19 Shea Way Suite 301, Newark, DE 19713
Tel: (302) 368-7824 Fax: (302)368-7830
http://www.bwtek.com • E-mail: info@bwtek.com

Application Note
Raman Sampling

B&W Tek offers several Raman probes for variety of applications. This application note addresses some technical issues related to the sampling.

Raman Excitation Wavelengths

B&W Tek offers various excitation wavelengths (in nm), 473, 488, 532, 633, 785, 830 etc. Longer wavelength Raman excitation normally has the advantage of minimizing background fluorescence interference, but at the expense of needing higher excitation power in order to compensate for the lower photon energies at longer wavelengths.

As a rule of thumb, excitation at 1064 nm will require four (4) times the laser power compared to 532 nm for achieving the same excitation energy with all other system parameters being the same. With the increased excitation power requirement at longer wavelengths, the focused laser beam will have a much higher power density. Shorter wavelength excitation alternatives may become necessary in situations where the high power density may damage the samples. In applications where fluorescence background is dominating the measurement a longer excitation wavelength is preferred.

Compression of Fluorescence Background

It is often required to measure samples in common containers, such as vials, plastic bags, etc. In other applications it is necessary that sampling be done through a sapphire or a quartz window. However, the container and window materials can fluoresce or exhibit Raman scattering under laser irradiations.

To minimize background interference, it is important to avoid placing these materials at the focal point of the laser beam. The greater the distance between the window materials and the laser focal point is, reduces the interfering background signal as acquired by the detection system. An increased focal length will also reduce the overall signal strength, so this is an optimum working distance must be considered.

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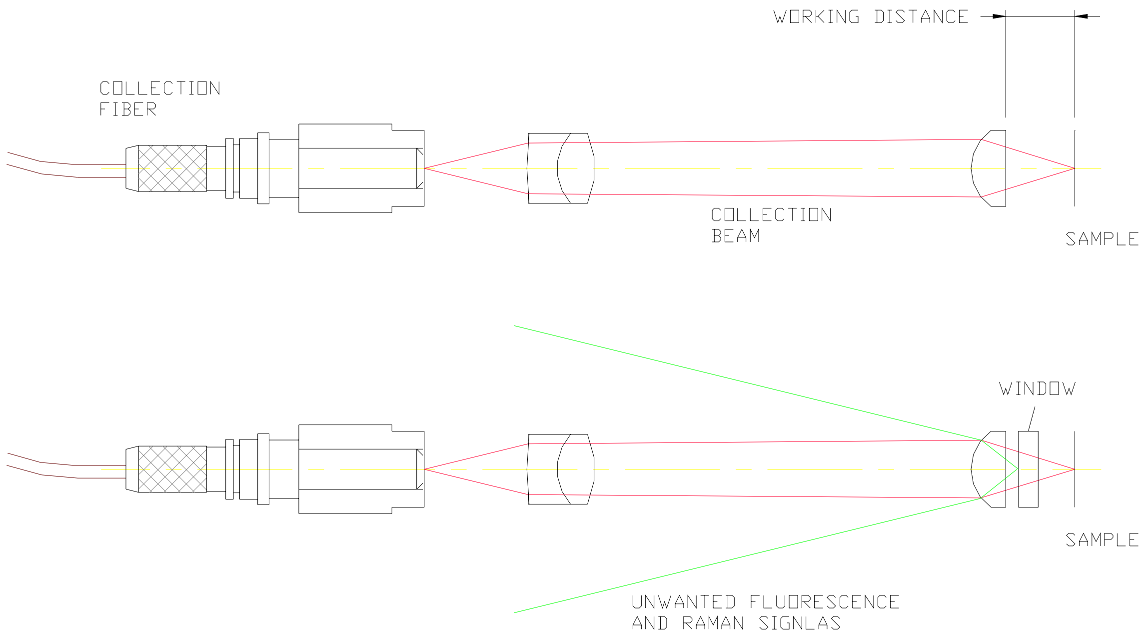

Figure 1 Fluorescence and Raman signals from window material

Figure 1 shows that when the window moves away from the focal point, most of the fluorescence and Raman signals associated with the window materials will miss the collection optics, then less unwanted background signal will be collected.

