

Choosing the Most Suitable Laser Wavelength For Your Raman Application

Over the years, dispersive Raman spectroscopy has increasingly been implemented for sample analysis including material identification, biomedical research, and art and archeology 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 532 nm, 785 nm and 1064 nm. The most popular is the 785 nm excitation system as it offers the best balance of signal strength, sensitivity to fluorescence, cost and overall performance, and can be used to collect the Raman spectrum of most organic materials quickly. When samples are fluorescent in the other wavelengths, the longer wavelength of 1064 nm is beneficial.

FACTORS TO CONSIDER

Some important indicators of performance for these

three wavelengths are listed below:

	532 nm	785 nm	1064 nm
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 532 nm is a factor of 4.7 more efficient than at 785 nm and 16 times better than at

1064 nm, effectively meaning that scan time at longer wavelengths needs to be much longer compared scan time to collect the spectrum using 532 nm, assuming that all other conditions remain the same.

$$P_{Scattered} \propto \frac{I_0}{\lambda^4}$$

Detector sensitivity is another concern. Since Stokes Raman is used for most instruments, Raman signals excited by a 532 nm laser are distributed in the visible range, where the response is best for most silicon-based CCD detectors. Meanwhile, Raman signals from 785 nm systems fall within the NIR range (750-1050 nm), where the response is still relatively good. For 1064 nm, however, since there is no response from silicon above 1100 nm, NIR-sensitive InGaAs array detectors are normally used for dispersive instruments. Further, a 512 pixel sensor is embedded for most dispersive 1064 nm Raman instruments (vs. 2048 for most others) due to cost control concerns, which leads to relatively less detector pixel resolution and potentially smaller Raman shift 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 photoluminescence mechanism. The Raman peaks maintain a constant separation from the excitation frequency; meanwhile, fluorescence is anchored at a specific frequency or wavelength, meaning that it does not shift with the excitation laser. Furthermore, the fluorescence bleaching effect makes the fluorescence signals drop over time. To minimize interference of fluorescence with a Raman spectrum, longer wavelength laser excitation is preferred. Fluorescence may be strong when measuring darker samples, dyes, and natural products.

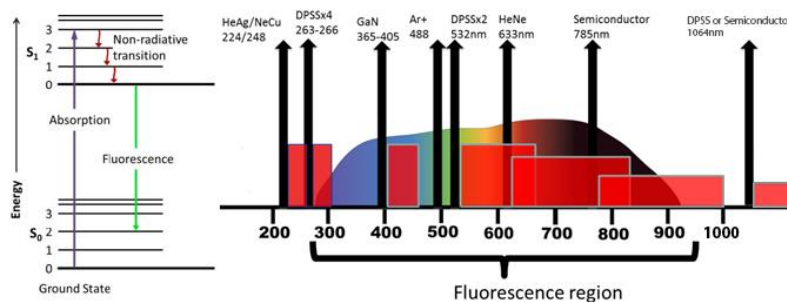


Figure 1. Energy diagram for fluorescence and lasers of different wavelength used across the fluorescence spectral range.

Laser energy absorption by samples must also be taken into consideration as this may cause sample heating and lead to changes in the sample. Generally, the longer the excitation wavelength, the more the sample absorbs light and is heated. In extreme cases, small volume liquid samples may be boiled, while colored, dark, or black samples may be damaged. Laser energy absorption-related sample damage may

be avoided or minimized, by rotating the sample, or lowering the laser power density at the sample, but these steps add complexity and/or increase the measurement time. Therefore, with certain incorrect measurement configurations, it is possible for sample damage to take occur due to improper handling even though Raman is a nondestructive technology. Other factors, such as the resonance Raman effect,

should also be taken into consideration when choosing a wavelength.

EXAMPLES

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, it is shown that the Raman spectrum of toluene can be measured readily using all three standard excitation lasers.

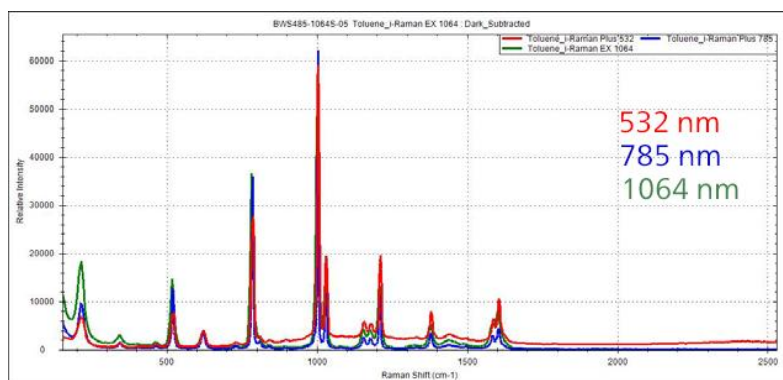


Figure 2. Raman Spectra of toluene measured with 532 nm, 785 nm and 1064 m laser excitation.

