



Using a Spatial Heterodyne spectrometer for Stand off Raman observations: The influence of the Raman collection probe.

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Abstract

This technical note describes the influence of the “spectrometer – optical probe” interface when using a Spatial Heterodyne spectrometer. The requirement to tailor the design and configuration of the probe to the individual environmental and sampling demands found in a diverse range of Raman measurement scenarios. Several sample and sampling parameters are identified and examined, and optimum probe types suggested. Three stand-off probe types are presented: two confocal monoaxial probes: one incorporating a dichroic mirror for laser turning and Raman collection filtering, and one using an independent laser turning mirror and thirdly a biaxial probe, where excitation laser and Raman collection optics of independently positioned and aligned. A series of Raman spectra are presented: a comparison of probe choice influence on capturing Raman spectra of freeze dried sugars; an examination of probe filtering effects when capturing highly translucent liquid samples and challenges when measuring highly opaque samples. Finally, an additional probe design is presented where Raman capture at stand-off distances between 500mm and 1500mm was readily facilitated. Raman spectra of paracetamol captured in 0.5 seconds at 1.0m stand-off distance is demonstrated.

Introduction

Raman spectroscopy is an established method for analysis and identification of chemical samples. One of the key advantages of Raman measurements is that the samples require no preparation; this makes the technique ideal for *in situ* measurement applications within the process industry. Raman scattering is a weak process, therefore collecting as much light as possible is critical if good quality observations are to be achieved. This issue is compounded when making observations from diffuse targets; as required for transmission Raman measurements. Additionally, if a large stand off distance is present in the observational environment, this can have a significant impact on the throughput that can be achieved. This has led to the development of high etendue spectrometers based on static Fourier transform instrument designs (e.g. spatial heterodyne spectrometer (SHS), RD1, RD2, RD3). This includes the IS-Instruments range of HES spectrometers which have been optimised for Raman applications.

The optical probe design and configuration (the instrument-sample interface) can have a significant influence on instrument performance. The probe must accurately collect light from the target sample with a high level of efficiency and excellent throughput, while eliminating unwanted returns from the sample holder or cuvette. To combat these effects, current commercially available systems have employed a range of solutions including: confocal microscope probes (RD4), fibre bundle collection systems used in a spatially offset configuration (RD5), and multi pass probes for liquid and gas samples. Additionally, the probe optics should be well matched to the analysing spectrometer. The ISI HES range of spectrometers offers both increased etendue and a greater depth of field. This demands careful optical probe design and/or selection. For example, the improved etendue offered by

the instrument can generate additional challenges in terms of extraneous light suppression; as background light is proportional to the instruments field of view.

As all molecular compounds provide a Raman signature, signal contamination from sample containers or extraneous material can be a major issue. As well as masking the primary signal, these unwanted returns increase the noise in the overall spectrum when adopting a SHS configuration due to the multiplex disadvantage (RD6).

This technical note will explore each of these issues and present some of the various probe options available. Specific probe designs for stand-off observations at distances up to 1.5 m are also presented. It will also examine how the data is presented in an SHS and effects of unwanted background light. Furthermore, techniques that can be used to improve the signal to noise ratio achieved with simple design changes are discussed. Key to this is adopting a philosophy where the probe and spectrometer are developed as one unit rather than separate optics systems.

Background

The total amount of signal returned by a Raman instrument is given by equation 1.

$$S = \frac{L_p A \Delta R \alpha \omega \Sigma e^{-2 \int \tau \delta r} \delta r}{\pi R^2} \quad \text{Equation 1}$$

Where L_p is the laser power, ΔR is the depth of the sample being analysed, α is the Raman scattering cross section, A the area of the telescope or collecting lens, ω is the instrument efficiency, and R is the distance to the target. The instrument efficiency is a combination of the optical transmittance and the detector quantum efficiency. τ is a function of the depth of the sample being examined.

This is a modified version of the LIDAR equation and assumes the target sample is a Lambertian scatterer. The equation takes no account of any directionality of the Raman scattering function that can influence the exact return.

The relationship between ΔR and τ is critically important to the choice of probe being used for any given application. The amount of light returned is proportional to the number of scattering centres intercepted by the laser beam which is determined by ΔR . Thus, the greater the depth probed by the instrument the stronger return.

However, the optical depth is also a function of ΔR , thus as the depth increases no further gains can be made. This effect is shown in *Figure 1*, where the relative signal strength is calculated for a fixed sample with a variety of different optical depth values. *Figure 1* shows that the linear relationship is observed with ΔR for an optical depth of 0.01 only.