In many cases, samples are measured by fiber optics Raman probes through some kind of window or container walls. Fluorescence free fused silica (not fused quartz) material should be used as the window or container material in Raman sampling. This is particularly important in situations where a weak Raman response requires a longer integration time. The danger is in that the long detector integration time may increase the spectral features originating from the window or container material.

Raman Probe Focal Length and Working Distance

B&W Tek offers several fore optic lenses with different focal lengths. For routine Lab applications, the Raman probes will employ typical focal lengths of 8.1mm or 12mm. For sample immersion (Industrial) Raman applications, a working distance of 5, 10 or 20mm are recommended. The working distance is depicted in Figure 1, and defined as that distance between the outer surface of the optical lens to the focal point.

Table 1 lists the focal lengths and working distance of B&W Tek' s probes.

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Table 1 Focal Length and Working Distance

	Focal Length, mm	Working Distance in Air, mm
Lab Probe	8.1	5.9
	12.0	10.6
Industrial Probe	13.3	5.0
	16.4	10.0
	30.9	20.0

The Raman signal collection can be maximized by selecting optimal focal length/working distance. The form of the sample is also an important factor effecting scattering intensity. The table below describes one such case between that of a liquid, acetone, and a solid, diamond. Solids exhibit symmetry elements which on one hand can offer spectacular results, but also are highly dependent on scattering geometry.

Table 2 Raman Intensity vs. Focal Length and Sample Type, 532nm excitation

Sample Type	Focal Length, mm	Maximum Intensity, counts
Liquid, Acetone	8.1	22,000
	12.0	18,700
Solid, Diamond	8.1	60,000
	12.0	16,100

It is evident from the data that maximum Raman signal intensity collected from a liquid sample is less sensitive to the focal length compared to that of the solid sample. Also, Raman signal collection for a liquid sample is less sensitive to the working distance variation compared to the solid sample case. Therefore liquid samples have much greater depth of field than solids. It is here that lies the true advantage that Raman spectroscopy can offer over infrared techniques, the ability to take advantage of symmetry and cofactor elements to greatly enhance the signal.

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Sampling Spot Size

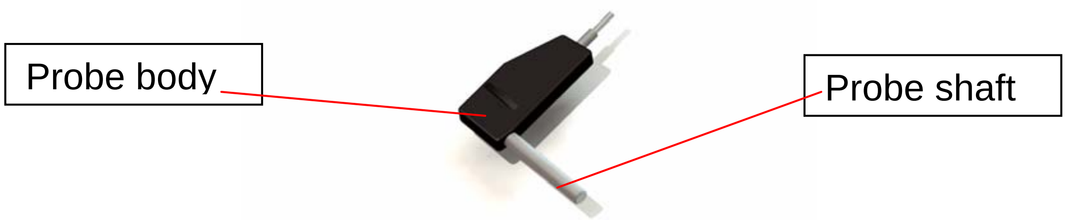

Figure 2 Probe body and probe shaft

B&W Tek offers many Raman probes and accessories, including options for different shafts (Figure 2). These include immersion shafts, high temperature/high pressure shafts, and a microscope sampling system with microscope objectives. A frequently asked question concerns the spot size produced by the probe shaft and sampling systems.

Spot size depends on the effect of the optics on the excitation laser beam, as illustrated in Figure 1. Two lens groups are used. The first lens group is to collimate the laser beam and the second lens group is to focus the beam onto the sample. If the two lens groups have effective focal lengths F1 and F2, the spot size D will be:

$$D = 105\mu m \times (F2/F1)$$

where, 105 µm is the core size of the input fiber.

F1 is 10mm as designed by B&W Tek. The second lens group is the variable item when a probe shaft is changed. If a microscope objective lens is used as the second lens group, for example, then F2 might be 5mm. And the spot size will be

$$D = 105\ \mu m \times (5/10) = 52.5\ \mu m$$

Immersion probe and Non-immersion Probe Shafts

The non-immersion probe shaft (B&W Tek Model No. BAC100-LPS) has a quartz lens window that is sealed and epoxied on a stainless steel shaft. Immersion of the probe into liquid might induce a leak into the shaft and result in a failure of the probe.

