

The Advantages of Echelle Spectrographs for Raman Spectroscopy



This technical note explains the design concepts behind the PerkinElmer® Raman echelle spectrograph. It describes the benefits of this unique approach to Raman spectroscopy systems that is the basis of the PerkinElmer 400 Series Raman instruments.

Dispersive Raman spectrometers use gratings to disperse the scattered light from a sample; the light is then focused onto a CCD. The major differences between dispersive Raman spectrometers are often the types and the configuration of the grating and CCD. There are two basic types of spectrograph in use for Raman spectroscopy, namely Czerny-Turner and echelle.

Czerny-Turner spectrographs are an older technology, found in almost all currently-available dispersive Raman spectrometers. Echelle spectrographs are more optically advanced; they are particularly useful in applications where rapid data collection, a wide spectral range with high resolution and a high level of reproducibility are all required. Czerny-Turner spectrographs can be used to obtain high resolution and full spectral range Raman spectra, but as described below there are several sacrifices that have to be made in terms of time and spectral quality. Echelle spectrographs can provide excellent spectral throughput while simultaneously providing full range and high resolution spectra faster and with no moving parts.

Czerny-Turner spectrographs

Traditional Raman spectrographs are based on the Czerny-Turner design and are sometimes known as monochromators and triplet spectrographs. The basis of a Czerny-Turner spectrograph is the dispersive element, or grating. This disperses the Raman signal into its constituent wavelengths, similar to the dispersion of visible light in a rainbow. As shown in Figure 1, light is focused into the spectrograph through a narrow slit and then directed using either lenses or mirrors onto the grating. The dispersed light is refocused onto a photosensitive CCD (typically 1024 pixels wide) that measures intensity at different wavelengths. This information is then used to generate the Raman spectrum.

At a fixed grating position, the number of data points is limited to the number of pixels on the detector. The spectrograph can focus the whole Raman spectrum onto the CCD as illustrated in Figure 2; in this case, the spectrograph can have up to 4000 wavenumbers dispersed over 1024 pixels. This gives approximately 4 cm^{-1} per pixel on average (often called pixel resolution),

resulting in spectral resolution of about 10 cm^{-1} . Higher resolution can sometimes be obtained, but only when using a very narrow entrance slit and this seriously compromises spectral throughput.

In order to achieve better resolution with a Czerny-Turner spectrograph, it is normal to increase the dispersion by switching to a grating with higher groove density. The result is a reduced range of wavelengths falling on the CCD but the pixel resolution will be increased. For example, if the spectral range is reduced from 4000 to 1000 cm^{-1} , the pixel resolution improves to approximately 1 cm^{-1} per pixel and the spectral resolution to about 4 cm^{-1} . The spectral resolution is improved, but the spectral range is severely compromised. Only a quarter of the spectral range can be detected in a single acquisition (see Figure 3). To obtain the full spectrum, the grating must be motorized and rotated. Reduced-range spectra are obtained by acquiring spectra in several portions, and the software stitches these pieces together to give the final, full-range spectrum, a technique known as 'scan and stitch'.

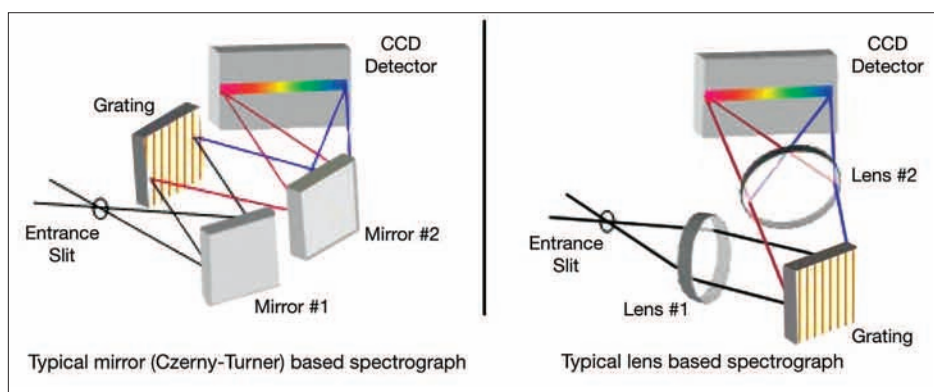


Figure 1. Mirror- and lens-based Czerny-Turner spectrographs.

