“Outside the box” Raman spectroscopy:

Remote measurements for bulk samples

Authors

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Introduction

The effectiveness of Raman spectroscopy depends, in general, on focusing the excitation laser onto the sample. However, there are many cases where a traditional spectrometer’s working distance is not sufficient to achieve this, in which case a focus-independent, long-distance collection proves invaluable. One potential application of this focus-independent “remote” measurement is high-throughput plastics recycling, where many differently sized plastics are passed along at a fixed distance and screened for specific material identification. Similarly, any potential use cases of samples inside a glove box or within a hazardous environment may benefit from long-distance collection, because the laboratory grade spectrometer can be kept clear of the sample enclosure while providing excellent spectral signal. It should be noted that each unique application comes with its own optical beam path and laser safety requirements.

In addition to this particular modality, the Thermo Scientific™ DXR3 Flex Raman Spectrometer provides excellent experimental versatility with micro scale, bulk sampling, and fiber probe collection modes also available. Shown below is a long-distance analytical setup in which the DXR3 Flex Raman spectrometer passes the unfocused laser beam through a quartz shielding window onto a polystyrene sample (Figure 1). The relationship between pathlength/sample mounting preparation and spectral signal is investigated below, to validate the use of a long-distance collection mode as a viable alternative to more traditional, focus-dependent analysis. It is worth mentioning the practice of standoff Raman spectroscopy, a technique designed to provide Raman data at distances ranging from 1 m to several hundred meters. However, these systems often require significantly different components than a standard Raman spectrometer, such as pulsed lasers, gated detectors, UV excitation wavelengths, and telescopic focusing elements.[1] The work described here performs measurements at a distance with a simple, off-the-shelf, benchtop spectrometer.

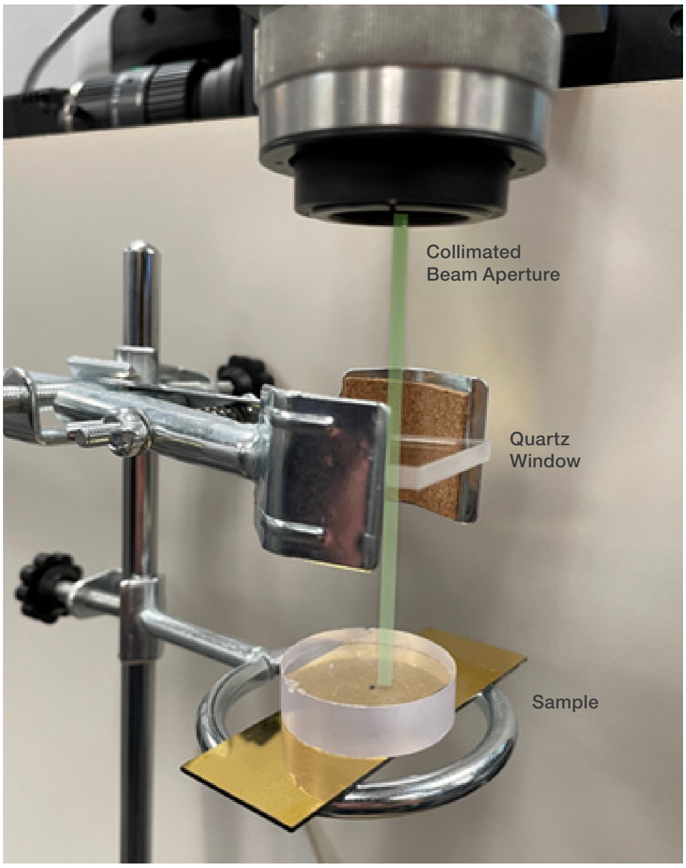

Figure 1. The generalized long-distance Raman spectroscopy design, with an inserted 1/8" thick quartz glass piece (to mimic shielding) inserted in the beam path and a 532 nm excitation laser at 40 mW with collection times of 2 s x 30 excitations (totaling 1 minute per spectra). The sample mounting is changed based on the substrate and sample being studied.

Polystyrene was used as a reference material to test five different experimental parameters: the overall sampling pathlength, the impact of the quartz shielding window within the path, the thickness of the sample, the presence of a reflective surface to bounce the beam back, and the angular orientation of the sample surface relative to the laser source. From these tests, optimal long-distance sampling parameters were determined and implemented on recycled plastics.