The immersion probe shaft (B&W Tek Model No. BAC100-IPS) has a quartz lens window sealed with an O-ring to prevent leaks into the shaft. As a precaution, the compatibility of the O-ring material should be verified before immersion into a liquid chemical of interest. The compatibility of the window and shaft materials should also be verified before use. The B&W Tek default design employs 316 stainless steel and a Kalrez O-ring. If you need information on the chemical compatibility of any immersion probe shaft and O-ring materials, please contact B&W Tek.

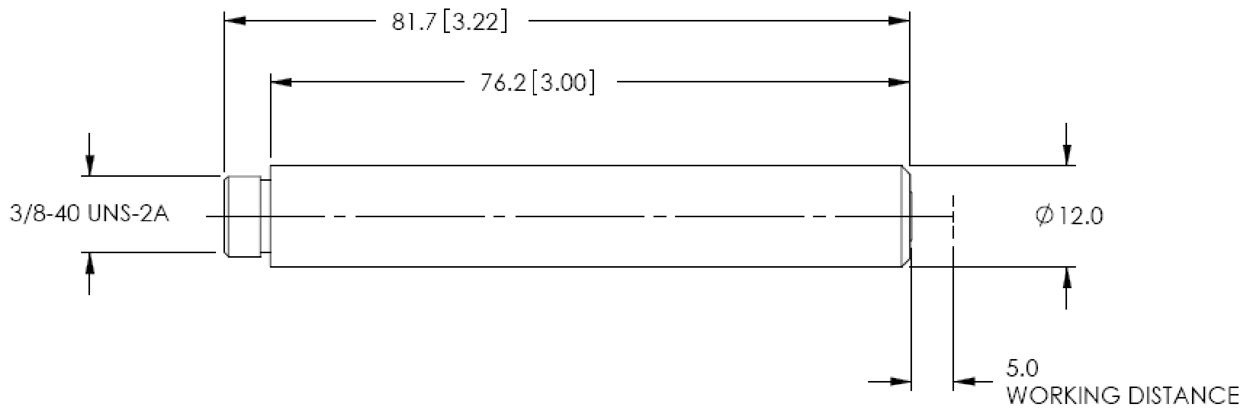

Figure 3 Raman Probe Immersion Shaft, BAC100-IPS

The non-immersion probe shaft has 3/8" shaft diameter and immersion probe shaft has 12mm shaft diameter. They are interchangeable by sharing the same 3/8"-40 TPI threads and the end-user can easily switch between these two shafts as desired.

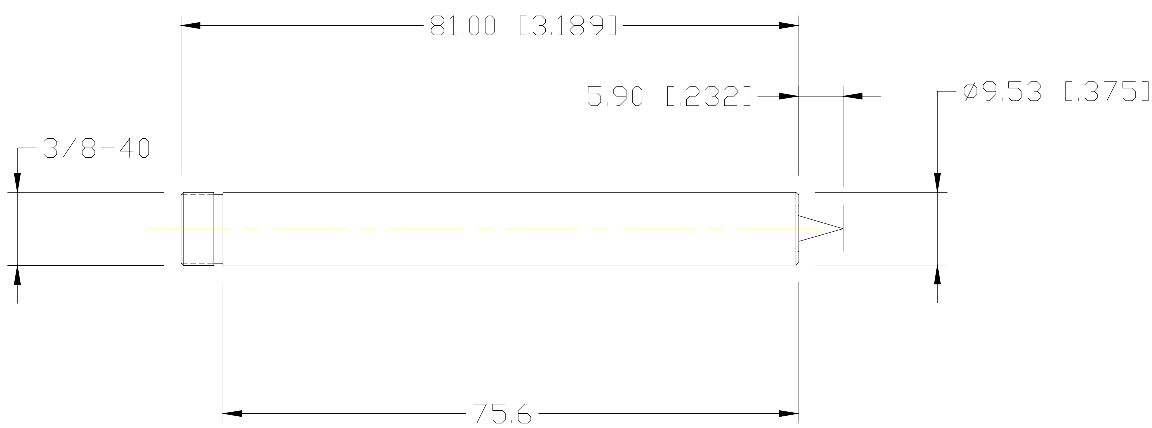

Figure 4 Raman Probe Non-Immersion Shaft, BAC100-LPS

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Vertical and Horizontal Probe Holders for Solids and Liquids

