TECHNICAL NOTE #13

Background Filtering in Fiber Optic Raman Sampling Probes

Introduction

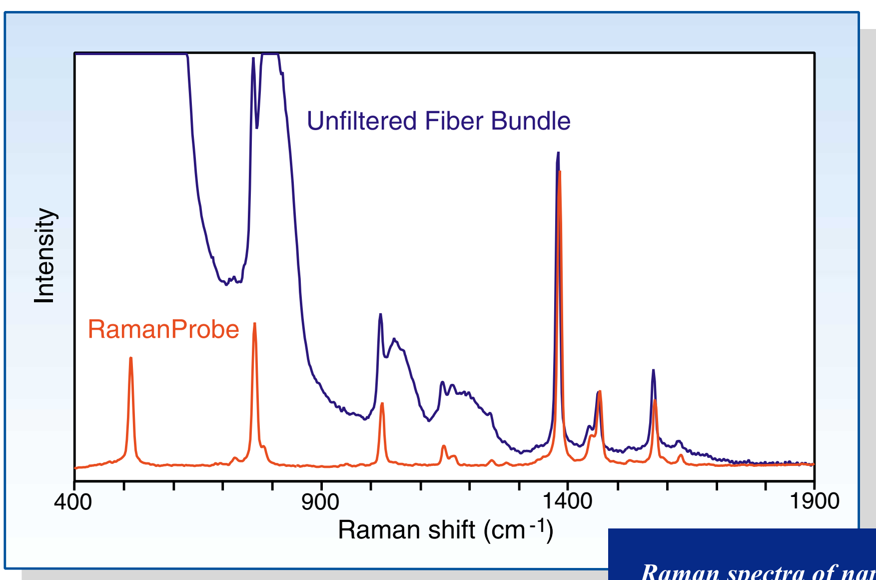
Raman spectroscopy is a unique technique that is complementary to infrared absorption spectroscopy. For remote analyses, the Raman experiment has an advantage in that it can be performed at wavelengths shorter than the "mid-IR" region, enabling the measurement of fundamental vibrational modes with more efficient fiber optic materials. For instance, when using an excitation source in the visible or near-IR region, silica fiber optics are able to efficiently transmit the laser light and collect the scattered radiation from the sample.

The simplest design of a fiber optic Raman probe consists of two single fibers mounted closely together. In this configuration, one fiber is attached to the laser excitation source and illuminates the sampling area. The other fiber collects the scattered light and transmits the energy to the spectrograph. The collection of light can be amplified by using more collection fibers or improving the overlap between excitation and collection fibers by adding focussing optics.