If the probe is designed to penetrate a set distance into the sample with a high optical depth, in a fixed optical arrangement the summation term in equation 1 is negated, and the amount

of signal can be reduced!. This issue can also be observed when the transmission and collection optics are not perfectly co-aligned.

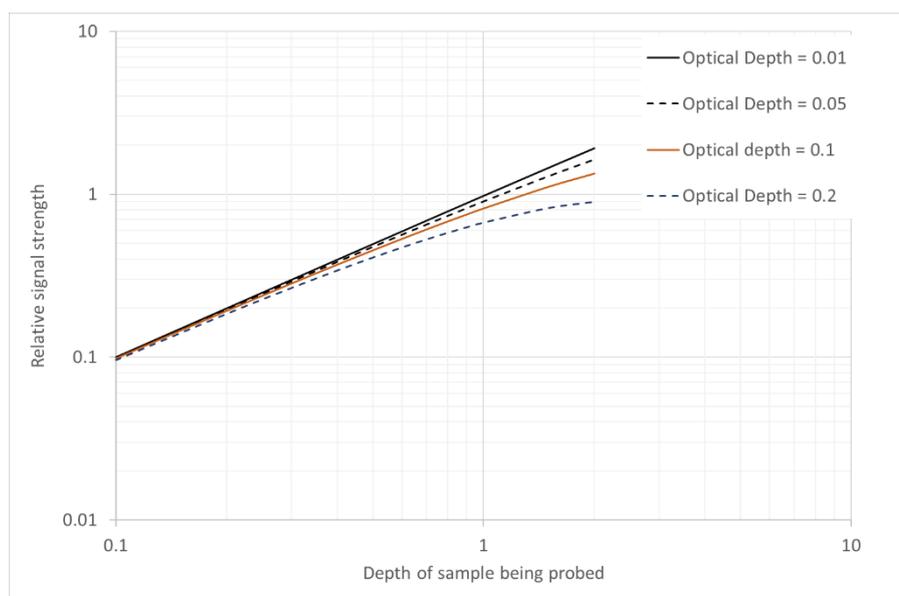


Figure 1 Relative signal strength as a function of optical depth.

The influence of samples

The range of samples that can be encountered by an instrument vary dramatically, and thus there is no one-size-fits-all probe solution. A specific type of probe setup may be ideal for just a small subset of possible measurements. The probes themselves can vary from simple backscatter arrangements, through to more complex scanning setups.

A probe may well be able to make a given observation but is not the best or most cost-effective solution. For example, scanning microscope probes are available from most manufacturers and can indeed perform observations of many samples. However, if a sample is predominantly homogenous in nature, or if there are time constraints (as is the case in many online observations) this class of system is not ideal, or even necessary. *Table 1* provides a guide on selection of a Raman probe to make the best observation of a given type of sample. Samples are considered in relation to the following parameters:

- (a) heterogeneity
- (b) volume,
- (c) thickness
- (d) within or without a container
- (e) scattering strength
- (f) opacity

spatially offset arrangement may be superior. Thin film samples are best probed with a micro-objective; however, complications occur when these samples are weak Raman scatterers. If a sample is highly opaque a transmission or spatially offset arrangements may give no response at all.

In the following sections the design of standoff Raman probes that may be adopted for online measurement problems are considered for use with a HES spectrometer. Confocal and biaxial Raman probes are considered and their performance compared. Finally, the specific problem of making observations at > 1 m are examined and a new probe design presented. Scanning and ring or multipass techniques are often more complex and therefore are beyond the scope of this report.

Instrumentation

Previous authors have discussed the strengths of an SHS when making observations of high etendue targets, specifically in applications such as transmission Raman (RD3). However, in many applications from laboratory based testing through to online measurements for industry, this type of arrangement is not possible.

In this report we consider measurement situations where the target is at least 50 mm from the target. The probe design is considered with the SHS as a unit, the susceptibility of the instrument to background light and stray Rayleigh scattering must also be considered. If this can be resolved outside of the spectrometer superior performance can be achieved.

The following three principle probe designs are now considered:

1. A confocal probe incorporating a dichroic mirror, acting to (a) turn the excitation laser and (b) filter the collected Raman signal.
2. A confocal probe incorporating an independent laser excitation turning mirror which, due to design limitations, the collected Raman signal becomes partially obscured.
3. A biaxial probe, where the excitation laser optics and the Raman collection optics are independently positioned and aligned.

