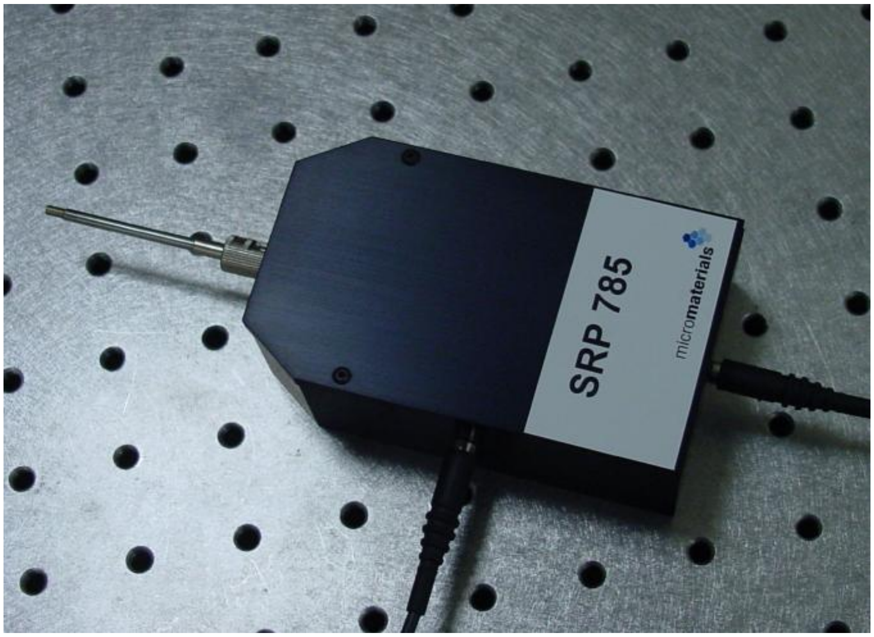
SELF-REFERENCING
RAMAN PROBE
User's Manual



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While Raman spectroscopy is a powerful technique for species identification, its application to precision measurements in the conventional manner is generally problematic. This situation arises because of the fact that the Raman signal observed depends on (among other things) the strength of the excitation light source as well as the efficiencies associated with the delivery of light from the source to the sample and of the Raman emission from the sample to the spectrometer, and it is exceedingly difficult to keep these factors constant over extended periods of time. The coupling of the excitation light into the Raman probe and the emission into the spectrometer in a fiber optic system is especially susceptible to variations because multimode fibers are typically used. For example, every time the output optical fiber from the probe is disconnected from the spectrometer and then reconnected, the Raman signal observed can easily change by 10% or more.

MicroMaterials' SRP series self-referencing Raman probes overcome these difficulties by interposing a length of sapphire fiber as an interface between the probe's optical compartment and the sample. The sapphire fiber produces its own Raman emission peaks. Since the Raman signal from the sapphire fiber shares the same optical path with that from the sample, the ratio of the two is unaffected by changes in the excitation laser's output power or coupling conditions between the probe and the laser or the spectrometer. Thus an internal standard is created.

A schematic of the self-referencing probe is shown in Fig.1. The probe tip consists of a single-crystal sapphire fiber protected by stainless steel tubing. The standard probe tip has a nominal length of 7 cm. The fiber produces three sharp Raman lines with frequency shifts of 418, 578, and 751 cm^{-1}. The availability of three reference peaks increases the probability that at least one will be free of interference from the Raman emissions from the sample.

