
A New Era in Affordable Raman Spectroscopy

This article overviews several recent advancements in Raman components that are enabling high analytical performance in low-cost Raman instruments.

Tony Lam

Raman spectroscopy is an ideal tool for chemical analysis due to its unique advantages over other analytical techniques. It is a nondestructive and noncontacting method of obtaining the fingerprint spectrum of materials, requiring no special sample preparation. Raman can analyze samples via sample plastic bags, glass vials, and in aqueous solution. It does not require a large amount of a sample to do analysis; the sample can be as small as 1–2 μm across. A short amount of measuring time, normally a few seconds, is required to obtain a Raman spectrum. Thus, it can be used to monitor chemical reactions in real time.

Despite the fact that Raman spectroscopy has so many advantages, it still is not in widespread use. The main reason is the high cost typically associated with Raman analyzer systems. Currently, a high-resolution and high signal-to-noise ratio Raman analyzer can be priced from \$40,000 and above. On the other hand, there is a market need for low-cost Raman analyzer systems as general laboratory tools. However, those systems usually are

equipped with low-resolution, low-power visible lasers, and low signal-to-noise ratios, which is not adequate enough to perform any high performance chemical analysis. Therefore, better-resolution and lower-cost Raman systems are key to increasing and enabling greater acceptance and usage of Raman spectroscopy.

This article presents a few key advancements in Raman components that will enable low costs and high performance. It also establishes the figure of merit to identify and characterize Raman systems in terms of high resolution and low cost. Finally, Raman applications and sample Raman spectra in pharmaceutical, petrochemical processing, and plastic recycling applications will be presented.

Modern Raman Systems

A typical laboratory Raman analyzer system consists of four major components: the excitation source, the collection device, the spectrograph, and the post-processing software. The excitation source must be strong enough to generate sufficient Raman signals, and



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monochromatic light to provide clean and uncomplicated spectra. A laser typically is used as the excitation source because it can provide a coherent beam of monochromatic light with high intensity. The collection device is the fiber-optic probe. It collects the scattered photons, filters out the Rayleigh scattering, and sends the Raman signals to the spectrograph. The spectrograph then separates the Raman signals by their wavelengths and transfers them to the light detector, which records the intensity of the accumulated photons at its own wavelength. These recorded data then are passed to the postprocessing software to display as a Raman spectrum.

Several types of lasers can be used as the excitation source for Raman spectroscopy. They are Ar⁺ ion (488.0 and 514.5 nm), Kr⁺ ion (530.9 and 647.1 nm), He:Ne (632.8 nm), Nd:YAG (1064 nm), and diode (630 and 980 nm) lasers (1). Due to recent advancements in diode laser technology, it is the best candidate to be utilized in low-cost, portable Raman analyzer systems because of its relatively low cost, compact size, high reliability (>10,000-h lifetime), and near-infrared (NIR) emission wavelength for fluorescence reduction. A typical diode laser used in a modern Raman analyzer system is a high power laser diode (>300 mW), with wavelengths ranging from 630 to 980 nm.

For any high resolution (<6 cm⁻¹) Raman system, the laser linewidth (ideally <1 cm⁻¹) of the excitation source plays a key role. Also, to avoid fluorescence interference, NIR wavelengths are preferred. Thus, diode lasers emitting at 785 nm (NIR) generally have been recognized as the industry standard in the past few years because of their coverage of nearly 3000-cm⁻¹ useful spectra when based upon a silicon charged-coupled device (CCD) detector. Unfortunately, without any frequency stabilization and linewidth narrowing, these diode lasers cannot be used in a high-resolution Raman system because of their free running spectral linewidth of ~25 cm⁻¹ and unstable center wavelength that causes random shifts in Raman spectra.

