



Choosing the Most Suitable Laser Wavelength For Your Raman Application

Over the years, dispersive Raman spectroscopy has increasingly been implemented for material identification 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. Even though the Raman shift of any material is only related to the material's specific chemical structure and is independent of the excitation wavelength, different wavelengths have their specific strengths and weaknesses. So how does one select a laser excitation wavelength for specific applications? There are many different options, but the three most widely used are 532nm, 785nm and 1064nm. Some important indicators of performance are listed below.

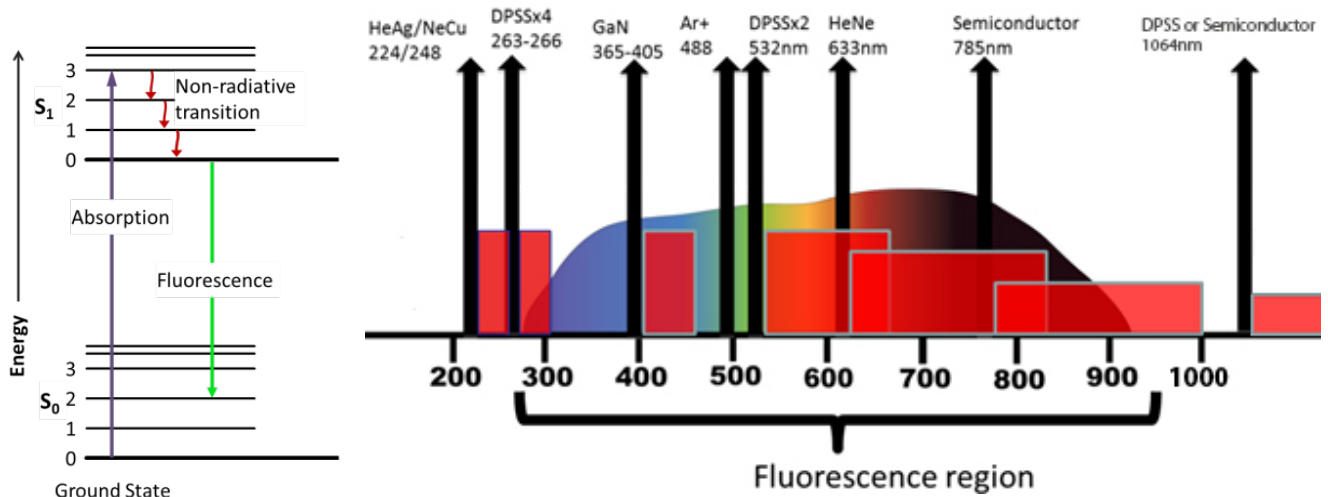
	532nm	785nm	1064nm
Excitation efficiency	high	medium	low
Fluorescence	high	medium	low
Heat absorption	low	medium	high

The most obvious is the difference in 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 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 such 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 fall within the NIR range (750-1050nm), where the response is still relatively good. For 1064nm, however, typically there is no response from the CCD above 1100nm, and therefore an IR sensor InGaAs detector, which has about 1/10 the efficiency of the 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 measures, which leads to poorer resolution and shorter spectral range coverage.

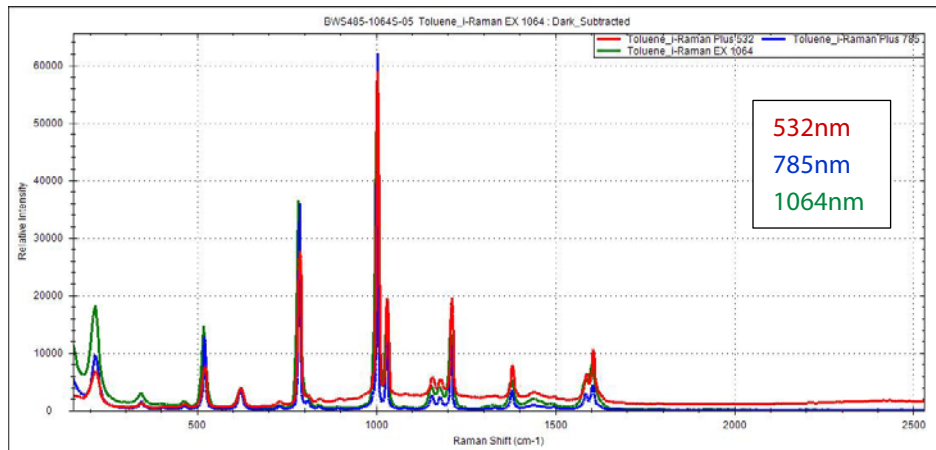
Another important phenomenon is fluorescence, which in most cases is a decisive factor when excitation efficiency can be sacrificed. Fluorescence is produced in a very similar process to Raman scattering but is based on a different mechanism. The Raman Effect can take place for any frequency of incident 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 a range. To minimize interference of fluorescence with a Raman spectrum, longer wavelength laser excitation is used.