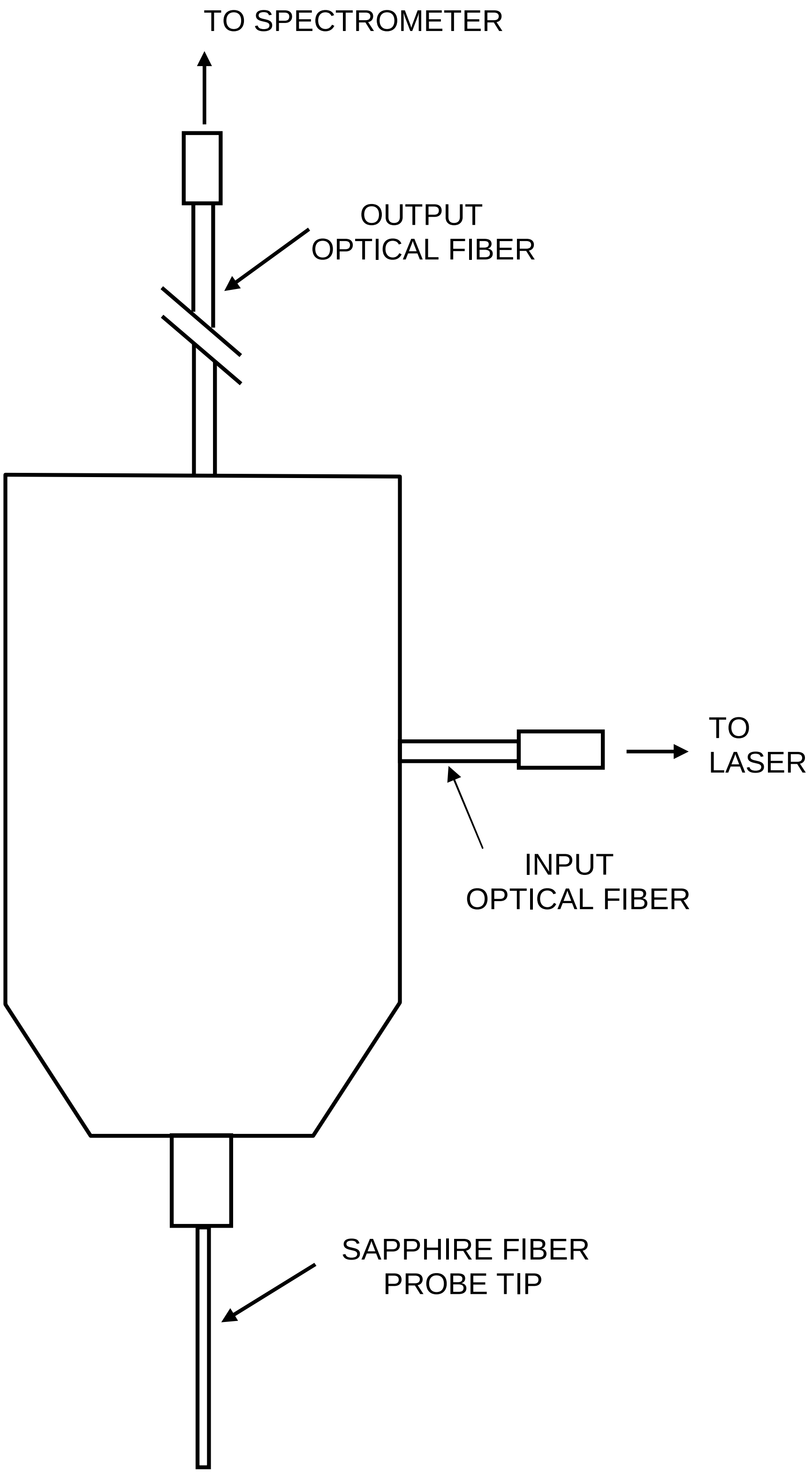
TO SPECTROMETER
OUTPUT OPTICAL FIBER
TO LASER
INPUT OPTICAL FIBER
SAPPHIRE FIBER PROBE TIP

FIG. 1

A typical Raman spectrum produced by the sapphire fiber is shown in Fig.2. A fiber-coupled single frequency laser which outputs approximately 60 mW of power at 780 nm served as the excitation source. The spectrometer used was a Mightex HRS-NIR-100 with an uncooled CCD and a 100 micron entrance slit. The data shown in Fig.2 is a dark subtracted spectrum obtained with an exposure time of 6.5 s and an averaging number of 5. The spectrum was then smoothed by applying a 15th order boxcar filter. The linewidths shown are mostly due to the resolution of the spectrometer and the subsequent smoothing operation.