The 532 nm laser excitation provides good sensitivity and is commonly used for carbon nanotube analysis, where the sample may burn at 785 nm. Of course, there is the option of lowering the laser power for the higher wavelength, but this will result in a lower SNR. The 532 nm excitation is also recommended for metal oxides or minerals and inorganic materials in general. The 532 nm instrument also has the benefit of covering the full range from 65 cm^{-1} to 4000 cm^{-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 between 2800 and 3700 cm^{-1} .

The 785 nm wavelength excitation is the most popular and common wavelength 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

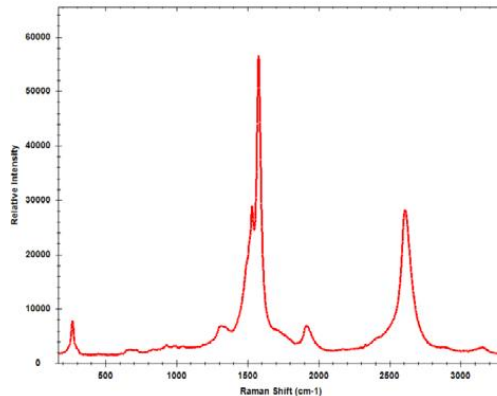


Figure 3. Raman spectrum of carbon nanotubes collected with 532 nm excitation.

may take anywhere from one second to several minutes. Between the 3 standard wavelengths, the balance of fluorescence reduction and spectral resolution makes the 785 nm the most popular choice.

In the spectra at left of heroin base scanned using 785 nm and 1064 nm excitation, the 785 nm spectrum displays more detail because of better resolution, but does have a sloping baseline due to fluorescence. It was also acquired using a much shorter integration time than the 1064 nm, 10 sec vs. high tens of seconds.

In most cases, 1064 nm laser excitation is chosen to minimize fluorescence.

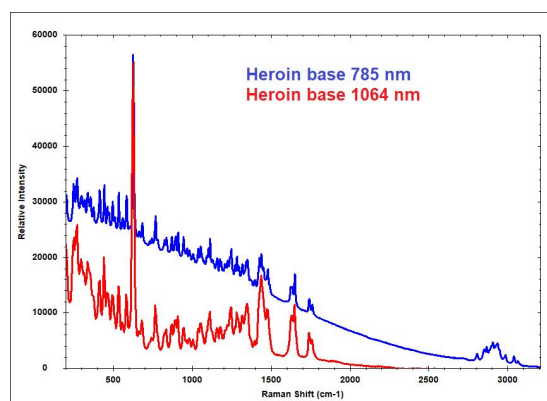


Figure 4. Raman spectra of heroin collected with 785 nm and 1064 nm excitation, showing that fluorescence is mitigated when using the longer wavelength.

For example, the Raman spectrum of sesame seed oil, a dark liquid, can be measured at 1064 nm excitation, but the Raman features in the spectra collected from

532 nm and 785 nm are masked by strong fluorescence.

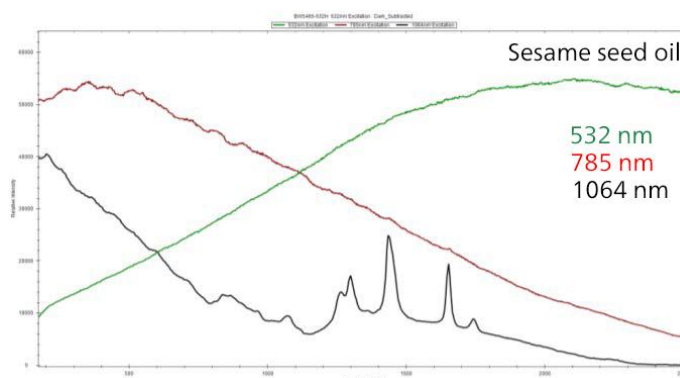


Figure 5. Raman spectra of sesame oil, overwhelmed by fluorescence when measured with 532 and 785 nm excitation, and with clearly evident Raman peaks at 1064 nm excitation.

Although there have been concerns in the past about fluorescence in cellulose, a good spectrum can be collected using 785 nm and 1064 nm, with lower background contribution using 1064 nm.

Fluorescence is detrimental for measuring the Raman spectrum of cellulose only when measured using 532 nm.