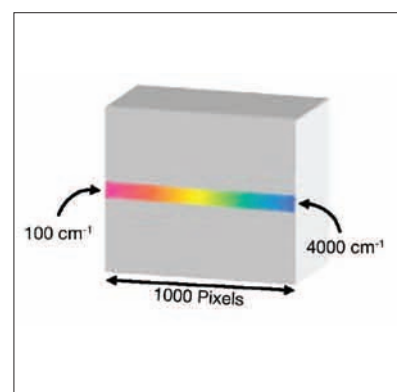


Figure 2. Dispersion of light in a basic Czerny-Turner spectrograph.

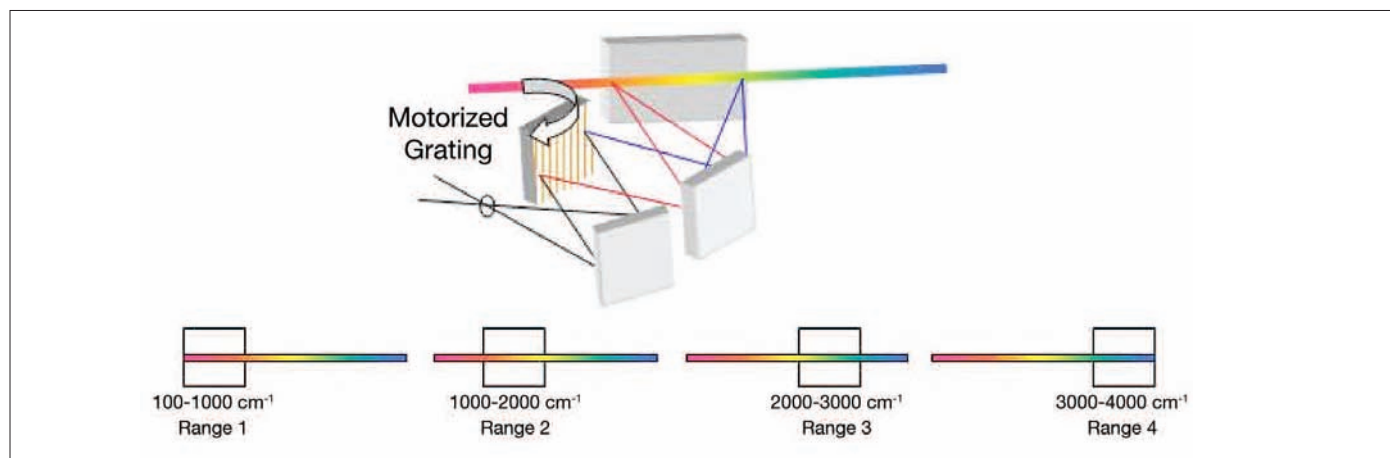


Figure 3. A high dispersion, motorized Czerny-Turner spectrograph.

There are four disadvantages to this approach:

- It takes time to move between grating positions, often around 3 seconds, although in extreme cases this can take up to 60 seconds. This means that it can take over 10 seconds to record a single spectrum with full spectral range, only 1 second of which is actual acquisition time. When a large number of spectra are recorded, for example, in chemical imaging or high throughput measurements, the total experimental time can become very long.
- The different parts of the spectrum are acquired at different times. This can be particularly problematic when analyzing dynamic systems for example reaction monitoring applications.
- Whenever an optic moves, it creates the opportunity for misalignment over time. A spectrograph with a moving grating requires periodic calibration to verify that the grating is indeed at the expected position. This is not the case with fixed optics.
- The moving of the optical components in motorized spectrometers makes intensity correction very time consuming and highly problematic.