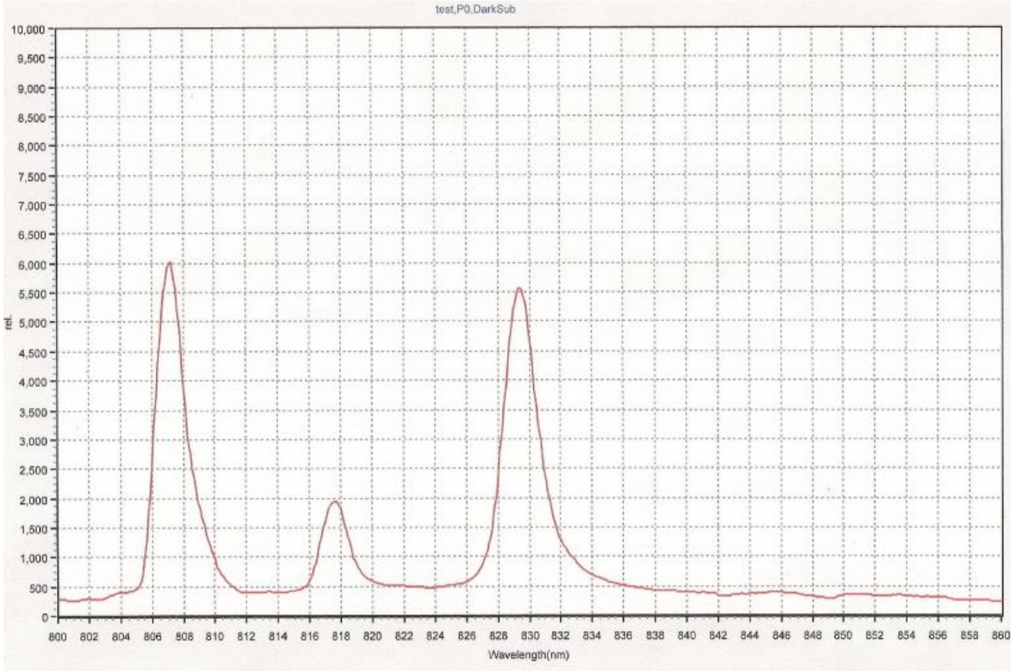

FIG. 2

As an illustration, the application of the probe to the determination of ethanol content in gasoline will now be described. To generate the calibration curve, the emission from ethanol-free gasoline obtained at somewhat reduced laser power was used as the “dark spectrum”. This was accomplished by backing out the output fiber of the laser in the mating sleeve connecting it to the input fiber to the spectrometer and at the same time monitoring the light output through the sapphire fiber. In the data to be presented, the power was reduced by approximately 20%. A spectrum was then taken with the probe immersed in the ethanol-free gasoline, and the height of the reference peak near 807 nm, selected because gasoline has negligible Raman emission there, was recorded (to be referred to as S_0). The same spectrum was then retaken as the "dark spectrum".

Next the ethanol-free gasoline was replaced by mixtures with different amounts of ethanol added. At each ethanol concentration the laser's output fiber was screwed in slightly, until it was all the way in. Thus, the laser power exiting the sapphire fiber was increased by approximately 25% at the end. The spectrum taken with 10% V/V ethanol is shown in Fig.3. The peak near 838 nm corresponds to the 880 cm^{-1} Raman transition for ethanol. In this case the sapphire peaks amounted to approximately 8% of those in the "dark spectrum". To make a precise determination of the peak heights at 807 nm and 838 nm, the baseline value was found by taking the average of the pixel readings in the intervals 800-802 nm and 842-844 nm. Then 10 pixel readings near each of the peaks at 807nm and 838 nm were fitted to quadratic forms, and the maximum values determined. The peak heights at 807 nm (to be referred to as S) and 838 nm (to be referred to as R) were then found by subtracting the baseline value. The normalized magnitude of the ethanol peak at 838 nm relative to the reference sapphire peak at 807 nm was finally calculated using the formula $M=RS_0/(S_0+S)$. The linear fit of the resulting data is shown in Fig.4. The good fit, in spite of a 25% spread in laser power, confirms the validity of the self-referencing approach.

