

Analytical Raman spectroscopy: a new generation of instruments

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Raman analysers provide information-rich spectra of materials in seconds, often on-line without touching the sample. Fully integrated analyzers with fiber optic probes for macro or/and micro analysis can carry out quantitative and/or qualitative analysis hundreds of meters away from the analyzer. An example, related to the polymer industry (determination of polymer crystallinity), is discussed.

Introduction

Raman analyzers have matured to the point that they are now viable outside the laboratory environment, and away from highly trained technical personnel. Automated Raman analyzers are currently running continuously in several different chemical production plants around the world as well as in analytical laboratories. This paper introduces analytical Raman spectroscopy and the instrumentation required for the field. We also briefly present the usefulness of Confocal Raman microprobe for the study of polymer crystallinity (PET).

Analytical Raman spectroscopy

Molecular vibrations shift the wavelength of a small fraction of the light that strikes a substance. This shifted light, called Raman scatter, can be used for quantitative and qualitative analysis. Quantitative analysis is based on the intensity of the Raman scattered light being proportional to concentration. Qualitative analysis is based on the wavelength shifts being different for a wide range of different molecular vibrations.

Raman spectroscopy is a scattering process, unlike the absorption process measured by mid-IR or NIR Spectroscopy. Both Raman and mid-IR measure fundamental molecular vibrations resulting in sharp, well-resolved bands. Raman spectral bands arise when a vibration induces a net change in polarizability whereas mid-IR bands occur from a net dipole change. Strong Raman scatterers contain

functional groups with highly deformable electron clouds. Examples include alkenes, alkynes, cyano, C-S, C-halogen and a wide range of inorganic species. Raman is very useful for measuring symmetric vibrations from the C-C backbone of polymers, diatomic molecules (N₂, O₂, etc.), and S-S bonds in proteins. Raman can be used to measure species dissolved or suspended in aqueous solutions. The Raman spectrum of water is relatively weak in the fingerprint region compared to the high absorption in the mid-IR or NIR. A Raman spectrum typically contains a large amount of information as sharp, well-resolved spectral bands. The band positions, intensities, and shapes provide an interpretable and fairly unique fingerprint for qualitative analysis. Quantitative analysis can often be done by simple band area measurement, but multivariate methods like partial least squares (PLS) often extract more information. The sharp, well-resolved structure typical of Raman spectra increases the robustness of simultaneous multi-component analysis.

The main strength of Raman spectroscopy for on line analysis (process control) and/or analytical applications is flexible sampling. Raman probes analyse material a fixed distance from the end of the probe. Transparent materials between the end of the probe and the sample do not hinder the measurement. As a result, Raman analysis can be done through quartz or sapphire windows or through closed transparent containers. The sample does not need to be touched, removed from the process stream, or perturbed in any way. The need for slip streams or grab samples is eliminated.

The Raman probe both delivers laser light to the sample and collects Raman scattered light from the sample. The use of optical fibers to connect the Raman probe to the Raman instrument allows remote analysis up to 500 meters. Confocal microscope probe head, immersion probe, window probe are easily coupled *via* optical fibers to a spectrometer and enhance the advantages of Raman spectroscopy.

Turnkey Raman instrumentation

Since its discovery in 1928, Raman spectroscopy has been recognized as a very powerful analytical tool capable of providing information not available from other analytical techniques. However, the traditional problems of Raman, such as, low probability of Raman scattering, rejection of the laser line, fluorescence, considerably limited the applications of Raman spectroscopy. In fact, because of these

considerations, a typical Raman setup formerly consisted of a high-power laser source (often water-cooled lasers) and a triple monochromator to prefilter and disperse the Raman spectrum. The low optical throughput of the triple monochromator further reduced the already weak S/N ratio. Also, the limitations and the complexity of Raman instrumentation dictated that Raman be almost exclusively relegated to the spectroscopy research laboratory.

