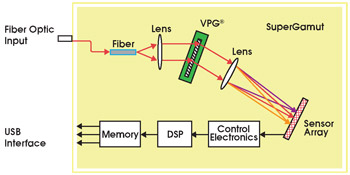
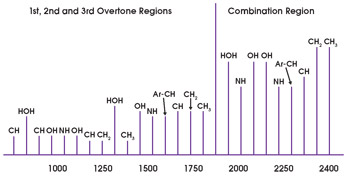
**Profiting from telecom investments: Taking advantage of the NIR First Overtone and Raman’s Spectral Fingerprints**

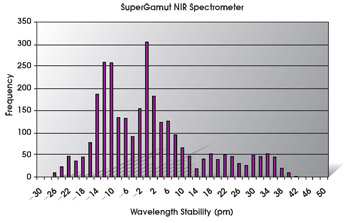
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Instrumentation professionals have long recognized great potential for near-infrared/Raman spectroscopic analyzers in application areas ranging from lab analysis to portable field monitors. Until now, however, near-IR and Raman process analytical instruments were too big, too expensive, too fragile and so sophisticated that they required highly trained operators for “real world” use. But recent advances in high-volume telecom device manufacturing have painted a new picture.  
  
Applications for near-IR and Raman instrumentation are far-reaching, promising to improve the efficiency of in-/at-line process monitoring on production lines and the safety of food and drugs, while at the same time enhancing quality control at each step of the product life cycle.  
  
**At work on the border**  
Government customs officials currently use handheld near-IR/Raman instruments at border points of entry to identify unknown substances quickly and with low cost of ownership. Pharmaceutical manufacturers are deploying near-IR/Raman instruments on production lines to monitor blending/drying conditions, fulfilling the promise of process automation technology initiated by the FDA earlier this decade.  
  
Fourier transform infrared (FTIR) spectrometers were developed for commercial use in the 1960s but tended to be used only in research labs because of their high cost and complexity of operation. Gradually, technology advancements in computers and instruments reduced the cost and enhanced their capabilities, making FTIR the industry standard for organic compound identification work in modern analytical laboratories.  
  
As sampling moves from the laboratory to the production line and points of entry, however, FTIR becomes impractical because of the size, complexity and cost of these systems.



***Figure 1.****A schematic diagram of a NIR dispersive transmission spectrometer. Images courtesy of BaySpec Inc.*

Dispersive infrared instruments are sometimes called grating or scanning spectrometers. A dispersive infrared instrument also has a source and mirrors. The source energy is sent through both a sample and a reference path, through a chopper to moderate the energy reaching the detector, and directed to a diffraction or transmission grating (Figure 1). The grating, similar to a prism, separates the wavelengths of light in the spectral range and directs each one through a slit to the detector. Each wavelength is measured one at a time, with the slit monitoring the spectral bandwidth and the grating moving to select the wavelength being measured. The X-axis of a dispersive infrared spectrum is typically nanometers, which can be converted to the wave numbers by dividing by 10 and taking the reciprocal. An external source of wavelength calibration is used, eliminating the need for high-precision laser wavelengths to reference in the system.  
  
**Spectral information**  
An understanding of near-infrared spectral information serves two purposes. It enables the prediction of where a particular chemical species should absorb and provides an assessment of near-infrared’s ability to perform an application.  
  
The near-infrared region can be broken into four sections:  
  
1) Transflectance: 800 to 1100 nm. Most suited to transflectance through a thick sample, such as seeds, slurries, liquids and pastes, the absorption bands result from third overtones of the fundamental stretch bonds in the mid-infrared region.  
  
2) Transmission: 1100 to 1800 nm. This section can be used for transmission through liquids and films as well as for diffuse reflectance measurements off samples with high water content. The absorption bands result from the first and second overtones of the fundamental stretch bonds in the mid-infrared region.  
  
3) Reflectance: 1800 to 2500 nm. This section is predominantly used for making diffuse reflectance measurements off ground or solid materials. The absorption bands result from combination bands; e.g., C-H stretch and bend combination bands.  
  
4) Raman: This technique looks at the fundamental molecular vibrations through an inelastic scattering process. It generates the so-called “spectral fingerprint” effect.  
  


*These are the overtone and combination spectral regions.*

The transflectance region is of particular interest in food analysis because it is suitable for measuring high moisture- and high fat-content products such as meat, dairy products, jams and conserves, dough and batters. Sample cells with longer path lengths can be used to collect the near-infrared spectra. Typically, a 10- to 20-mm path can be used, making sampling easier and enabling viscous and nonhomogeneous samples to be scanned without further processing.  
  
A major advantage of measuring in transflectance as compared with reflectance is that the spectra represent the variation in components throughout the entire sample, not just the surface. In reflectance, the first 1 mm contributes as much as 99 percent of the spectrum. Uneven distribution of components (in the sample, egg, drying at the surface, or separation of a water or oil layer at a glass window) results in reflectance spectra that do not represent the entire sample.  
  
The advantages of using transmission spectroscopy, however, are evident in that the intensity of near-infrared bands is approximately an order of magnitude higher than the transflectance region, allowing for relatively long path lengths. The reflectance region also provides an additional 10× improvement over the transmission region.   
  