Collection Probe

The preferred choice of Raman collection probe for many applications is a confocal arrangement. This type of probe is easy to use with the excitation and collection optical paths coaligned. This usually requires a dichroic filter to be integrated into a probe. When using a HES spectrometer the probe should have a filter inserted ahead of the fibre to eliminate any unwanted Raman / fluorescent light. Given the sensitivity of the HES instrument to background light, any unwanted Raman scattering should be removed at source. Therefore,

the ISI confocal probe uses a focusing mirror to direct and collect the light from the target rather than a lens which can itself be a significant Raman scattering source.

A schematic of this probe is shown in *Figure 2*. The advantages of this approach is that no light is lost due to obscuration. This makes the design highly robust and flexible. The design can be adapted to fit a micro-objective allowing for very small samples to be probed at reduced focal depth thereby eliminating unwanted scattering sources (e.g. from the sample container).

The probe etendue must be matched to that of the analysing spectrometer if no light is to be lost. This can become a significant limitation in dispersive systems. The ISI confocal probe is fibre coupled, so has the advantage of decoupling the optical systems making the design of both parts more flexible.

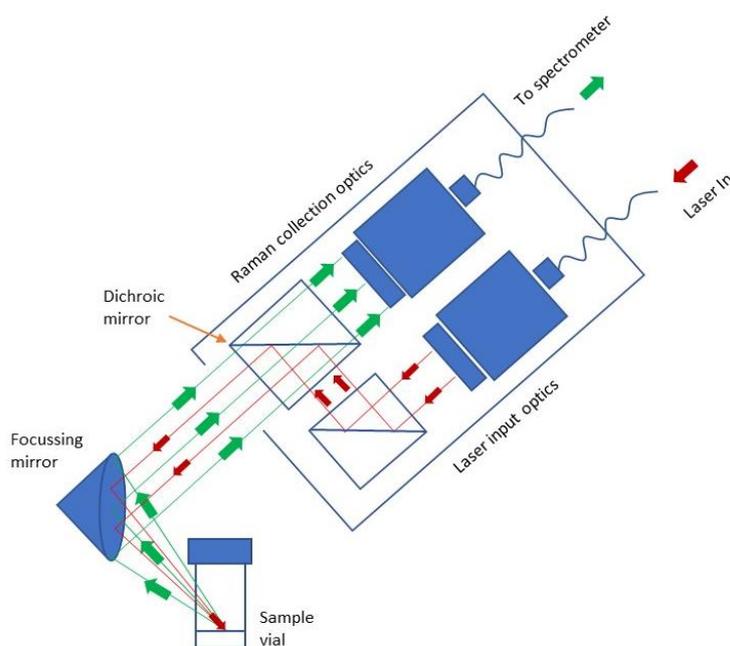


Figure 2 IS Instruments confocal Raman probe

An alternative confocal probe arrangement is given in *Figure 3* here the dichroic filter is replaced with a turning mirror. This is less efficient than the example given in *Figure 2* as the excitation laser turning mirror partially obscures the return signal and in most cases provides inferior performance. However, this arrangement can provide advantages when attempting to study samples within a container. If the sample has a sufficiently different focus position, then the turning mirror can act as spatial filter with respect to the walls of the container.