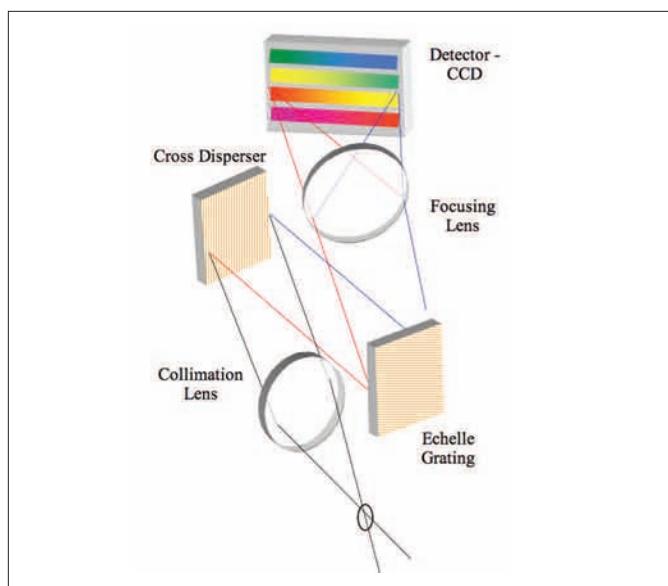


Figure 4. Optical layout of an echelle spectrograph.

In summary, there are two basic Czerny-Turner designs. The first is a rugged and reliable system with complete spectral coverage but with a limited spectral resolution of 10 cm^{-1} . The second is a system capable of higher resolution, but at a cost of mechanical complexity. When a full spectral range combined with higher spectral resolution is required, a motorized Czerny-Turner spectrograph can represent a compromise solution.

Echelle spectrographs

An alternative dispersive technique, which addresses the shortcomings of Czerny-Turner spectrographs, is to acquire the entire spectrum in one scan, while maintaining high spectral resolution. This is achieved using an echelle spectrograph.

Echelle spectrographs are commonly found in spectroscopic applications where wide spectral range and high resolution are required. These applications include Inductively Coupled Plasma (ICP) spectrometers and in astronomy applications, such as the Hubble space telescope. Echelle spectrographs for ICP applications are designed to operate with plentiful light and where discrete elemental bands are being studied; complete spectral coverage is not required. Raman spectroscopy differs significantly from this. As Raman is a low light technique, every photon is valuable. Furthermore, as Raman is a molecular spectroscopy technique, complete spectral coverage is highly advantageous.

In PerkinElmer's Raman echelle spectrograph, the dispersed light is focused onto the CCD creating a two dimensional pattern, known as an 'echellogram'. This echellogram consists of multiple strips of light stacked one on top of the other like the rungs on a ladder. This is where echelle spectroscopy gets its name, 'échelle' being the French word for ladder. In many respects, echelle spectrographs are similar to Czerny-Turner spectrographs with the primary difference being that, as shown in Figure 4, they have two dispersive elements and these elements disperse the light perpendicular to one another.

The resultant echellogram image taken from the CCD is subsequently processed into a Raman spectrum. This technique is known as ‘echelle data reduction’ and results in a full range, high resolution (better than 4 cm⁻¹) Raman spectrum being generated in one acquisition and with no moving grating. As an additional benefit, the echelle data reduction incorporates relative intensity correction using the Standard Reference Material from NIST (National Institute of Standards and Technology). Use of the NIST standard removes spectral artifacts which would otherwise be present when using a CCD system.

Echelle in practice

As the echelle spectrograph is designed to detect all wavelengths simultaneously, there is extremely efficient usage of the weak Raman signal with no time wasted in moving optical components. This full spectral coverage at high resolution is also obtained using a large and optically efficient spectrograph entrance aperture. A spectrum of laser printer ink toner obtained in one second is shown in Figures 5 and 6. This spectrum exemplifies both the range and resolution achieved with the echelle spectrograph.