Sampling pathlength

To determine the largest feasible pathlength, for either very large samples or convenient instrument placement relative to the sampling line, the test sample was analyzed at a series of distances increasingly farther away from the beam aperture (Figure 2). In this study, the quartz shield location was held constant, and the sample was oriented normal to the excitation laser beam with a metallic background.

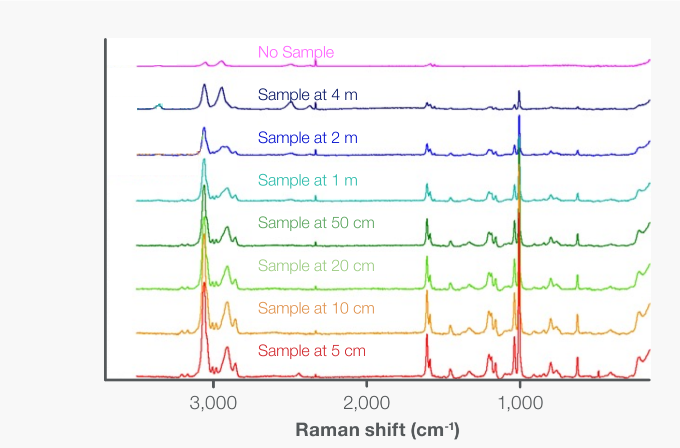

Figure 2. Spectra collected from a 9 mm thick polystyrene reference standard mounted on a gold-coated substrate. The quartz window was maintained at a fixed 1 cm distance from the laser aperture. The sample surface was measured relative to the quartz window, varying from 0.05 to 4.0 meters. The pink spectrum is included for reference and was collected in the absence of any sample, representing the Raman peaks for reflections from the quartz window, internal optics, and ambient dark laboratory conditions.

Although the sample signal is readily detectable up to 4 m (based on the presence of the 1001 cm^{-1} peak in Figure 2), it falls off at an exponential rate of decay in relative signal intensity over increasing distance. To better quantify the decreasing signal strength, Table 1 and Figure 3 indicate the sample's Raman intensity with the peak height ratio between the dominant polystyrene peak at 1001.7 cm^{-1} and the dominant background peak at 2943 cm^{-1} (taken from the spectra in Figure 2).

Sample Distance (m)	Peak Height Ratio
0.05	**23.610**
0.1	**23.574**
0.2	**21.488**
0.5	**15.806**
1.0	**10.430**
2.0	5.587
4.0	0.926
No Sample	0.027

Table 1. Sample distance vs the peak height ratio between the polystyrene sample peak at 1001.7 cm^{-1} and the background signal peak at 2943 cm^{-1}. The bold values represent a strong signal from the sample.

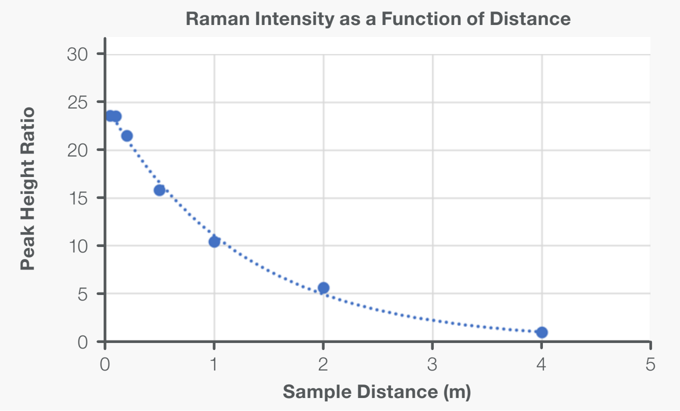

Figure 3. A graphical representation of the data in Table 1. The displayed trendline in an exponential function.

This provides great insight into the relationship of pathlength and Raman signal, although the functional maximum pathlength will be very sample- and experiment-dependent. A recommended maximum pathlength of 1 m is proposed here, which should be sufficient for all but the largest samples.

Location of the quartz shield

Given that the best practice seems to be keeping the sample within a 1 m pathlength, the next question is how the location of a quartz window shield within that pathlength might affect the overall signal. Since the beam is not perfectly collimated, the largest concern with the shield placement is that there may be some dependence on the light scattering at the window surface due to the beam width. The quartz was moved in 10 cm increments, with the distance measured from the laser aperture with a sample at a fixed distance of 1.0 m (Figure 4).