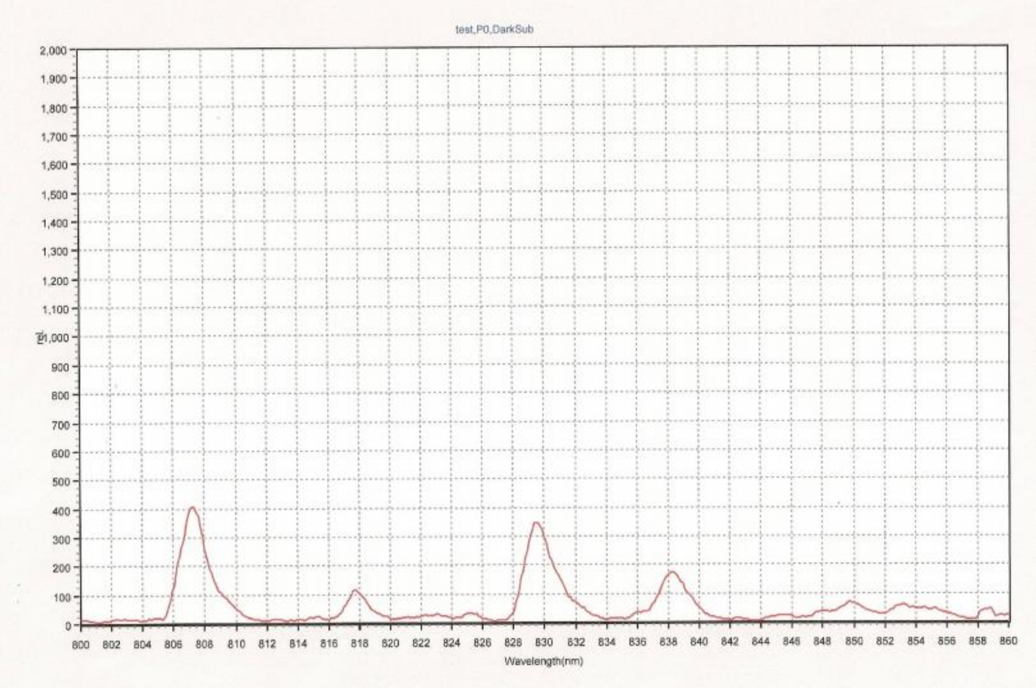

FIG. 3

To determine the ethanol content of an arbitrary gasoline, one cannot use just any ethanol-free gasoline to provide the “dark spectrum” because the blending of the fuel varies from one station to another. Instead, one must first extract the ethanol from the gasoline of interest. This can be done easily by mixing the gasoline with water in roughly equal parts in a small vial and shaking vigorously for a few minutes. Once the two phases have separated (in another few minutes), the gasoline phase on the top will be free of ethanol and can be used to generate the “dark spectrum”. Then the same procedure as described above is followed to determine the normalized magnitude of the ethanol peak. This was done for a regular E10 gasoline obtained from one of the major-brand stations, and the result is shown as the dashed line in Fig.4. It is seen that the gasoline contained 9.5% ethanol. The uncertainty of the measurement is estimated to be +/- 0.5%.