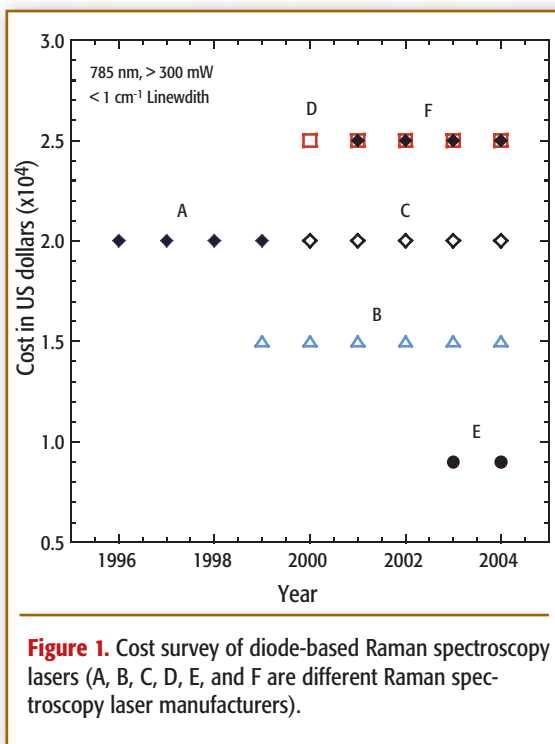


Figure 1. Cost survey of diode-based Raman spectroscopy lasers (A, B, C, D, E, and F are different Raman spectroscopy laser manufacturers).

Recent developments in diode laser wavelength stabilization and linewidth narrowing have been very dramatic. Current wavelength stabilization designs include Littrow with traditional gratings, Littmann with traditional gratings, fiber Bragg gratings, volume Bragg gratings, distributed feedback lasers (DFBs), distributed Bragg reflector lasers (DBRs), and master oscillator power amplifier lasers (MOPAs). Some designs also integrate a bandpass filter or amplified spontaneous emission (ASE) reduction technique to remove the unwanted ASE interference that often is seen in a high-power diode laser. All these lasers should

at least provide 150 mW in optical power, a stabilized center wavelength within a tenth of a wavenumber, and a spectral linewidth of less than 1 cm⁻¹ for a high-resolution Raman system. A laser linewidth (~3–4 cm⁻¹) close to the spectrometer's resolution is not ideal because the system's overall spectral profile or response will be the convolution of the two responses (laser linewidth and spectrometer's resolution). Thus, any laser spectral profile changes due to temperature, current, or any other nonlinearities will affect the overall system spectral profile and cause inaccuracies in chemometric prediction. Figure 1 depicts a cost survey over the past eight years for wavelength-stabilized, 785-nm, 300-mW, 1-cm⁻¹ linewidth Raman spectroscopy laser systems on the market.

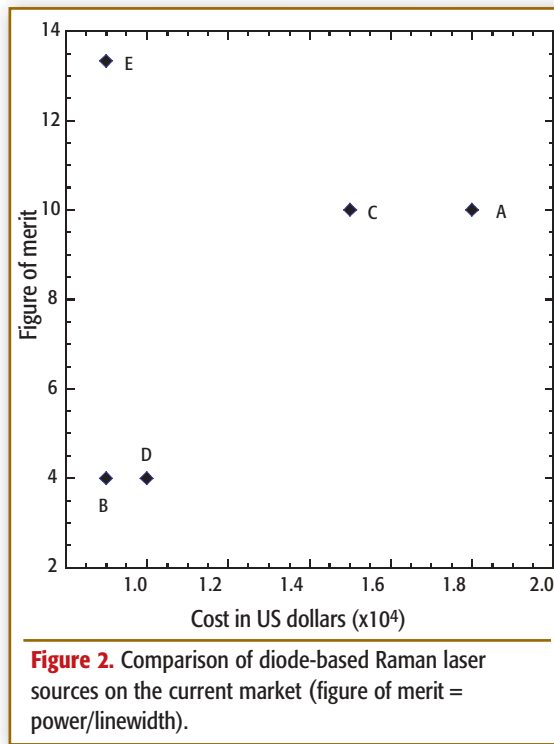


Figure 2. Comparison of diode-based Raman laser sources on the current market (figure of merit = power/linewidth).