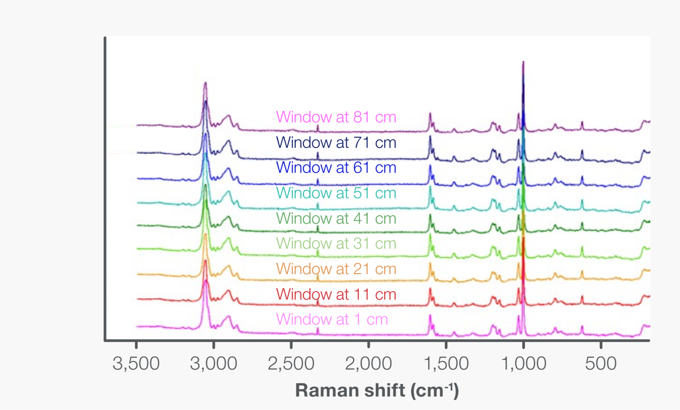

Figure 4. Spectra taken from a fixed sample while moving the quartz window shield along the beam path in 10 cm increments.

There is no discernible difference in the Raman signal as an effect of the quartz shield placement. This allows for great flexibility in the placement of a piece of shielding relative to the instrument and sample (although the beam path should pass normally through all windows).

Sample preparation - thickness and substrate

Since the laser beam in this configuration is collimated and has no specific focus, the beam will continue indefinitely. As such, the sample and/or sample substrate must be considered in terms of how efficiently it scatters the Raman-shifted photons back to the detector. For opaque, relatively thick samples, the incident laser beam will scatter/reflect off the sample surface. In this case the substrate will not affect these measurements. However, the laser beam will pass through most transparent materials. In this case, the substrate may also produce a Raman signal; this makes substrate selection very important. As such, the optimal substrate would be a Raman-inactive surface like a pure metal. This has the additional benefit of being highly reflective and returning the incident and scattered light directly along the initial path, improving the signal. Similarly, the thicker the sample being tested, the more Raman signal will be returned. This data is shown in Figure 5 where sample thickness was varied both with and without a reflective gold-coated substrate.

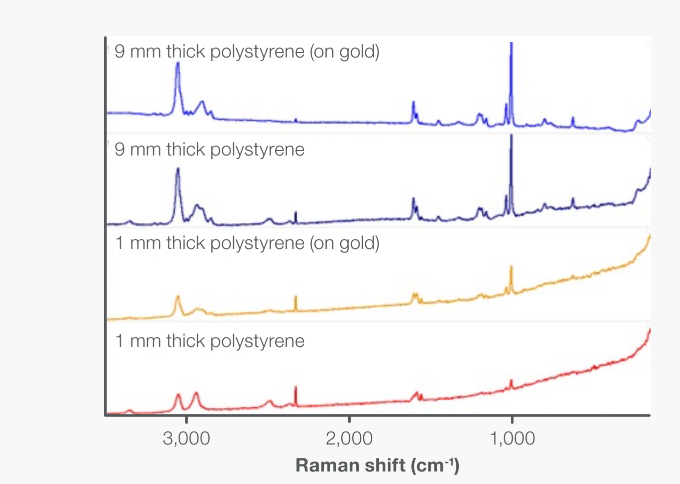

Figure 5. The thickness or amount of material significantly affects the overall signal, especially when compounded with other factors such as the presence of a reflective surface and the sampling pathlength. These spectra were collected at 50 cm from the laser aperture. By decreasing the sample thickness by a factor of 9, the intensity of the 1001 cm^{-1} peak decreases by a factor of 11. Removing the reflective gold coating behind the sample reduces the intensity by an average factor of 2.9.

Although any Raman-active sample will produce a Raman signal and the presence of a reflective, Raman-inactive background is not required, it is important to consider how these factors may influence the overall signal for a given sample. When possible, a reflective, Raman-inactive substrate should be used.

Angular orientation

In a similar vein, most samples will not present a flat, even surface and will scatter light widely. By testing a flat sample at various angles, the effect of presenting a flat sampling surface normal to the orientation of the collection beam is tested. Raman scattering occurs omnidirectionally so any sample orientation will return a signal (as seen in Figure 6). However, for flat surfaces, an orientation normal to the beam does produce a slightly stonger signal.