It is only recently that new technologies, in the field of optical components, detection systems (CCD), solid state lasers, optical fibers, have finally enabled the development of compact Raman spectrometers. A major breakthrough was the development of holographic notch filters, which efficiently block the laser light. This enabled Raman to be performed with a single-stage Raman spectrograph. Further more, high performance holographic transmission gratings enabled these spectrographs to be designed with a very low f -number and very simple optical configuration. The resultant increase in optical throughput allowed to take advantage of the low noise Charge Coupe Device (CCD) array detectors. Another key element was the development of compact, solid-state lasers with the stable, narrow line performance required for Raman spectroscopy. Finally, optical fibers technology brought to Raman the ideal sampling method. This new generation of Raman instruments allows to open new fields of applications to Raman spectroscopy. Today, it is easy for a non-specialist to set up, calibrate, and operate a Raman system. Fully integrated Raman instruments with fiber optic probes and user-friendly software have made Raman spectroscopy a useful analytical tool for non-specialists in industrial analytical laboratories and at chemical production plants.

Figure 1 shows a schematic diagram of a fully integrated Raman system [1]. The only external connections are a serial port to a computer, the power connection, and the fiber optic cable to the Raman probehead. Raman scattered light is dispersed by a spectrograph and detected by a charge-coupled device (CCD) detector. The spectrograph shown in figure 1 is a $f/1.8$ axial transmissive spectrograph [2] with volume transmission grating [1,3].

Transmission gratings can be stacked one after another to extend their operating range, as shown in figure 2. This technique allows coverage of a wider wavelength region than would be available with a single grating without a loss in spectral resolution. The grating fringes are tilted and the gratings rotated slightly so that light from one grating is deflected upwards and the light from the other downwards. The effect is to increase the frequency coverage of the grating system without reducing dispersion. The spectrum with this type of gratings appears on the CCD detector as two pieces, each of different regions of the detector. These two pieces are spliced together via appropriated software, so that the user sees only one continuous high resolution Raman spectrum.

Transmission grating allows for simple spectrometer geometry (axial) which allows for higher throughput by limiting the number of optical components in the spectrometer.

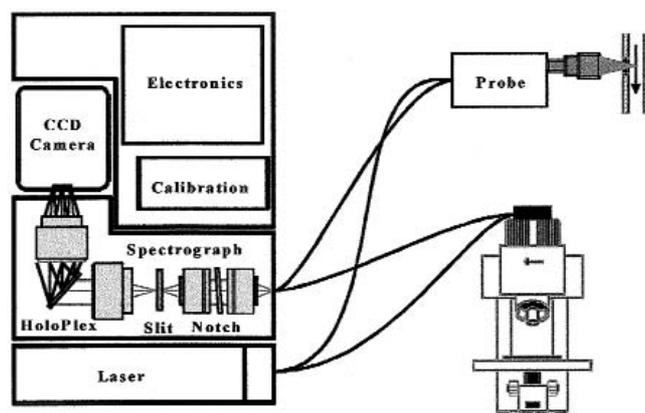


Figure 1. Integrated Raman analyzer.

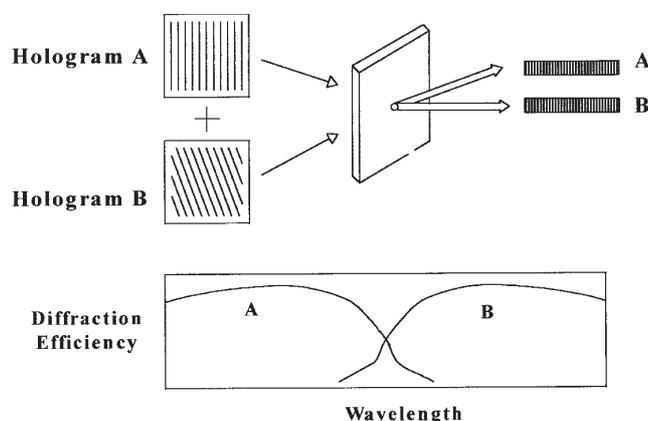


Figure 2. Schematic of transmission grating.