Due to the recent development of a silicon CCD camera, the CCD sensor has replaced the single channel detector, photomultiplier tube (PMT) and avalanche photodiodes (APD), as a multi-channel photon detector in the spectrograph. It can detect radiation from 400 to 1100 nm (2). In addition, the CCD sensor will reduce integration time because it allows spectrum multiplexing. A typical integration time of the CCD spectrograph is less than 30 s.

A general laboratory Raman probe is composed of two fibers. The excitation fiber is used to deliver the excitation source to a sample. The collection fiber is used to collect Raman signals and deliver it to the spectrograph. Normally, the bandpass filter and band-reject filter are integrated into

the fiber-optic probe head to remove the laser Rayleigh scattering, silica Raman interference from the fiber, and ASE from the laser excitation source.

The data collected from the spectrograph then are sent to the software. The software then converts the data into the Raman spectrum and displays it on an x - y chart. The x axis of the chart is the wavenumber, while the y axis is the intensity of the spectrum.

Resolution of Raman Systems

Three basic bandpass filters are used in a typical Raman measuring system to determine the overall Raman spectrum quality (that is, resolution). These three bandpass filters are: laser linewidth bandpass, spectrometer bandpass, and sample bandpass (natural linewidth) filters.

Ideally, a laser linewidth bandpass filter should be much less than the spectrometer bandpass filter. In this case, the spectrometer will be the only factor in determining the Raman system's bandpass filter. If the bandpass filters of the two (that is, laser and spectrometer) are close, the system's bandpass filter will be a convolutional bandpass filter of the two components. Generally, a spectrometer bandpass filter's profile is much more stable than the laser bandpass filter profile, thus a much narrower laser linewidth bandpass filter is preferred and could make a system much more stable.

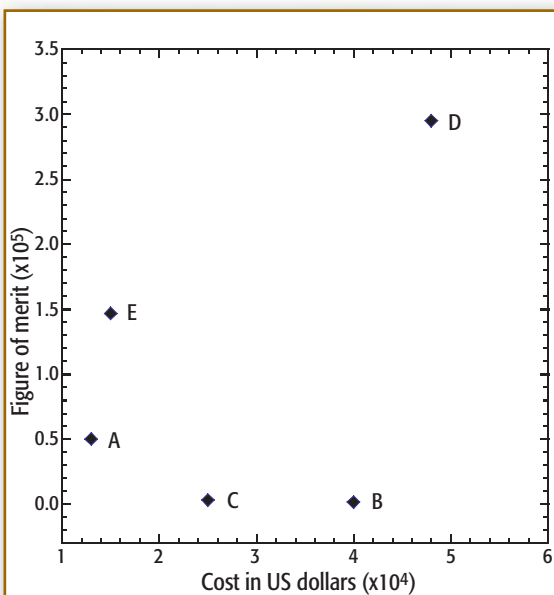


Figure 3. Comparison of laboratory Raman systems on the current market (figure of merit = [coverage x power]/[resolution]).

For most Raman applications in solid and liquid samples, a system resolution of 6 cm^{-1} or less is sufficient. Unfortunately, any high-resolution ($<6 \text{ cm}^{-1}$) Raman system usually is highly priced primarily because of the high cost of the high power ($>300 \text{ mW}$), wavelength-stabilized, and linewidth narrowed ($<1 \text{ cm}^{-1}$) Raman spectroscopy laser.

Costs of Raman Systems

To compare the cost of different Raman systems currently on the market, a figure of merit is adopted as a way to normalize different features and performances for a fair comparison. The higher the figure of merit, the better the system's performance. This section of the article compares the costs of the laser sources and the overall Raman systems. The cost

of laser sources is compared because the laser still is the major cost component for a Raman system. The figure of merit of the laser is defined as the laser power inversely proportionally with the laser linewidth:

Figure of merit = power/linewidth [1]

Using Equation 1, the figures of merit of lasers (A–E) are calculated and mapped in Figure 2.