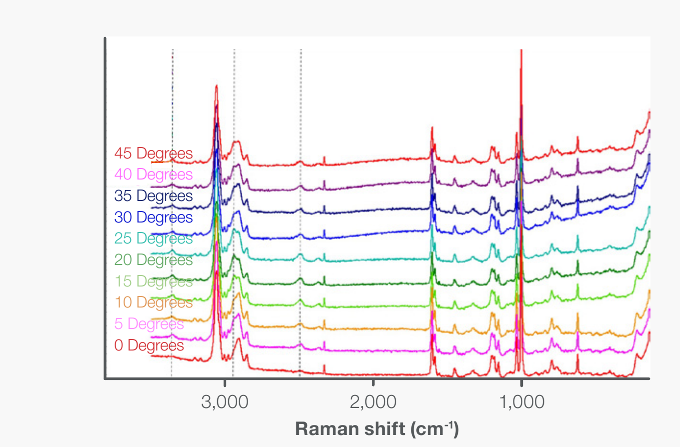

Figure 6. Polystyrene samples (mounted on a gold substrate) were held 50 cm from the laser aperture and then rotated from 0 degrees (normal to the incident light) in ΔΘ=5^0 increments up to 45^0. The reflective substrate made it easy to track the reflected beam (moving in 10^0, 2*ΔΘ increments) although the Raman scattering occurs in all directions and is not correlated to the direction of reflection.

Any angle beyond 0^0 has a relative increase in the signal of the background peaks (seen at the dashed vertical lines and due to a decrease in the returned polystyrene signal) which is an easy indication of less efficient Raman scattering from the sample. The weakest polystyrene signal is at 20^0 and does not decrease at larger angles. Since there is a very similar polystyrene signal intensity at any orientation, this indicates that rough or multifaceted samples will produce equally clear results given that the sample orientation does not noticeably impact the results.

Practical use case: recycled plastic identification

One of the major benefits of this long-distance measurement technique is being able to handle samples of various sizes and thicknesses without needing to adjust the laser focus for specific samples. The following results simulate a potential use case where remote Raman spectroscopy is used to rapidly identify the plastic materials of various sizes. The samples were fixed at a 50 cm pathlength, and collection times were set at 10 s.

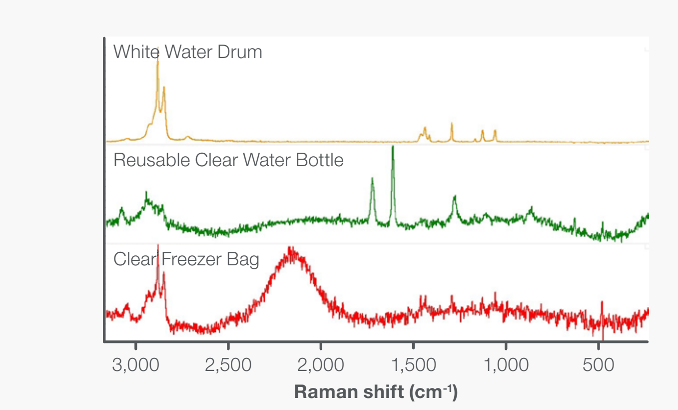

Figure 7. Recycled plastics, collected with a 10 s excitation of 532 nm incident light at 40.0 mW. Each spectrum was baseline corrected to remove fluorescence and background. The signal-to-noise ratio (SNR) is linked to the material thickness where the water drum was 8 mm thick (SNR 75.81), the water bottle is 2 mm thick (SNR 13.61), and the freezer bag is 0.2 mm thick (SNR 4.06).

All three samples show clear and identifiable Raman signals. The plastic drum is identified as polyethylene, while the water bottle is a specific, BPA-free polycarbonate alternative. The plastic bag is multilayered, with signals from both polyethylene and polycarbonate, along with a visible fluorescence peak at 2150 cm^{-1}. All of these different polymers are spectroscopically identifiable, and at a range of different sample thicknesses. These results provide an excellent view into the use of this technique on non-reference samples. This is just one example of a potential use for the long-distance collection mode, a mode which enables much greater versatility in experimental design and instrument placement.

Citations:

1. Alison J. Hobro, & Bernhard Lendl. (2009). Stand-off Raman Spectroscopy. TrAC (Trends in Analytical Chemistry), 28(11), 1235-1242. *https://doi.org/10.1016/j.trac.2009.08.008*

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