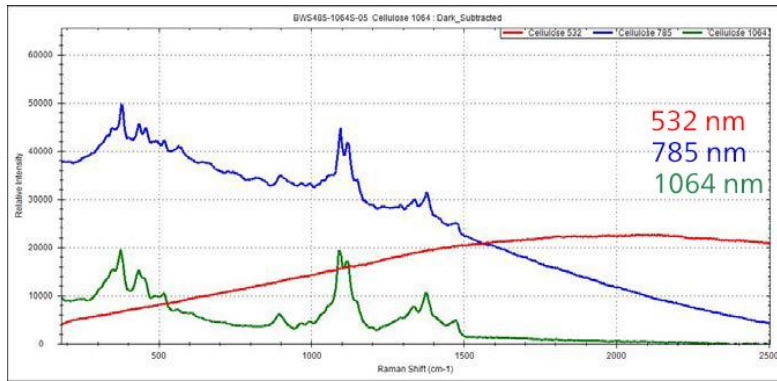


Figure 6. Raman spectra of cellulose measured with 532 nm, 785 nm and 1064 m laser excitation.

SUMMARY

- The 532 nm laser provides the highest energy to bombard the sample structure, leading to higher fluorescence, making it ideal for inorganic materials;
- The 785 nm 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 1064 nm laser performs with the least fluorescence but also requires a relatively longer acquisition time to get adequate levels of signal to analyze, while having a higher probability of heating a sample if no special care is taken. This makes it a better fit for colored and darker materials such as natural products, dyes, oils, and colored polymers.

FURTHER READING

[Carbon Analysis with High Signal-Throughput Portable Raman Spectroscopy](#)

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CONFIGURATION



Spectromètre Raman portable i-Raman Plus 532H

L'i-Raman® Plus 532H appartient à notre série primée de spectromètres Raman portables « i-Raman », équipée de notre technologie de spectrométrie intelligente et innovante. Faisant appel à un détecteur à barrette CCD à haute efficacité quantique, avec refroidissement thermoélectrique et une gamme dynamique élevée, ce spectromètre Raman portable fournit des performances exceptionnelles avec un bruit réduit, même avec un temps d'intégration atteignant 30 minutes. Ainsi, les signaux Raman faibles peuvent aussi être mesurés.

Le i-Raman Plus 532H offre la combinaison exclusive d'une large gamme spectrale et d'une haute résolution avec des configurations autorisant des mesures de 65 cm^{-1} à $3\,400 \text{ cm}^{-1}$. Le faible encombrement et la légèreté de structure de ce système peu énergivore lui permettent d'effectuer partout des analyses Raman de qualité recherche. Équipé d'une sonde à fibre optique pour faciliter l'échantillonnage, l'i-Raman Plus peut être utilisé avec un support de cuvette, un microscope vidéo, une table de translation XYZ avec support de sonde ainsi qu'avec notre logiciel d'analyse à variantes multiples BWIQ® et le logiciel d'identification BWID®. Avec le i-Raman Plus, vous avez une solution Raman pérenne de haute fidélité pour l'analyse qualitative et quantitative.



Spectromètre Raman portable i-Raman Plus 785S

L'i-Raman[®] Plus - 785S appartient à notre série primée de spectromètres Raman portables « i-Raman », équipée de notre technologie de spectrométrie intelligente et innovante. Faisant appel à un détecteur à barrette CCD à haute efficacité quantique, avec refroidissement thermoélectrique et une gamme dynamique élevée, ce spectromètre Raman portable fournit des performances exceptionnelles avec un bruit réduit, même avec un temps d'intégration atteignant 30 minutes. Ainsi, les signaux Raman faibles peuvent aussi être mesurés.

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Spectromètre Raman portable i-Raman EX

i-Raman[®] EX fait partie de notre série primée de spectromètres Raman portables i-Raman dotés de notre système breveté CleanLaze[®] avec une excitation laser de 1 064 nm. Utilisant un détecteur à matrice InGaAs haute sensibilité avec réfrigération TE, une plage dynamique élevée et une conception de spectrographe à haut débit, ce spectromètre Raman portable offre un rapport signal/bruit de fond élevé sans induire d'autofluorescence, ce qui permet de mesurer une large gamme de produits naturels, d'échantillons biologiques (tels que les cultures cellulaires) et d'échantillons colorés.

i-Raman EX offre une gamme de couverture spectrale allant de 100 cm⁻¹ à 2 500 cm⁻¹, permettant de mesurer sur toute la région des empreintes digitales. Le faible encombrement du système, sa conception légère et sa faible puissance absorbée garantissent des capacités d'analyse Raman de qualité recherche en tout lieu. Pour des capacités d'analyse étendues, il peut être utilisé avec notre logiciel exclusif Vision ainsi qu'avec le logiciel d'analyse multivariée BWIQ[®] et le logiciel d'identification BWID[®]. Avec i-Raman EX, une solution Raman de haute précision est toujours disponible pour des analyses qualitatives et quantitatives sans fluorescence.

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