Also, stability and accuracy of the instrument is improved by avoiding the need for certain mechanical components, such as grating scanning motors, multiple gratings shaft or turret, required to respond to the constrain of spectral coverage and/or resolution.

Laser light is coupled to the probehead through a single optical fiber. Raman scattered light from the sample is returned to the Raman instrument through a second optical fiber. These optical fibers can be hundreds of meters long, if necessary.

Fiber optic probe performance is crucial to most applications. The probe needs to deliver the laser light to the sample, collect Raman scattered light efficiently from the sample, interface easily to reactors, pipes, sight glasses, or exposed samples, and eliminate any spectral artefacts caused by the optical fibers. An optical diagram of one such probe [1,4] is shown in figure 3 below.

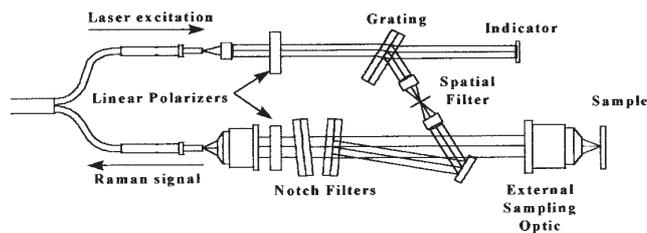


Figure 3. Schematic diagram of a Raman fiber optic probehead.

The combination of a volume holographic transmission grating and a spatial filter in the excitation path of the probehead assembly acts as a monochromator. The monochromator removes silica Raman scattering and luminescence produced by the laser light travelling through the optical fiber. Volume holographic notch filters [5] reject elastically scattered laser light before the Raman scattered light is injected into the return fiber. Permanent alignment inside the probehead ensures that the collection optical path and the excitation optical path are always properly aligned, regardless of the external sampling optic used. Numerous external sampling optics for the probehead are available, ranging from simple immersion lenses to research-grade microscope lenses and long focal length lenses. The spectrograph can accept multiple fiber optic inputs for simultaneous multi-channel analysis.

Confocal Raman microscopy

In Raman microscopy, a research grade optical microscope is coupled to the excitation laser and the spectrometer thus producing a platform capable of obtaining conventional visible images and in addition generating Raman spectra from sample areas approaching the diffraction limit (1 micron). The combination of a Raman microscope and a motorized X, Y and Z stage allows for the generation of 2-D or 3-D maps which can yield information on the distribution of materials in a heterogeneous sample over a defined area. Areas of interest include polymer laminates, silicon strains, pharmaceutical material, etc.

When a laser is focused in air a beam waist and beam length, related to the numerical aperture of the lens and wavelength of radiation, is produced. If a laser is instead focused onto surface of a condensed phase material then the beam length below the surface will be effected by the refractive index of the material, the materials absorption characteristics, etc. Raman scattering thus will occur along the beam length and all this radiation will be collected by the collection lens. Therefore, the spectrum measured from a single X, Y point on a surface will actually be the convolution of information from several Z planes (both above and below the "surface"). By employing a technique known as "confocal microscopy", it is possible to probe discrete Z-planes [ref. z]. In this technique, a conjugate aperture –

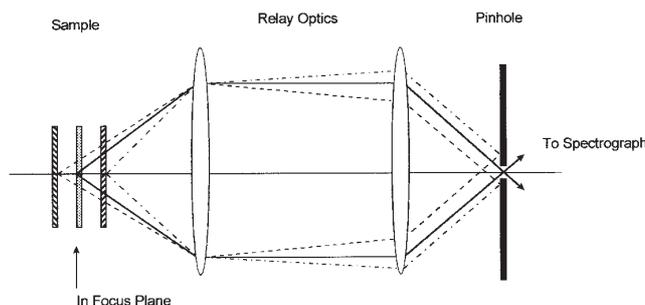


Figure 4. Confocal arrangement.