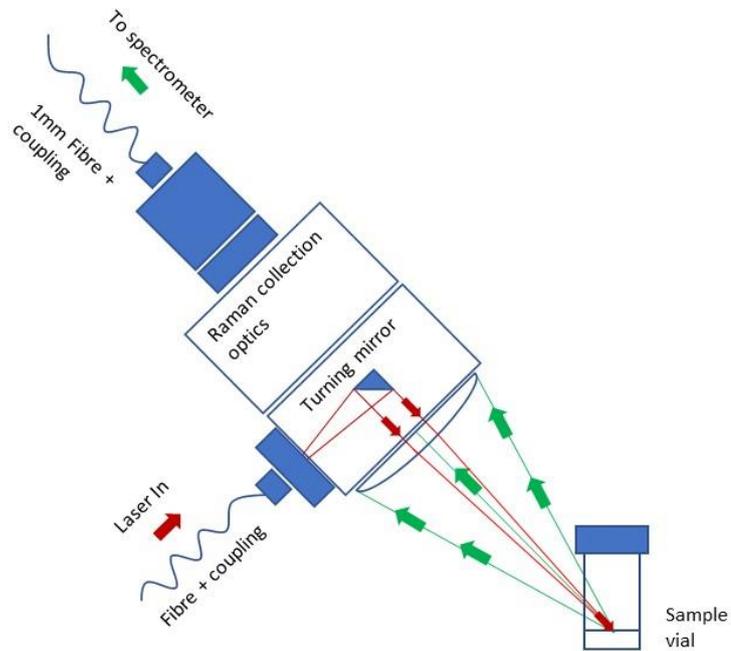


Figure 3 IS-Instrument mono axial probe arrangement

Figure 4 shows a decoupled arrangement which could be considered optically biaxial. This setup is more complex to arrange and is not ideal for hand held applications, however for online monitoring it can provide the best solution, as it efficiently removes any unwanted light and can accurately target samples inside a given container, where only the Raman signal from the target source is collected.

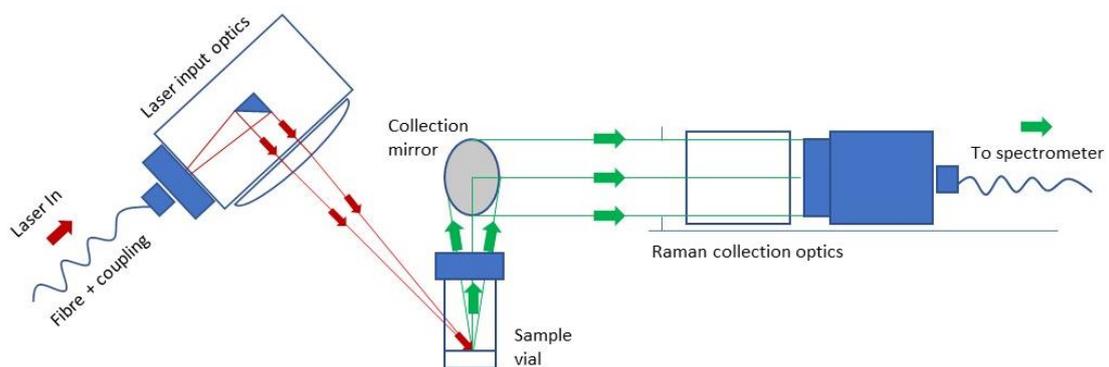


Figure 4 IS-Instrument Bi-axial Probe arrangement.

Raman probes for challenging sample capture

The following section presents a series of Raman measurements demonstrating the application of tailored probe designs. With configurations to optimise the capture of Raman scattered light into the spectrometer. For a series of challenging sample types and sampling conditions.

In each case the light collection section of the optical probe was coupled via a 1mm fibre to an ISI HES spectrometer. A 785nm PDL D Boxx Raman excitation laser was coupled via a 100 μm fibre to the transmission section of the optical probe. The laser power at probe output at the sample was approximately 250 mW.

Measurement of solid samples within a glass container

Figure 5 (a) and (b) show Raman spectra of two freeze dried samples: A and B, in both instances measurements were captured through a crimp top glass sample vial container, thereby negating the requirement to remove the sample from the container and expose the material to the ambient environment.

Previous work showed the sample container gave a strong Raman signal itself and was likely to contaminate the measured spectra. Figure 5 shows the spectra acquired with the 3 probes shown in Figure 2- Figure 4. Demonstrating the strengths and weaknesses of each of the probes. The confocal probe with the dichroic mirror shows a very large peak from 1200 cm^{-1} – 1600 cm^{-1} . This is due to the efficiency of the probe collecting the majority of the scattered light both from the target and the sample container. In this instance the efficiency of the probe is working against our objective to observe only the sample. The spectra recorded using the confocal monoaxial probe shows good ability to capture the spectra. However, both spectra A and B show a baseline lift toward the LHS, indicative of unwanted laser light from the input laser optics interfering with the collected Raman signature. In the confocal probe with a dichroic mirror, this lift has been removed. However, the performance is still superior to the classical confocal.