*The SuperGamut has sub-50-pm repeatibility.*

The performance of near-infrared greatly depends on the ability to control and acquire data from the instrument and to calibrate and analyze it. Optical path length is a key parameter of the near-infrared instrument, which has been thoroughly discussed in univariate quantitative analysis in the presence of photometric errors. Although multiple wavelengths can provide more chemical information, it is difficult to determine a single path length that is suitable for each wavelength region. Therefore, availability of full near-infrared wavelength ranges is necessary.  
  
Vibrational modes that are inactive in mid-infrared absorbance are active for Raman scattering, and vice versa. The bands are about as narrow and distinctive as mid-infrared absorbance bands. For this reason, it is extremely useful for elucidating molecular structure from first principals and from library spectra, in the same way as mid-infrared spectroscopy. However, bands tend to be weak and subject to interference by fluorescence from the sample. New availability of surface-enhanced Raman spectroscopy substrates and nanoparticles – especially the newly developed dispersive 1064-nm Raman instruments – solves these issues.  
  
**Portable near-IR/Raman instruments**  
Today’s state-of-the-art near-infrared/Raman spectral engines borrow largely from the massive investments made in telecom-grade components over the past 10 years. These include transmission holographic volume phase gratings, linear array image sensors, miniature lasers and light sources, and solid-state computer chips. Collectively, these are now assembled into ultracompact, no-moving-parts, low-power-consumption, hermetic, reliability-tested spectral engines that can run on batteries in a handheld form factor.  
  


*At left is BaySpec’s SuperGamut near-infrared spectrometer engine.*

There are four parameters that describe the capability of a spectrometer: spectral range, spectral bandwidth, spectral sampling, and signal-to-noise ratio (S/N). Spectral range is important to cover enough diagnostic spectral absorption to solve a desired problem.  
  
A spectrometer must measure the spectrum with enough precision to record details in the spectrum. The S/N required to solve a particular problem will depend on the strength of the spectral features under study because the S/N is dependent on the detector sensitivity, the spectral bandwidth and the intensity of the light reflected or emitted from the surface being measured. A few spectral features are quite strong, and a signal-to-noise of only about 10 will be adequate to identify them; others are weak, and an S/N of several hundred (or higher) often is needed. In addition, device-device repeatability is now effective with manufacturing lot-lot consistencies learned from higher volumes.  
  
Today’s spectral engines are designed to meet real-world challenges for best-in-class performance, long-term reliability, compact size and ultralow-power consumption at affordable prices. Near-infrared/Raman spectrometers use telecom reliability-tested components and feature no moving parts for long-term reliability and lifetime calibration in the field.  
  
This new type of affordable, accurate and rugged spectral device is helping to fulfill the promise of near-infrared/Raman spectroscopy.   
  
**Meet the authors**  
  
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**Why Raman?**  
  
The transition of Raman spectroscopy from a technically demanding research technique to a useful practical method of chemical analysis started in the late 1990s because of the development of and more general access to various lasers, thin-film coatings, holographic optical components, semiconductor detector/optoelectronics and small, fast computers. The development of the optical telecommunications industry in the past 10 years has not only accelerated the transition but also revolutionized the Raman instrumentation. Today, Raman instruments are becoming ubiquitous analytical tools.  
  
The beauty of Raman is that it uses optical wavelengths but can obtain vibrational spectroscopic information of molecules – the spectral fingerprint – that was previously achievable only by long-infrared spectroscopic techniques. It has the best of both worlds.  
  
The energy-level diagram below shows the states involved in the Raman signal. Line thickness is roughly proportional to the signal strength from the various transitions.

**Why Near-Infrared?**  
  
The near-infrared spectral region – 800 to 2500 nm – is the “overtone and combination” region of the mid-infrared (see chart below). Near-infrared spectra contain absorbance bands mainly the result of three chemical bonds; i.e., C-H (fats, oil, hydrocarbons), O-H (water, alcohol) and N-H (protein). Other chemical bonds may exhibit overtone bands in that region; however, they generally are too weak to be considered for use in analysis of complex mixtures such as those mentioned above. Near-infrared is ideal for the quantitative determination of oils, protein and moisture. In addition, high scatter coefficients allow for excellent diffuse reflectance spectra of solids.  
  
The sensitivity and directivity of any spectroscopic measurements depend on band intensities. Short wavelengths, such as the visible region – 400 to 800 nm – are what spectroscopists call “third overtones,” which have considerably weaker band intensities – 103 less – when compared with the second overtone region – 800 to 1100 nm. This is even weaker – another 103 – compared with the first overtone region – 1500 to 1800 nm. Overtones in the short wavelength region of 400 to 1100 nm of various molecular stretches also diminish the spectral fingerprint effects, which render no spectral discrimination, making it harder to identify molecular information. So it is advantageous to use near-infrared instead of visible or infrared.  
  
Near-infrared spectra do not have the resolution of the mid-infrared spectra but can usually be collected off or through materials without sample preparation. They also are suitable for measuring high and low water-content materials. And, whereas mid-infrared is mainly a qualitative technique, near-infrared is mainly a quantitative one.

**Components and Instrumentation Advantages**  
  
Near-infrared offers other practical considerations when compared with other wavelength ranges, including:  
  
\* Sampling cells can be made from glass; mid-infrared requires sodium chloride or potassium bromide (expensive preparation devices and rigorous sample preparations).  
  
\* Relatively little sample preparation.  
  
\* Path lengths up to 10 to 20 mm may be used because of low molar absorptivity and high-energy throughput in this region.  
  
\* Commercial availability of light sources.  
  
\* Compatibility with fiber optic cables for portable quality control analyses.