historically a pinhole) is used to reject out of focus radiation originating from different Z-planes from reaching the detector. The underlying principle of this method is graphically shown in figure 4. In figure 4, the radiation originating from above the sample surface is not brought to a focus before the pinhole and thus the measured signal from this layer is significantly attenuated by the aperture. The signal from the surface is brought to a focus at the aperture and passes without significant attenuation. Out-of-focus light from below the surface is brought to a focus before the aperture and thus is minimized (the opacity of the sample determines how significant a problem this is).

The advantages of using a confocal aperture can be summarized as:

1. spatial discrimination of the experiment to a well defined area of a heterogeneous sample;
2. for small inclusion/contamination/layers minimizing signal from the matrix;
3. minimizing effects of stray light;
4. rejection of fluorescence.

Application of confocal Raman microscopy [6,7,8]

Poly(ethylene terephthalate), or simply PET, is one of the worlds most widely used polyester polymers. It is formed from the condensation reaction between dimethyl terephthalate and ethylene glycol. PET can be found in fiber and film form and is used for blow-molded containers (such as soft drink bottles), food packaging materials, textiles and touch keypads. PET exists from an amorphous state up to an approximately 60 % crystalline state. The molecular chain orientation ranges from random (isotropic), or arranged along one (uniaxial) or two (biaxial) axes. Only orientated, semi-crystalline PET displays the appropriate clarity, strength and barrier properties required for commercial applications. The correct balance of physical properties, derived from the polymer crystallinity and molecular orientation, are achieved during manufacture by controlling factors such as draw temperature, speed, and cooling rate.

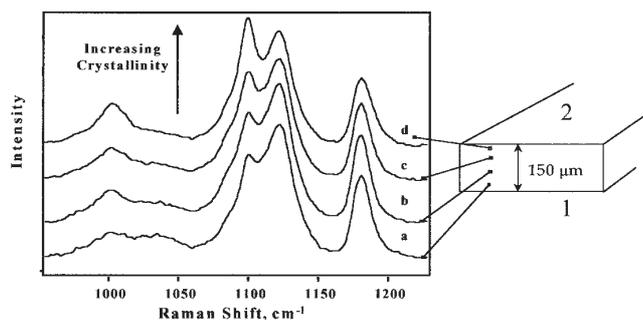


Figure 5. Raman spectra acquired across the front face of a uniaxially drawn PET film. Data was taken with a confocal microscope using 532 excitation. (Data Courtesy of ICI).

The Raman microscope provides spectral information with high spatial resolution. This makes it ideal for investigating the microstructure of processed films and fibers. Polarized Raman spectroscopy can measure not only polymer crystallinity, but the molecular orientations within a polymer matrix on the micro scale. This provides unique insights to enable the establishment of better production methods and improved product quality.

Figure 5 shows the Raman spectrum taken from a uniaxially drawn PET film. As the excitation spot is stepped across the face of the film, the crystallinity can be seen to change from side 1 to side 2 as evidenced by the increase in the band around 1100 cm^{-1} . Obviously, a bulk measurement or a transmission measurement would not yield this type of detailed spatial information. Based upon this analytical information, the source for the variation from side 1 to side 2 was postulated to be the temperature difference between the two rollers used to draw the film.

Conclusions

Raman spectroscopy is a powerful analytical technique for providing chemical information about many different polymeric systems. Modern Raman instrumentation is compact, robust and sensitive, ideal for use in research laboratories as well as in the production environment. The spectral information contained within the Raman spectrum may be used to predict polymer physical properties such as density (crystallinity) and melt index (viscosity). Future applications within the polymer industry will continue to expand due to the high information content that the Raman spectrum contains combined with the sampling flexibility provided by fiber optic coupling.

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