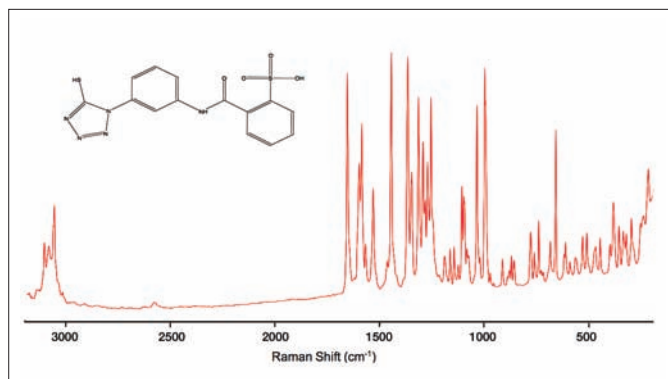


Figure 5. Raman spectrum acquired in one second using the PerkinElmer echelle spectrograph.

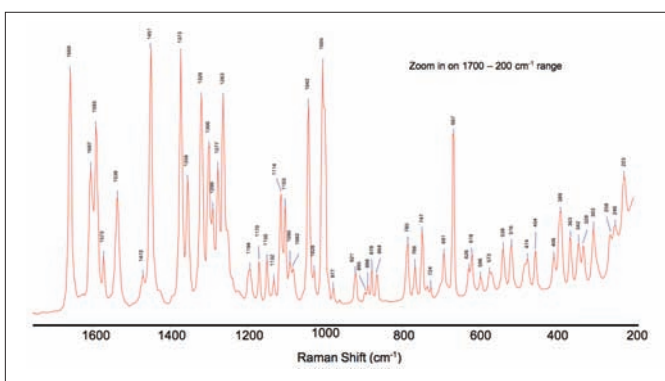


Figure 6. Zoom-in on fingerprint region (1700-200 cm⁻¹) of spectrum in Figure 5, demonstrating the high resolution detail of the Raman spectrum.

The advantage of recording spectra at 4 cm⁻¹ resolution is clearly illustrated in Figure 7. This figure shows the spectra of polystyrene run at 8 cm⁻¹ on a Czerny-Turner system compared to a 4 cm⁻¹ spectrum run on an echelle instrument. This additional resolution can be very important when differentiating between spectrally similar materials such as polymorphs.

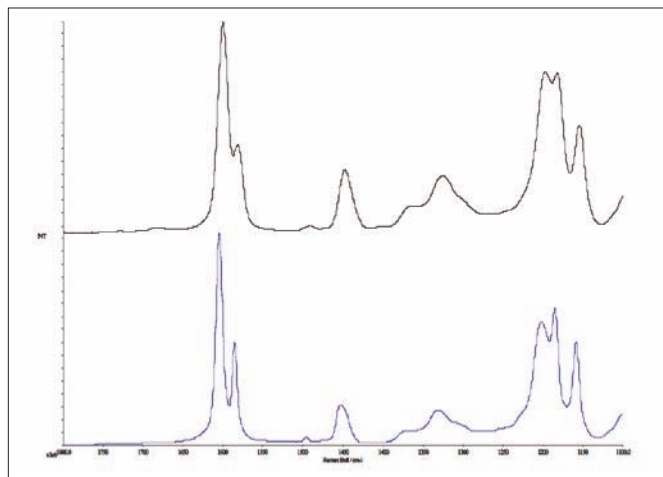


Figure 7. Polystyrene recorded at 8 cm⁻¹ (top) and 4 cm⁻¹ (bottom) resolution.