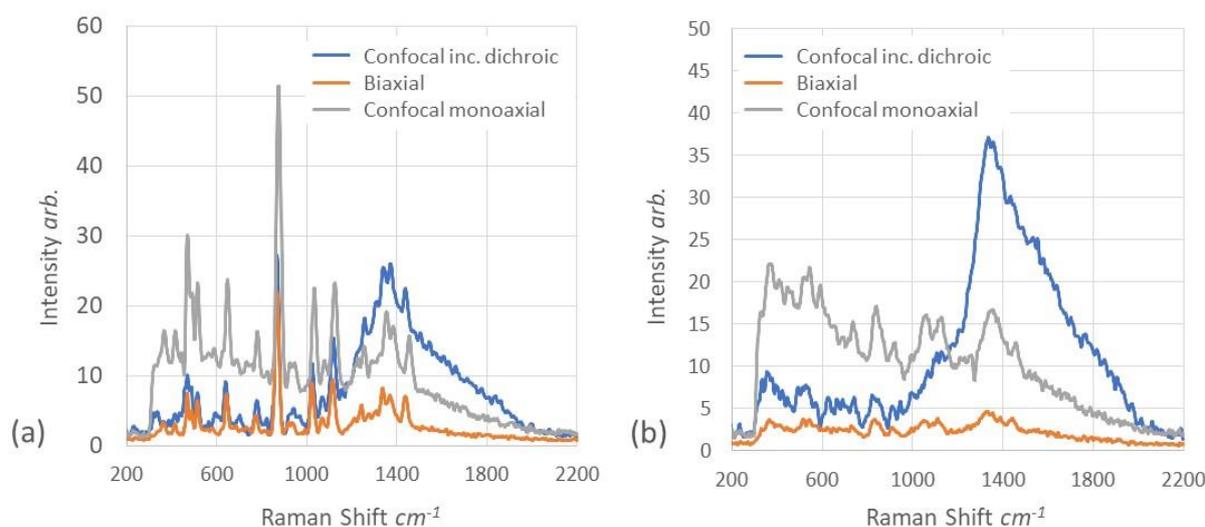


Figure 5 The acquired spectra of freeze dried samples through a crimp glass vial container

The biaxial probe resolves both of these issues in this instance. The collection optics are focused only at the target and due to being non-coaligned surface scattering becomes spatially filtered. In Figure 5(a) the spectra is clearly presented. However, the mechanical alignment of the system is more challenging and thus some light is lost.

Measurement of a liquid sample - water

The observations discussed above are of solid samples mounted within an optically obscuring container. Liquid samples can also provide challenges for Raman measurement. In this section an observation is considered, where the container is conveniently shaped, and therefore the confocal Raman probe, shown in Figure 2 was used. Furthermore, the large depth of field inherent to HES instruments (due to large etendue), allows ΔR to be increased for translucent liquid targets such as water; allowing more photons to be captured and observed.

The resulting raw data observation is presented in Figure 6, where no data processing has yet been applied. The probe was initially fitted with a 785nm long pass (LP) filter as labelled. The integration time was 4 seconds with approximately 250 mW laser excitation power at the target. The water peak can be clearly observed at 1600 cm^{-1} . Using equation 1 the observed signal can be compared to a simulation of the expected instrument performance.

Using a confocal F2:1# probe, the estimated depth of focus is 10 mm. From (ref) the Raman cross section of the water spectral peak at 1600 cm^{-1} is $3.35 \times 10^{-31} \text{ cm}^2\text{Sr}^{-1}\text{mol}^{-1}$ at 785 nm. The instrument used an ANDOR IVac 324 detector with as QE of 30 % at 1600 cm^{-1} , and the optical transmission taking account of the losses with the fibre coupling, filter and beam splitter is estimated as being 20%. This suggest 820,000 photons will be observed within the 1 integration time. The detector sensitivity is 6.7 photons per count, therefore the detector count rate is 122,000. The actual observed photons is 116,000, this is within 5 % of the

computed value. This demonstrate that the HES2000 instrument is achieving excellent performance when combined with the confocal probe.

However, the noise in the signal is relatively large, this is due to the multiplex effect when using a Fourier based device (RD5). To further illustrate this an 880 nm bandpass filter has been added with 70nm band width. The filter has a 70 % transmission. Although the resulting spectra has a lower signal the observed signal to noise ratio is higher by a factor of 1.8. Integrating the light observed from $50\text{ cm}^{-1} - 700\text{ cm}^{-1}$ shows that approximately 3.4 times more photons are observed without the bandpass filter, suggesting that this would contribute a factor of 1.84 in additional noise to the capture of water Raman spectra. This is in excellent agreement with the observation. This result illustrates how the performance of the system can be refined to provide optimum performance for a given observational condition.

