Fiber Optic Sampling Using a Dispersive Raman Spectrometer and Fiber Optic Probes

TN-00117

Michael Longmire, R.C. Wieboldt, Francis Deck, Thermo Nicolet Spectroscopy Research Center, Madison WI, USA

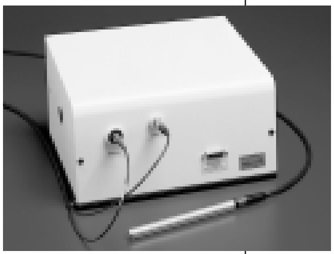
KEY WORDS

Raman
Pharmaceutical
Polymer
Forensic
Solid
Liquid
Powder
Fiber Optic Probe with trigger handle

INTRODUCTION

Dispersive Raman spectroscopy is an excellent technique for fiber optic sampling applications. The fundamental vibrational chemical information that is available from Raman spectroscopy provides a molecular fingerprint. This spectral information can be interpreted to clarify chemical and bonding interactions, perform chemical identifications or carry out reaction monitoring.

In addition, sampling can often be done directly through a glass or plastic sample container or through the reaction flask, without having to prepare the sample. This is because Raman is insensitive to thin polymer films and glass, making fiber optic measurements a natural extension of Raman analysis.



Many companies have recognized the benefits of chemical analysis and chemical identification by Raman spectroscopy. The ease of sampling, combined with the extensive chemical information that Raman provides, make it an ideal choice for many analyses. With very little effort, data can be collected and the spectra used to unambiguously identify chemical compounds by spectral interpretation, comparison to knowns or by performing library searches. The ability to use fiber optics only enhances this ease of use, making it possible to analyze samples that are too large or of a sufficiently uncommon shape that they cannot fit in the standard spectrometer sample compartment. Additionally, fiber optics allow safe remote measurements of toxic compounds and permit analysis of compounds that require special environmental considerations, such as elimination of oxygen or water. In these cases, the measurement can be made either in the controlled environment or through the sample container without compromising the sample or disturbing the normal operation of the spectrometer.

To implement the advantages of fiber optic measurements in Raman spectroscopy, Thermo Nicolet has developed a fiber optic accessory specifically designed for use with the Thermo Nicolet dispersive Raman systems. The accessory consists of the fiber optic launch geometry, which fits in the sample compartment, and a number of wavelength specific fiber optic probes. In addition, an ergonomically designed handle can be added to the fiber optic probe for ease-of-use and to bring spectrometer controls, such as initiation of data collection, to the sample.

EXPERIMENTAL

The following section describes the results of several Raman measurements utilizing the Raman fiber optic probe. All data in this section were collected on Thermo Nicolet's Almega™ dispersive Raman spectrometer using a 785 nm laser and a 5-meter low OH silica fiber with a stainless steel probe head.

For fiber optic analysis by Raman spectroscopy, it is important to minimize the extraneous Raman scatter and fluorescence that can be introduced by the silica fibers themselves. Since the excitation laser travels the full length of the fiber, a significant background signal can be introduced into the spectrum from the interaction between the laser and the silica fiber. Likewise, the scattered radiation contains not only the Raman signal of interest but also the intense Rayleigh scatter that could further interact with the silica return fiber.

To minimize silica effects, the probes that Thermo Nicolet offers incorporate appropriate filters at the tip of the fiber probe. Placing filters in the probe tip effectively removes all silica background from the excitation laser, providing a clean monochromatic excitation source. They also remove the Rayleigh scatter from the collected Raman signal before it enters the return fiber.

To function properly, the filters must be optimized for the excitation laser wavelength. For this reason, Thermo Nicolet offers a different fiber optic probe optimized for each laser wavelength available on the dispersive Raman systems. However, all of the fiber optic cables use the common Thermo Nicolet Raman fiber optics launch configuration.

To demonstrate the versatility of the Thermo Nicolet Raman fiber optics configuration, a number of samples of different physical states were analyzed.

Figure 1 presents a spectrum of cyclohexane, a clear organic solvent contained in a glass bottle. Spectrum A demonstrates the quality of data that can be collected with the fiber optics probe. For comparison, Spectrum B shows cyclohexane collected in a standard Raman sample compartment. Figure 1 demonstrates that Raman fiber optics sampling can easily collect representative data and it shows that the background introduced by the fiber probe is minimal. This indicates that the probe filters effectively remove all unwanted signal due to the silica fibers. It is important to remember that if the fiber optic probe is immersed in the sample to be measured, care must be taken to clean the probe thoroughly between analyses to avoid cross-contamination. Consideration should also be given to the compatibility of the stainless steel probe tip with the sample solution, particularly when corrosive samples are to be measured. The safest approach is to sample directly through the sample container.

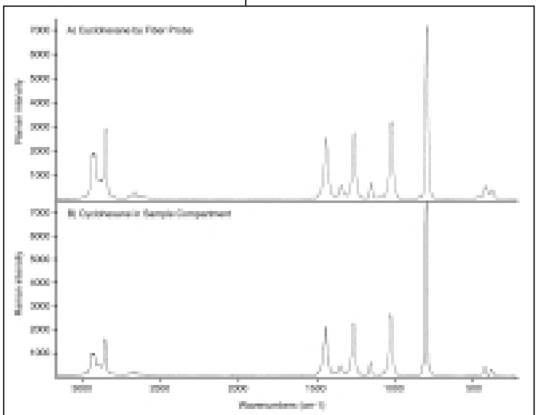


Figure 1: dispersive Raman spectra of cyclohexane collected a) through a 785 nm Thermo Nicolet Raman fiber optic probe and b) in the standard Almega dispersive Raman sample compartment

Raman fiber optic analysis is also highly effective in analyzing powdered samples. The technique is advantageous because it does not require that the powder be removed from the glass bottle or manipulated in anyway. An alternate approach is to place the probe tip in contact with the surface of the powder sample and collect the spectrum directly.