Observing the figure-of-merit chart (Figure 2), the laser excitation sources are divided into three groups. One group is the high performance and high cost group, including A and C laser sources. The second group is the low-performance and low-cost group, including B and D laser sources. The last group, E laser sources, is the high performance and low cost group.

The figure of merit of the Raman system is defined as the product of the spectral range (coverage) and the laser power divided by the system resolution:

Figure of merit = (coverage x power)/(resolution) [2]

Using Equation 2, the figures of merit of Raman systems (A–E) are calculated and mapped in Figure 3.

Observing the figure-of-merit chart of the Raman system (Figure 3), the A and E Raman systems are considered to be the medium-performance and low-cost systems. The B and C systems are considered to be low-performance and high-cost systems. The D system is considered a high-end system, high performance versus high cost. It is the

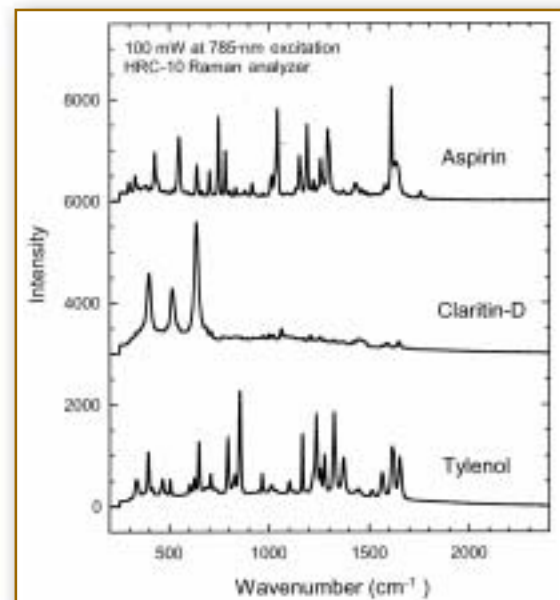


Figure 4. Raman spectra of OTC medicines.

Raman spectroscopy applications that determine which Raman systems should be used, but for most of the applications, a Raman system that has a 6- cm^{-1} spectral resolution is sufficient (1).

Applications of Affordable Raman Systems

With high-resolution and low-cost Raman systems, many Raman spectroscopy applications in chemical analysis become feasible. To name a few, Raman spectroscopy is useful in drug identification for the pharmaceutical industry, the control of octane level in gasoline, and the classification of plastic in the plastic recycling industry. To demonstrate the feasibility of using a low-cost Raman instrument in these applications, the HRC-10 Raman analyzer with less than 6- cm^{-1} system resolution, manufactured by EnWave Optronics, was chosen to collect Raman

spectra of some over-the-counter medicines, unleaded iso-octane levels of Chevron gasoline, and some plastic samples.

Pharmaceutical. One of the advantages of the Raman system is its ability to measure down to 50 cm^{-1} in spectral range compared to the mid-IR system that can only reach approximately 400 cm^{-1} . The feature is very attractive to the pharmaceutical industry because most of the spectra of drug lattices are below 200 cm^{-1} (3). Raman spectroscopy finds its application in lattice vibration study for the characterization of the solid state of a drug and especially for the investigation of polymorphism and amorphous systems. In addition, it finds application in analysis and quantification of drug blends, and in the examination of drug formulations and drug excipient incompatibilities.

Petrochemical. The gasoline purchased from any local gas station has the methyl-*tert*-butyl ether (MTBE) (4) content added to improve the octane number. The octane number is an experimentally determined property of petroleum fuel that defines the quality of engine antiknocking. Raman spectroscopy can be used to identify the octane level within gasoline. An example of the octane level in Chevron unleaded gasoline is shown in Figure 5. Also, Raman systems can be used to measure oxygenate material in the gasoline. According to the U.S.