Another advantage of echelle is the ability to acquire a large number of spectra in a short time frame, without compromising range or resolution. Figure 8 shows a chemical image of a headache tablet, and, as can be seen, each data point in the chemical image contains a complete high resolution spectrum.

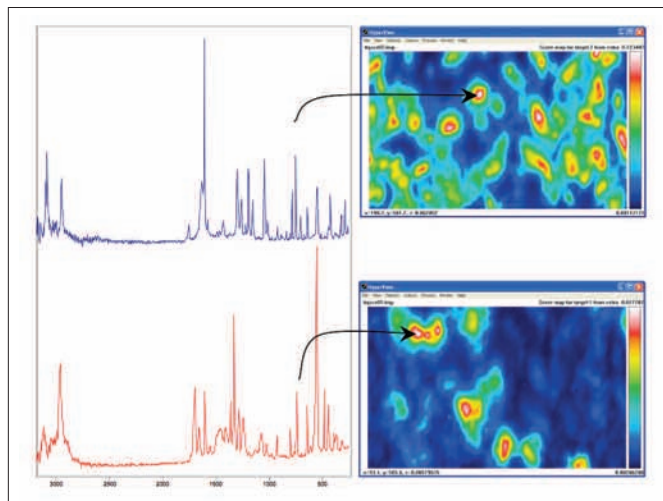


Figure 8. Raman chemical image showing distribution of aspirin (blue) and caffeine (red). Data point in the image takes 1 second to acquire at high resolution and full spectral range.

The ability of the echelle to acquire a full-range, high detail spectrum in a single acquisition is vital when analyzing dynamic systems such as reaction monitoring where the whole spectrum is generated simultaneously. The complete spectrum (Figure 9) is acquired so no important data is lost, and by zooming into the spectrum the high spectral definition is demonstrated, enabling simple study and understanding of the course of the reaction.

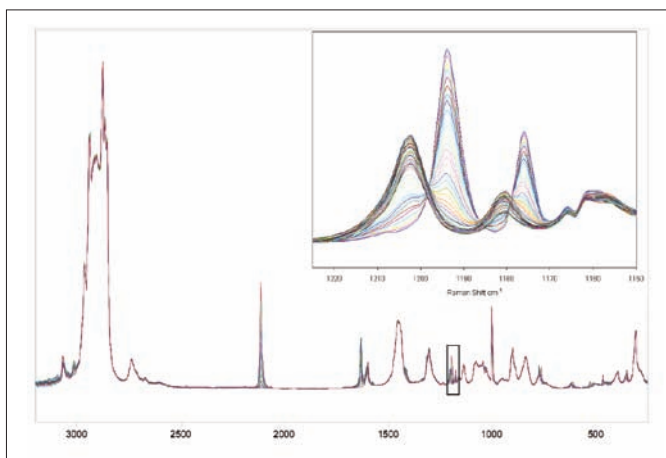


Figure 9. 30 overlaid spectra from a hydrogenation reaction carried out in heptane solvent. Inset is the high resolution spectral detail hidden in the spectrum. This inset shows the detail between 1220 and 1150 cm^{-1} .

Summary

The PerkinElmer echelle spectrograph combines:

- Full spectral range 3500-95 cm^{-1} ensuring no important spectral features are overlooked
- High spectral resolution (better than 4 cm^{-1}) giving better specificity when analyzing spectrally similar materials. This is important for spectral comparisons and library searching.
- No moving parts giving a more robust instrument that requires no alignment and less calibration.
- Fast acquisition times (less than 1 second). This has advantages when doing imaging or reaction monitoring experiments.

The net result is a highly stable, reliable instrument requiring no alignment which generates optimum spectral performance, in a minimum of time.

Further reading

RamanStation 400/400F brochure

Raman Flex 400/400F brochure

Application note on reaction monitoring at elevated temperature and pressure using fiber optic Raman spectroscopy

Application note on chemical imaging of solid dosage forms

To access recommended reading and further information, visit www.perkinelmer.com/raman