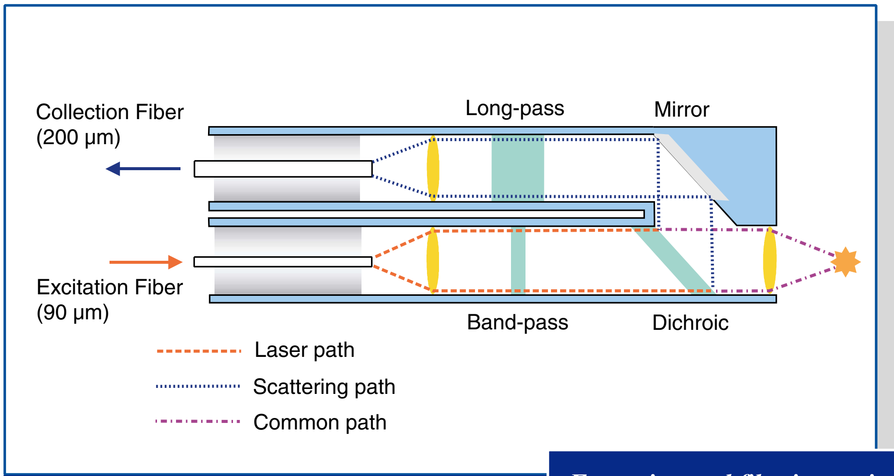
Fiber Background

Silica fiber optics are readily available for transmission in the near-IR and visible regions of the spectrum. In the Raman experiment, a laser source is shone through a fiber optic cable. At the opposite end of the fiber, the laser line is transmitted with little attenuation from the fiber; however the light output also contains Raman bands arising from the silica fiber material itself. After excitation of the sample, the large majority of scattered light intensity is at the same frequency as the incident laser beam (Rayleigh line). After collection and subsequent transmission through a second fiber, the silica Raman bands are significantly more intense than the bands arising from a typical sample. Other than using spectral subtraction after the measurement, there is no way to remove these interfering bands or "fiber background" from the resulting data. Depending upon the scattering intensity from the sample and the length of the fiber optics, the silica background can completely overwhelm the resulting spectrum.

A thorough method to remove fiber background from a Raman spectrum is precise optical filtering. The filtering is a two step process since the bands must be filtered/prevented from *both* fibers; this is achieved by incorporating various filters between the excitation and collection fibers. These optics allow only the laser line to impinge upon the sample and also efficiently remove the Rayleigh line before the scattered light is transmitted through the collection fiber.



Raman spectra of naphthalene measured with filtered and unfiltered fiber optic probes.



Focussing and filtering optics within the RamanProbe.

- The coaxial design ensures maximum overlap between excitation and collection fibers by using a common lens; the excitation and collection fibers are imaged to the same point in space.
- Having a focussed beam enables precise positioning of the sampling location; measurements can be made through a thick glass container by focussing beyond the vessel's walls.
- Single fibers can be extended by direct coupling to an additional fiber; this also enables broken probe cables to be salvaged.

Coaxial Design with Efficient Filtering

The RamanProbe™ is based on a patented design (U.S. Patent 5,112,127) that optimizes optical throughput while completely removing fiber background. It is a coaxial, two-fiber probe; one fiber is used for excitation and another for collection. The overlap between the two fiber ends is optimized by using a lens to both focus the laser and collect the scattered radiation.

The beam path is shown in the accompanying diagram. At the end of the excitation fiber, a lens is used to collimate the laser light. A band-pass filter removes the silica Raman bands, transmitting only pure laser light. The dichroic filter also transmits the laser line to be focussed by another lens onto the sample. The same lens gathers the light that is scattered 180º from the laser direction (backscattering geometry). The collected signal is then reflected by the dichroic filter through a long-pass filter assembly that transmits only the Stokes scattered light. This last filter set attenuates the Rayleigh band by a factor of 10^8, thereby preventing the observation of silica Raman bands that would arise in the collection fiber. Finally, another lens is used to focus the light, now consisting of bands only from the sample, onto the outgoing fiber. All of these optics are contained in a 0.5" (25.4 mm) diameter stainless-steel housing, ideal for hand-held use and amenable to custom modifications.

The filtering in the RamanProbe is so efficient that the complete spectral range, including laser line, can be imaged onto a CCD chip without additional filtering in the spectrometer. The optical components are able to withstand elevated temperatures (*ca.* 200ºC) and, with the addition of an extension tube, can be moved further away from the sample for even higher temperature applications.

Single-Fiber *Versus* Bundle Collection

A coaxial probe has numerous advantages over a bundle design:

- Having optical filters in the collimated beam path between the collection and excitation fibers is the most effective way to eliminate fiber background.
- Light leakage between the excitation and collection fibers (known as "cross-talk") is not possible since the fibers are inherently isolated from each other.

Summary

Unfiltered bundle probes are feasible over very short lengths (*e.g.* < 1 m) and when measuring highly scattering samples. In cases where scattering is weak and longer cable lengths are required (*e.g.* 100 m or more), a coaxial probe with efficient filtering can provide high quality Raman spectra without any silica background. The RamanProbe incorporates a minimum number of optical components in a small, robust probe-head for optimum performance and experimental versatility.

If you would like additional copies of this note, or if you would like to speak with a member of our technical staff, please contact us at:

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