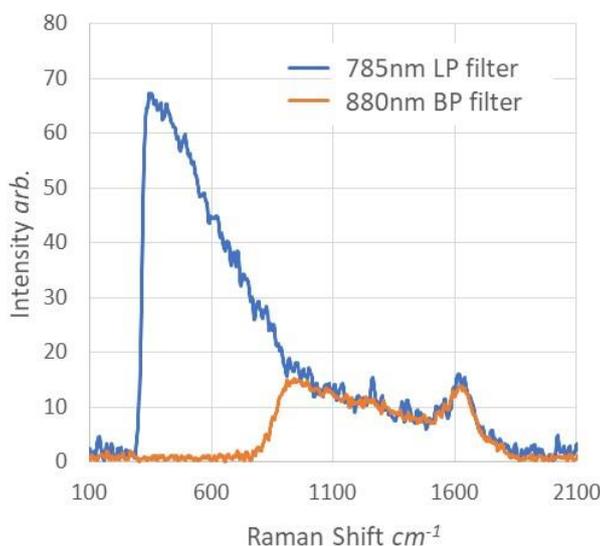


Figure 6. Raman spectra of water captured using a 785nm long pass filter and a 70nm bandwidth 880nm band pass filter.

Opaque targets - Graphite

There are situations where a small depth of focus provides the maximum amount of returned light, due to massive attenuation of the sample as indicated by *Figure 1* . One such case is when making Raman observations of graphite. Graphite is an opaque material as shown in *Figure 7*



Figure 7 Example of a Graphite block.

The IS-Instruments range of HES spectrometers are typically designed to collect light from a 1 mm diameter spot. Matching the collection probe to this spot size typically gives a depth of field of several mm. This is more than sufficient for most liquid and solid samples to provide a good Raman signal, assuming a laser power in excess of 100 mW at 785 nm. Graphite is known to have a large Raman cross section (RD7).

As with the water observation the confocal Raman probe was used. However, when making observations of the graphite poor quality Raman spectra were obtained as shown in *Figure 8*). The general background slope observed from 400 cm^{-1} – 2000 cm^{-1} is indicative of light being reflected back from the surface and exciting the fibre. The expected peaks at $\sim 1300 \text{ cm}^{-1}$ and 1600 cm^{-1} although visible are very weak in comparison. It was noted that the surface did have a significant reflective sheen.

The observation was repeated on a roughened surface of the graphite, with dust from the graphite being present. the captured Raman spectra is shown in *Figure 8*(b) where both of the predicted peaks are clearly observed.

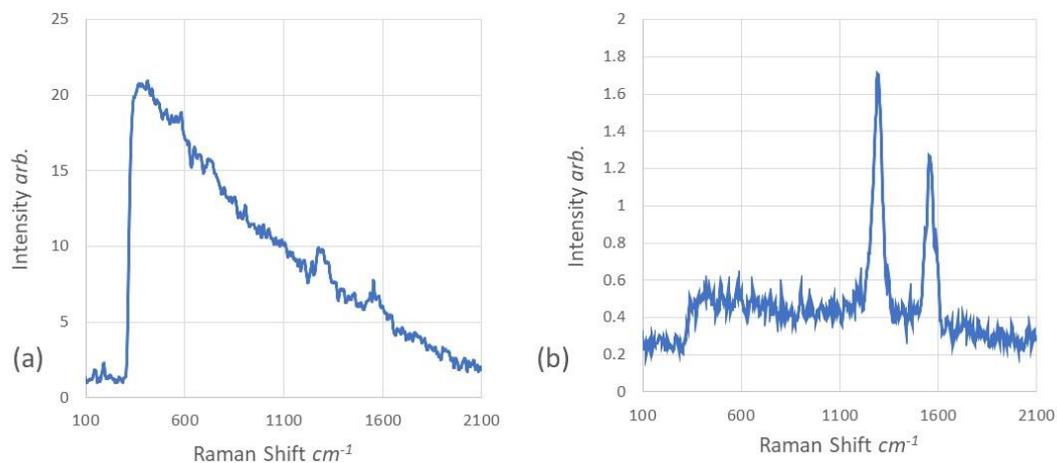


Figure 8 Graphite Raman observations on (a) smooth surface and (b) roughened surface

This implies that the surface itself has had an impact on the measurement. Examining the results in more detail the actual Raman peaks are similar in relative strength and shape in both cases, however in the roughened case the background lift is far less. Also, the length of time to acquire the data was in excess of 10 seconds despite the large scattering cross section of graphite. This can be explained by the significant optical depth of sample with surface penetration being estimated as being no more than 50 μm . Further when observing the smooth surface the total amount of light collected is significantly greater than when measuring the roughened face.

The smooth surface has a reflective sheen, and this produces many more Rayleigh scattered photons. This reflective sheen is indicative of the face having specular reflective properties. Therefore, a significant increase is observed in the amount of unwanted laser light being collected, this in turn excites the glass with the probe producing the unwanted background response. In this case a micro-objective with a much smaller etendue may provide superior results as these unwanted photons are spatially filtered and thus do not contaminate the observation.