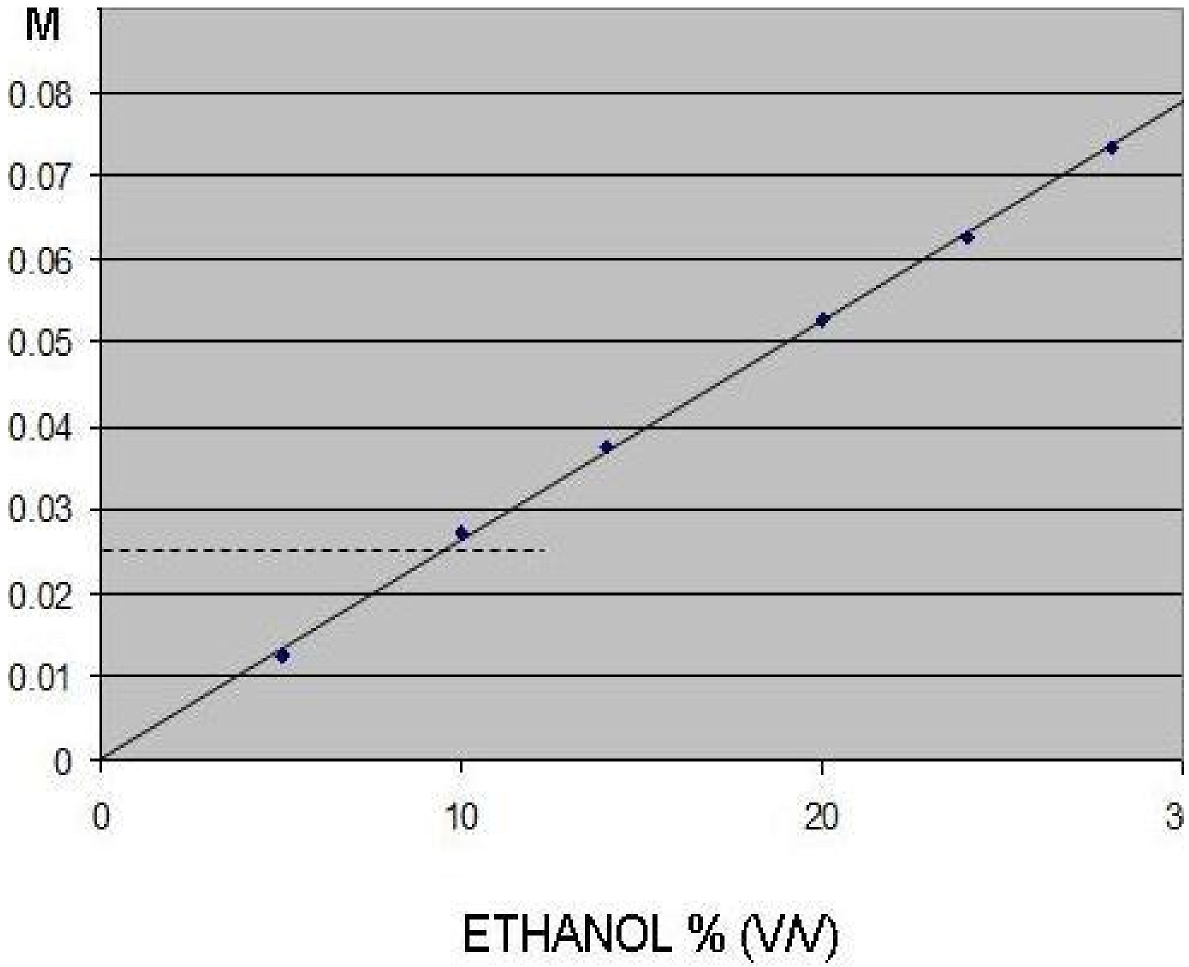

FIG. 4

Note that the changing of the coupling between the laser and the spectrometer in the generation of the calibration curve is clearly not a requirement. It was done in the illustration only to show the effectiveness of the self-referencing approach. In practice, even without touching anything there will still be an inherent variation of the order of a few percent in the Raman emissions acquired in a typical system. Thus, one would still gain in measurement accuracy by using the normalization procedure. Also, the Mightex spectrometer was used to show the kind of results that can be obtained with even a very basic unit. Superior results can be expected for spectrometers with cooled CCD and greater versatilities.