

Choosing the Most Suitable Laser Wavelength For Your Raman Application

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Over the years, dispersive <u>Raman spectroscopy</u> has increasingly been implemented for sample analysis including <u>material identification</u>, <u>biomedical research</u>, and <u>art and archeology</u> due to its portability and sampling flexibility. When choosing a Raman instrument, one of the primary concerns is the wavelength of the laser that is integrated into the Raman spectrometer system. The Raman signature and the specific peak position of any material is related to the material's unique chemical structure and is independent of the excitation wavelength, so the molecular fingerprint will be the same regardless of the excitation laser wavelength. However, different excitation wavelengths provide specific strengths and weaknesses allowing a user to optimize the measurement of different samples by their choice of Raman excitation laser wavelength. So how does one select a laser excitation wavelength for particular applications? There are many different excitation options, but the three most widely used are 532nm, 785nm and 1064nm. Some important indicators of performance for these wavelengths are listed below:

	<u>532nm</u>	<u>785nm</u>	<u>1064nm</u>
Excitation efficiency	high	medium	low
Fluorescence	high	medium	low
Heat absorption	low	medium	high

The most obvious difference is the excitation efficiency. Raman scattering efficiency is proportional to λ^{-4} , where λ is the laser wavelength. For example, Raman scattering at 532nm is a factor of 4.7 more efficient than at 785nm and 16 times better than at 1064nm, effectively meaning that scan time is much longer at higher wavelengths as compared to 532nm, assuming that all other conditions remain the same.

$$P_{Scattered} \propto \frac{I_o}{\lambda^4}$$

Detector sensitivity is another concern. Since Stokes Raman is used for most instruments, Raman signals excited by a 532nm laser are distributed in the visible range, where the response is best for most silicon-based CCD chips. Meanwhile, Raman signals from 785nm systems fall within the NIR range (750-1050nm), where the response is still relatively good. For 1064nm, however, typically there

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is no response from the CCD above 1100nm, and therefore an IR sensor InGaAs array detector, which has typically about 1/10 the efficiency of a CCD, is used. Further, a 512 pixel sensor is embedded for most dispersive 1064nm Raman instruments (vs 2048 for most others) due to cost control concerns, which leads to poorer resolution and shorter spectral range coverage.

Another important phenomenon that occurs and interferes with the measurement of the Raman spectrum is fluorescence, which in most cases is a decisive factor when excitation efficiency is very important. Fluorescence is produced in a very similar process to Raman scattering but is based on a different mechanism. The <u>Raman Effect</u> can take place for any frequency of incident light while maintaining a constant separation from the excitation frequency; meanwhile, fluorescence is anchored at a specific frequency or wavelength, meaning that it will shift if the excitation laser is different. Furthermore, the fluorescence bleaching effect makes the fluorescence signals fluctuate across the range. To minimize interference of fluorescence with a Raman spectrum, longer wavelength laser excitation is used. Fluorescence may be strong when measuring darker samples, dyes, raw herbal materials, essentials or extracts, especially for those chemical bonds containing elemental nitrogen.



Laser absorption must also be considered as this may cause sample heating and lead to changes in the samples. Generally, the longer the excitation wavelength, the more the sample absorbs light and is heated. In extreme cases, liquid samples may boil and colored, dark, or black samples may burn or ignite. There are some ways to avoid this, or at least minimize this, such as rotating the sample or lowering the laser power, but these steps either add complexity or increase the measuring time while worsening the signal-to-noise ratio (SNR). Therefore, with certain incorrect measurement

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configurations, it is possible for users to damage some materials even though Raman is a nondestructive technology.

Other factors, such as chemical bond resonance, should also be taken into consideration when choosing a wavelength.

Below, we show some sample spectra that exhibit the different performance of various excitations.



It must be noted that there are many materials that can be scanned using any wavelength without a problem. In the example above, it is shown that the Raman spectrum of toluene can be measured readily using all three standard excitation lasers.

The <u>532nm</u> laser excitation provides good sensitivity and is commonly used for <u>carbon nanotube</u> <u>analysis</u>, where the sample may burn at <u>785nm</u>. Of course, there is the option of lowering the laser power for the higher wavelength, but this will result in a lower SNR.



The 532nm excitation is also recommended for metal oxides or minerals and inorganic materials in general. The 532nm instrument also has the benefit of covering the full range from 65cm⁻¹ to 4000cm⁻¹, which may be an important consideration for certain applications where there are distinct signals in the higher Raman shift region, including the –NH and –OH functional groups at 2800 and 3700 cm⁻¹.

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The <u>785nm</u> wavelength excitation is the most popular and common wavelength currently in use, as it performs efficiently for over 90% of Raman active materials with limited interference from fluorescence. Depending on the sample and the strength of the corresponding Raman signal, a single scan acquisition may take anywhere from one second to several minutes. Between the 3 standard wavelengths, the balance of fluorescence reduction and spectral resolution makes the 785nm the most versatile choice.



In the above spectra of Norcodeine scanned using 785nm and <u>1064nm</u> excitation, the 785nm spectrum displays more detail because of better resolution. It was also acquired using a much shorter integration time than the 1064nm.

In most cases, the only reason to choose 1064nm is to minimize fluorescence.





For example, the Raman spectrum of sesame seed oil can be measured at <u>1064nm</u> excitation, but the spectra collected from <u>532nm</u> and <u>785nm</u> are masked by strong fluorescence.



Although there have been concerns in the past about fluorescence in cellulose, a good spectrum can be collected using both 785nm and 1064nm, with fluorescence only playing a part at 532nm.

In addition to the three most widely used excitations, the 633nm single mode laser is used for most biomedical applications which require precision in regards to excitation power and region while not damaging the sample, nor illuminating fluorescence. As such, most of the previously published work using Raman in this field is done with this excitation wavelength.

In summary:

- The 532nm laser provides the highest energy to bombard the sample structure, leading to higher fluorescence, making it ideal for inorganic materials;
- The 785nm laser provides a balance of performance with less excitation efficiency but also lower fluorescence, giving the best economic performance and making it the best choice for most chemicals;
- The 1064nm laser performs with the least fluorescence but also takes the longest amount of time to get adequate levels of signal to analyze, while having a higher probability of overheating the sample. This makes it a better fit for materials such as dyes, oils, and colored polymers when used properly.



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Additional Resources

<u>i-Raman Plus datasheet</u> <u>i-Raman EX datasheet</u> Further Reading: <u>Intro to Raman spectroscopy</u>

If you have any questions about the application or would like to know how Raman would work for your application, please contact us at appnote@bwtek.com or call us at +1 (855) 297-2626 to speak with an expert.