Laser absorption cannot be disregarded as this may cause sample heating and lead to changes in the samples. Generally the longer the excitation wavelength, the more the light is absorbed and the sample heated. In some specific 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 configurations, Raman may still damage some materials even though it is a non-destructive technology.

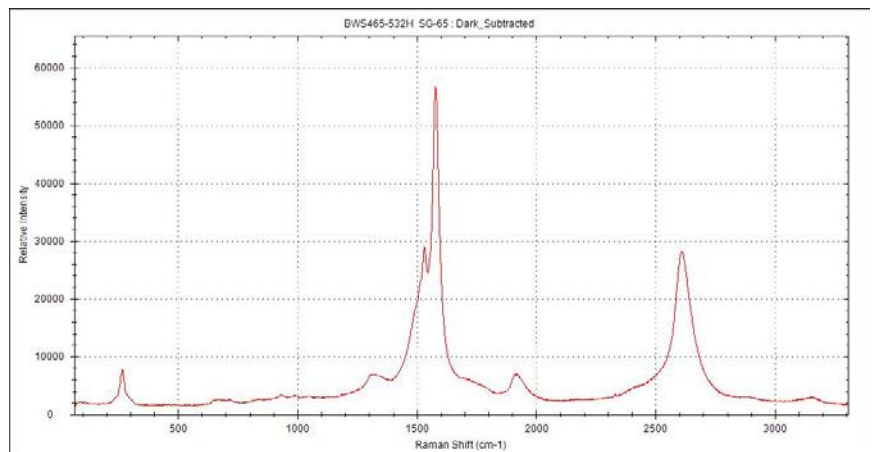
There are certain other factors, such as chemical bond resonance, that should also be taken into consideration when choosing a wavelength.

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 with any wavelength without a problem. An example is toluene, where the Raman spectrum can be measured readily using all three standard excitation lasers.

The 532nm laser excitation provides good sensitivity and is commonly used for carbon nanotube analysis, where the sample may burn at 785nm. 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 is also recommended for metal oxides or minerals and inorganic materials in general.