Figure 2 compares a polymer measured using a Raman fiber optic probe, to a representative spectrum of the material collected in a traditional fashion. The two spectra compare very favorably. This suggests that an identification, quality control method or quantitative analysis would be possible utilizing a fiber optic probe in conjunction with Raman spectroscopy.

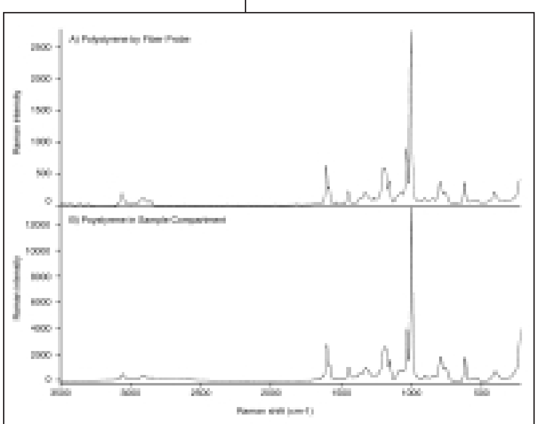


Figure 2: a) polystyrene measured by a Raman fiber optic probe, b) spectrum of a pure polystyrene spectrum collected in the sample compartment

As a final example, two unknown materials were analyzed using the dispersive Raman fiber optics probe. The resulting spectra are shown in Figures 3 and 4. Spectra collected from the fiber optic probe are of exceptional quality, making it possible to attempt identification of the unknown materials. One powerful method for identifying unknown compounds is through spectral library searching.

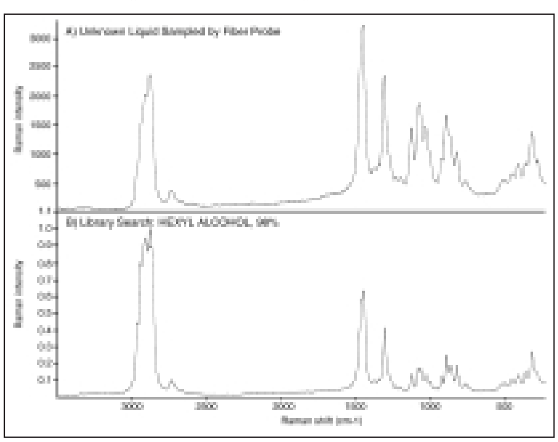


Figure 3: a) a spectrum of an unknown liquid sample collected through its sample bottle and b) the library search result of the best match from the Thermo Nicolet Aldrich Raman Condensed Phase Library

Using the 14,033 compound Thermo Nicolet Aldrich Raman Condensed Phase Library, the two unknowns were easily identified as hexyl alcohol and a styrene/butyl methacrylate copolymer. This analysis indicates that the fiber optic probe can be a useful tool for identifying unknowns or as a quality control tool for routine chemical composition validation.

CONCLUSION

A Raman fiber optic probe is easily used with a Thermo Nicolet dispersive Raman system to provide high quality spectra very rapidly with no sample preparation. The fiber optic probe can be used several feet away from the spectrometer. Analyses can be carried out in controlled environments or near reaction vessels, eliminating the need to collect the sample for analysis in a lab.

The Thermo Nicolet fiber optic configuration installs quickly into the sample compartment and supports industry standard fiber optic connectors. Since using fiber optics converts the system from a Class I laser product to a Class IIIb laser product, the launch configuration includes safety interlock connections and lockout switches to facilitate laboratory compliance with Class IIIb laser products. In addition, an ergonomically designed fiber optic trigger handle is available for use in applications where frequent use of the probe is anticipated or in situations where the integrated trigger handle and indicator diodes offer desired remote control of select instrument functions.

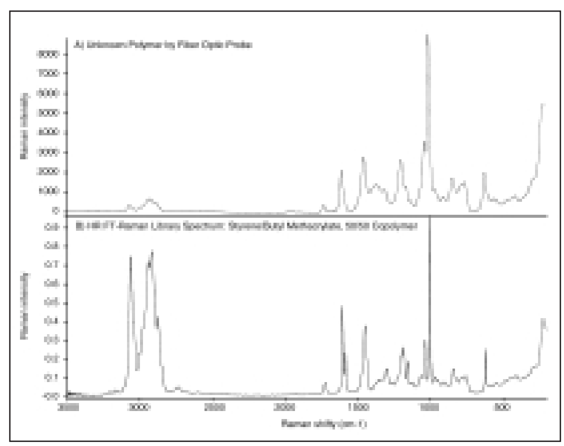


Figure 4: a) a spectrum of an unknown polymer and b) the library search result of the best match from the Thermo Nicolet Aldrich Raman Condensed Phase Library

Thermo Nicolet

5225 Verona Road • Madison, WI 53711-4495 • U.S.A. • TEL: 800-201-8132, 608-276-6100
FAX: 608-273-5046 • E-MAIL: nicinfo@thermonicolet.com • WEB: www.thermonicolet.com

A Thermo Electron business

TN-00117 11/00