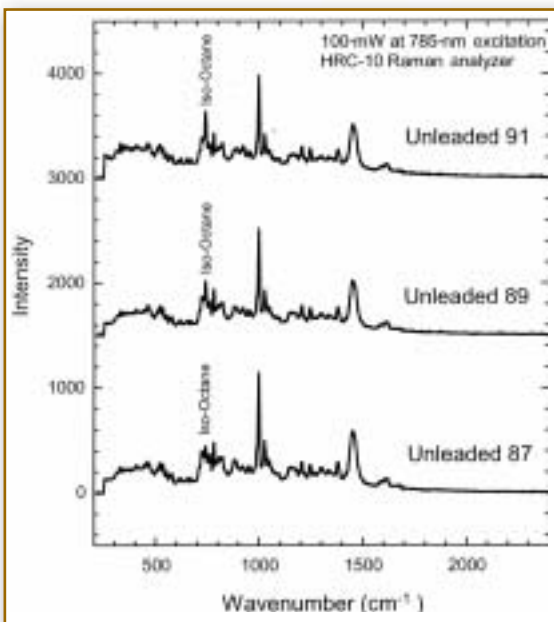


Figure 5. Raman spectra of Chevron unleaded gasoline with various iso-octane levels.

Environmental Protection Agency (EPA) (3), to reduce the levels of carbon monoxide in the air, the government entity requires the use of oxygenate additives to the gasoline. The petroleum manufacturers have been maintaining and monitoring the oxygenate level accurately in the gasoline during refinery process. Raman spectroscopy systems have been a favored approach for qualitative identification of oxygenate materials.

Plastics. Plastics are used extensively and vastly in many common materials. Plastics consist of seven different kinds of polymers. They are polyethylene-terephthalate (labeled as PET, and number 1 under recycling symbol); high density polyethylene (HDPE, 2); polyvinyl chloride (PVC, 3); low density polyethylene (LDPE, 4); polypropy-

lene (PP, 5); polystyrene (PS, 6); and “other,” labeled as 7 (5). In the plastics industry, Raman spectroscopy systems find application in real-time monitoring of polymerization reactions to control the processing time, in quantitative compositional analysis of polymer melt streams, and in plastic identification for recycling purposes. Figure 6 shows an example of plastic Raman spectra.

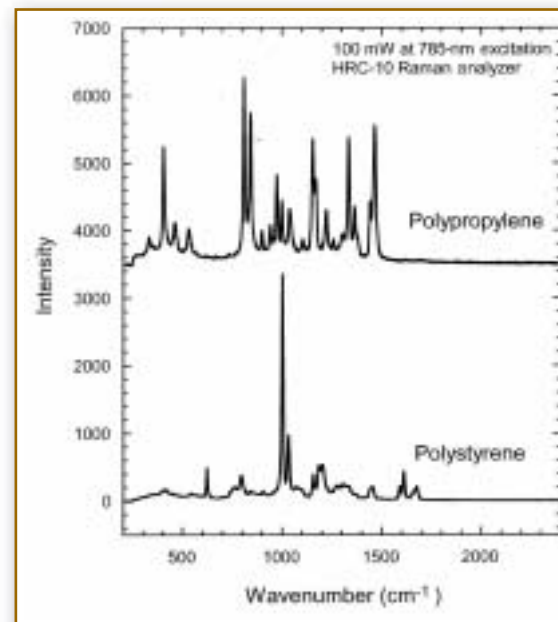


Figure 6. Raman spectra of polypropylene and polystyrene plastics.

Conclusion

With the current advancements in diode laser technology, Raman systems have been improved on two fronts:

cost and resolution. Raman excitation sources now can be made with a lower cost. In addition, laser wavelength stabilizing and linewidth narrowing have improved the resolution of Raman systems. Consequently, these advancements have eliminated the high costs associated with the high-resolution system and brought this novel technology to every corner of life. It signifies a new era in Raman spectroscopy. Perhaps, within five years, it will find itself within many potential applications that have not been considered previously for chemical analysis.

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