The stand-off challenge

In many process applications, interfacing a Raman system to a manufacturing facility can be a challenge. Often it is not possible to have the system in close proximity to the target sample. In this case if there is a line of sight, a stand-off probe can be used. However, this provides significant challenges to the spectrometer. As shown in equation 1 the strength of the signal is $\propto 1/R^2$ furthermore, the instrument etendue can become a limiting factor. Particularly if the distance to the target is not fixed. The ISI HES range of spectrometers have a factor of up to 500 gain in the etendue (RD3) over classical dispersive systems. Giving it a clear advantage in making observations of this nature.

The extended distance is likely in most cases to require an extended integration time to acquire the spectrum from the target. This in turn will increase the prominence on any unwanted background signals. One issue often not considered is the Raman response from the lenses used within the probe. For integration times beyond 10 seconds this signal can be significant, therefore any standoff Raman instrument must consider this effect in the design.

In a stand-off probe it is desirable to increase the size of the receiving optics, to maximise the collected signal. However, the filter technology can restrict the maximum diameter than ce be used to < 100 mm diameter. For stand off applications a monoaxial design as shown in Figure 9 is normally adopted. It should be noted that in this design the turning lens is mounted behind the main collection lens. For larger apertures this lens has a thickness in excess of 10 mm. This can result in additional Raman or fluorescent response being emitted as illustrated in [Figure 9](#).

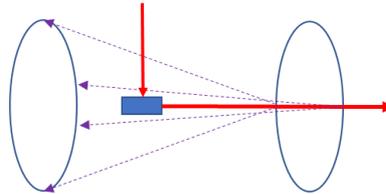


Figure 9. Illustration showing effect of a large FOV on collected Raman or fluorescence response

The solution to this issue was to move the turning lens to a position, 'after' the main collecting lens. This has the effect of eliminating any internally excited photons. Figure 10 and [Figure 11](#) show IS-Instruments Ltd stand-off probe built around this concept.

The folding mirror can be clearly observed after the main light collecting elements. The probe uses a 100mm diameter lens, with an adjustable focus from 50mm to 1500mm. The laser etendue is controlled to match the collecting spectrometer (i.e. 1 mm spot diameter at the target).