B&W Tek fiber optic sample probes can be hand-held, but for highest quality results, two different sample probe holders are offered. A vertical probe holder is suitable for solids and sheet samples (B&W Tek Model number BAC150). A horizontal probe holder (B&W Tek Model number BCR100), on the other hand, is suitable for liquid or powder sampling through a standard cuvette.

Cuvette Sample Holder and Raman Flow Cells

For liquid samples, a 10mm cuvette sample holder or a Raman flow cell can be selected as a sampling accessory. The cuvette sample holder is flexible and lab-friendly since the 10mm cuvette is commonly used in Spectrophotometry. However cuvette sample holders can be prone to material and sample positioning variations. Raman flow cells on the other hand are process-friendly, offering high repeatability due to reduced positioning errors.

Effective Optical Path Length

Figure 4 shows how the effective working distance can be affected by inserting a transparent material, such as window, cuvette or other optical media into the optical path.

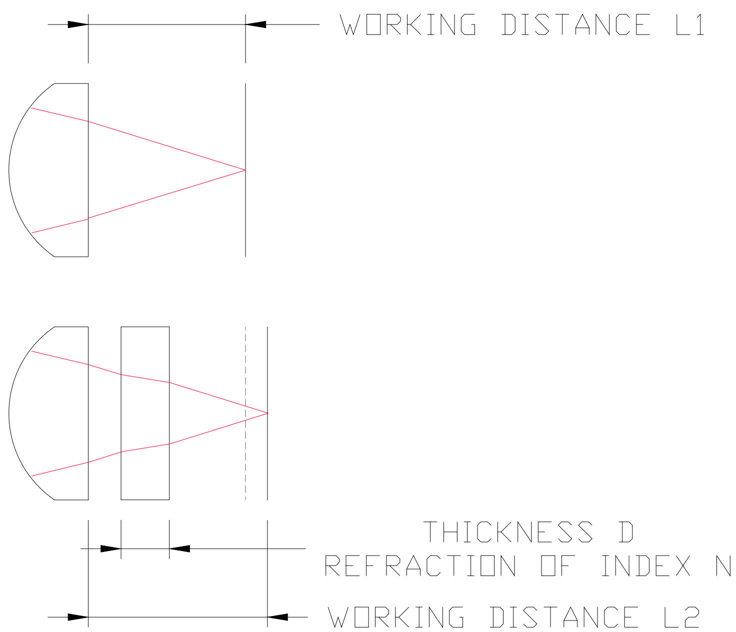

Figure 5 Optical Path Length as Effected by a Window

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All working distances in Table 1 refer to the optical path in air. If a thick optical plate is inserted into the optical path, the effective working distance L2 needs to be recalculated taking into account the properties of the plate material. The new working distance is computed by:

$$L2 = L1 + D * (N-1)/N$$

where; D is the plate thickness and N is its index of refraction

For example: if the probe working distance in air is 5.9mm and a 4mm thick BK7 (N=1.517) glass plate is inserted in the optical path, then effective working distance L2 is 7.3mm.

Table 3 lists the refraction index of common transparent materials used in Raman measurements.

Table 3 Index of Refraction

Material	Index of Refraction, Nd	Note
Fused Silica	1.458	
Fused Quartz	1.544	
Pyrex Glass	1.474	
Sapphire	1.768	Crystal, N Ordinary
Water	1.333	
BK7	1.517	
B270	1.523	
CaF2	1.434	Crystal, N Ordinary
Polycarbonate	1.585	
PMMA	1.492	