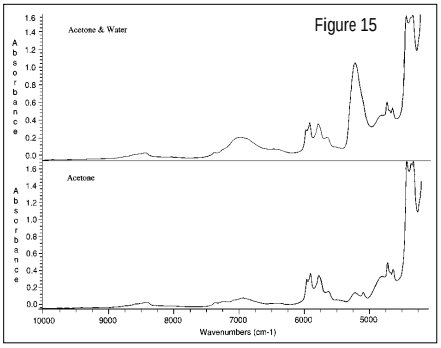
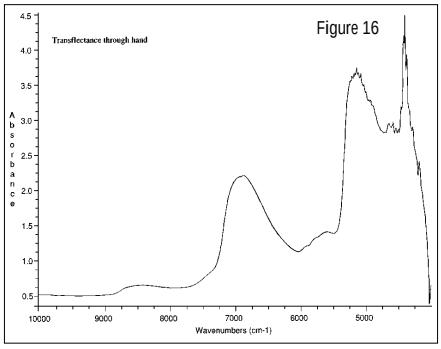


Figure 16 shows a transflectance spectrum taken through the thin area of a human hand between the thumb and first finger. While this is certainly not optimal, it demonstrates how the system might be used for biological applications.



CONCLUSIONS

A Nicolet Magna-IR spectrometer with a fiber optic sampling accessory can be quickly configured for use in near-IR spectroscopy applications. This report demonstrates the performance of the system with various types of samples. The flexibility of the spectrometer and the OMNIC software allow the user to easily acquire and process data for a specific application. The high performance of the Magna-IR system provides a level of confidence when evaluating applications in unfamiliar areas. Finally, FT-IR provides consistent and reliable wavelength accuracy to near-IR measurements.

While mid-infrared spectroscopy is still the technique of choice for many applications, the ability to rapidly switch over to near-IR operation provides a new window of opportunity.

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