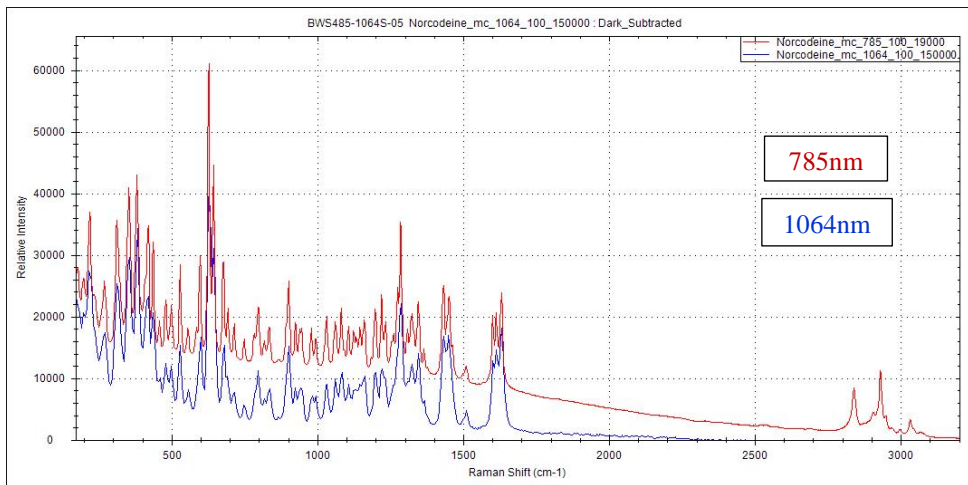


The 532nm instrument is the only one that can cover the full range from 175cm⁻¹ to 4000cm⁻¹, which may also be an important consideration for certain applications where there are distinct signals in the higher Raman shift region, including the –NH and –OH functional groups.

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.

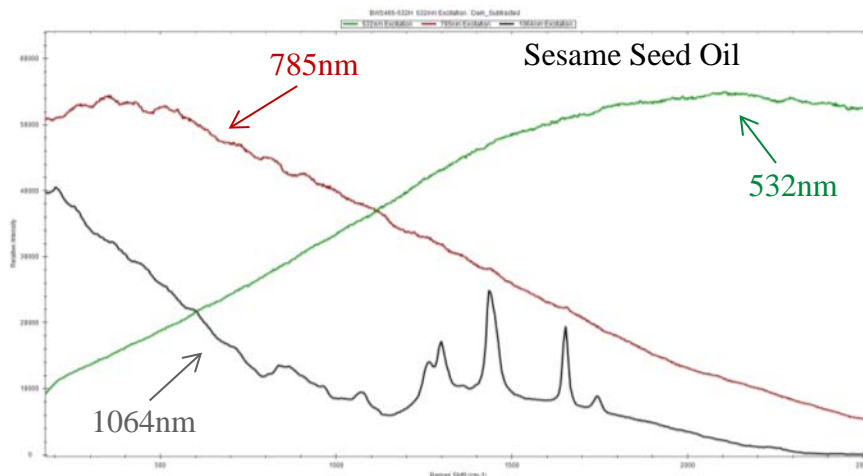


The 785nm wavelength excitation is the most popular and common wavelength currently in use, as it performs efficiently for over 90% of chemicals with limited interference from fluorescence. Depending on the sample and the strength of the corresponding Raman signal, a single scan acquisition may take 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.

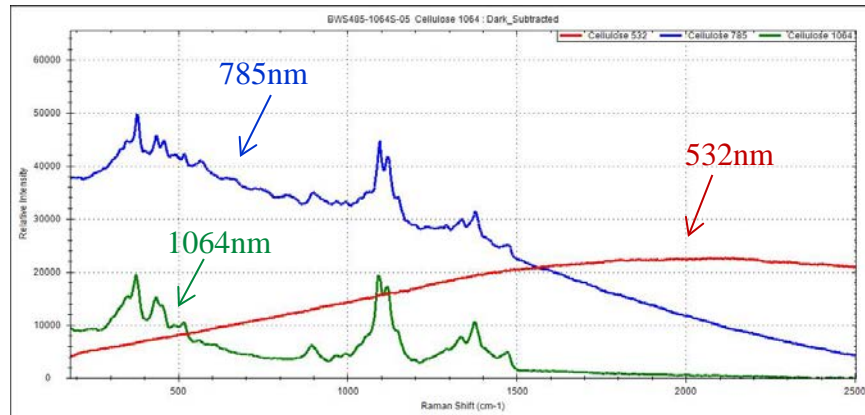


From the spectra above for Norcodeine scanned using 785nm and 1064nm excitation, the 785nm spectrum displays more detail and was acquired using a much shorter integration time than 1064nm.

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



For example, sesame seed oil works at 1064nm excitation, but the spectra collected from 532nm and 785nm 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 sum:

- 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 enough of both sides, with less excitation efficiency but also lower fluorescence, giving the best economic performance and making it the best choice for most chemicals;
- The 1064nm performs with the least fluorescence but also takes the longest time to get adequate levels of signal to analyze while having a higher probability of overheating the sample, making it a better fit for materials such as dyes, oils, and polymers when used properly.