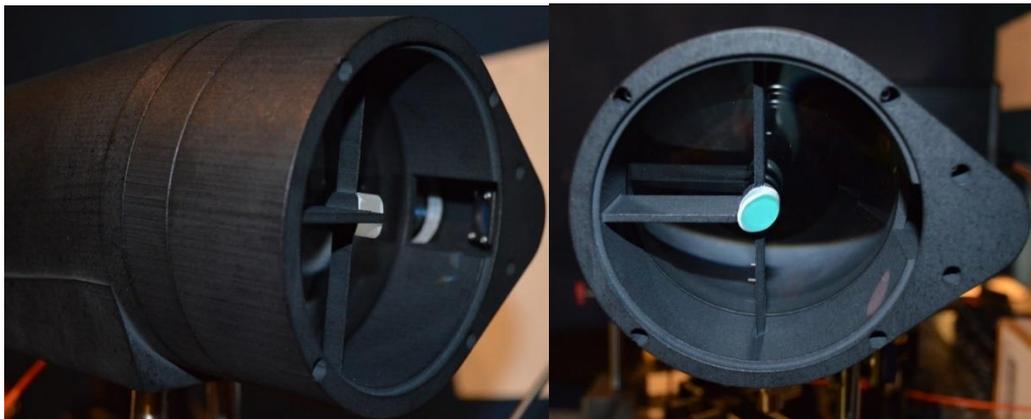


Figure 10. Stand off Raman probe: Stand off distance 500 smm – 1500 mm

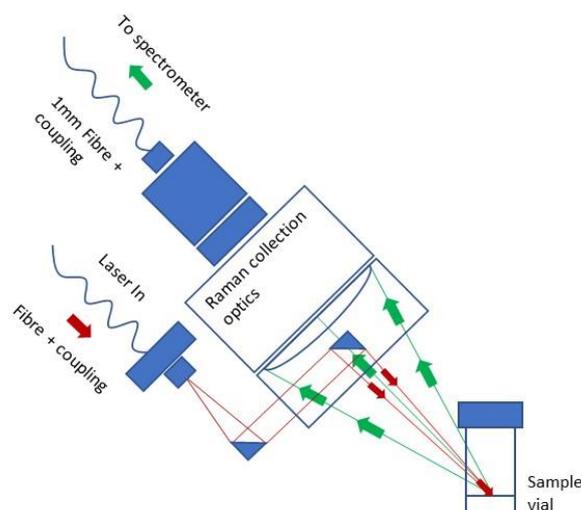


Figure 11. Schematic showing ISI-Instruments 500-1500mm standoff probe

The performance of the probe was tested by examining a sample of paracetamol at a stand-off distance of 1m. The resulting spectra are presented in [Figure 12](#). Observations were made using a HES 2000 instrument, with an integration time of 0.5 seconds and 1 second respectively, with an average of 10 observations as shown in Figure 12 (a). The observed signal to noise ratio is excellent. The high etendue offered by the HES instruments allows the device to maximise the return from the target. The difference between a single shot and the averaged observation is presented in Figure 12(b).

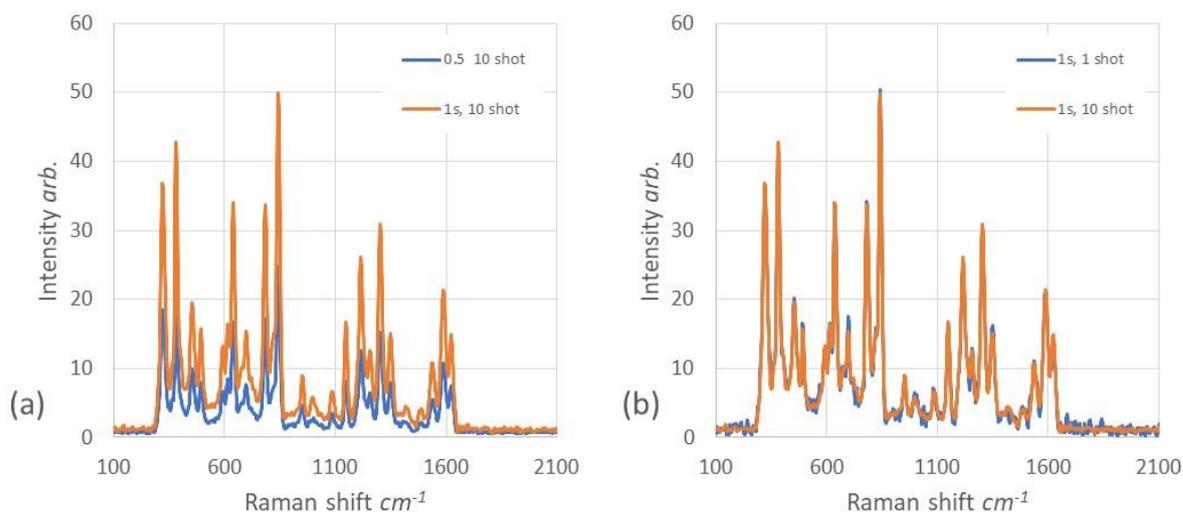


Figure 12 Paracetamol Raman spectra measured at a distance of 1 m using ISI stand off Raman probe. (a) average of 10 observations at 0.5 and 1 second integration times. (b) 1 second integration time with single shot and 10 average observation)

The spectra presented have had no processing applied, and show no residue fluorescent or Raman signal from the probe demonstrating the excellent performance that can be achieved with the HES 2000 even at a distance of 1 m and an integration time of less than 1 second.

Summary and conclusions

- Tailoring the probe specification to the demands of the sample and sampling environment is shown to be very critically important for optimising the performance of the Raman measurement.
- A series of probe types are presented and their suitability for capturing Raman spectra from a series of challenging samples and sampling conditions is discussed.
- A comparison of 3 different optical probes used to capture Raman spectra of a freeze dried sample within a glass vial highlighted the strengths and weaknesses of each, indicating in this instance that a biaxially configured arrangement was optimum.
- Raman spectra of a translucent liquid and an opaque solid are also presented, where probe specifications for each were optimised to capture the best measurement.
- A new confocal monoaxial optical probe is also presented, where the undesirable effects caused by optical component induced Raman capture is addressed, where the partially obscuring excitation laser turning mirror is placed externally from the Raman collection optics. This probe is shown to reliably capture Raman spectra at a standoff distance of up to 1.5m.

The HES2000 spectrometer and Raman probes are now available from IS-Instruments, for further information please visit our website:

www.is-instruments.com or contact us on info@is-instruments.com

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