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Technical series

Near infrared spectroscopy

A versatile analytical technique

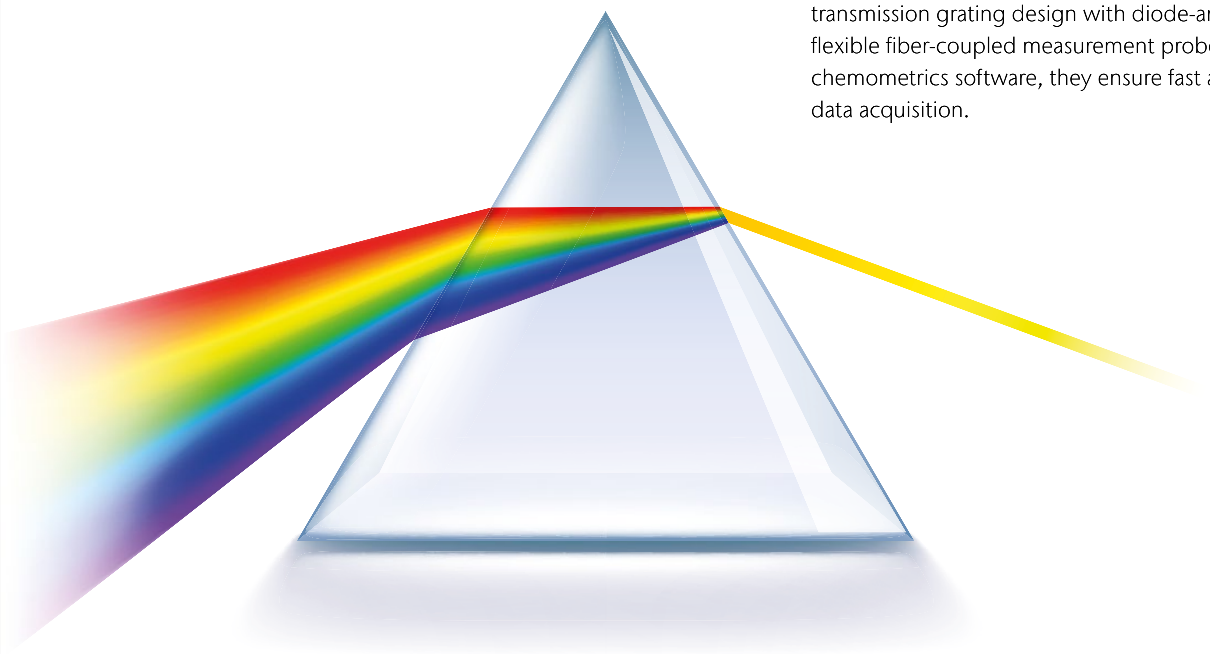
How to optimize usage of raw materi-als, energy, and production process?

NIR spectrometers offers you versatile applications

Infrared (IR) radiation was first discovered in 1800 by William Herschel, a musician and very successful amateur astronomer (he was first to find the planet Uranus). He wanted to know if there was a particular color of light associated with heat from sunlight. Herschel used a prism to separate the colors of the light and held a thermometer as a detector beyond the red end of the visible spectrum. He found the heat maximum there. With no visible light present, Herschel surmised that there must be an unseen form of light beyond the red light of the visible spectrum.

Scientists and engineers now use much more sophisticated versions of Herschel's spectrometer to precisely measure infrared spectra for chemical and process analytic applications. One of the most versatile and useful types of IR spectrometers is the near-infrared (NIR) spectrometer covering wavelengths just beyond the visible from 780 nm to 2500 nm. Sophisticated chemometrics software is often paired with the NIR spectrometer to provide critical quantitative information and enable feedback for process control. Compliance with product specifications or regulatory requirements is often the driving force to implement NIR process control. Applications exist in a wide range of industries including food and feed, agricultural and seed, dairy, pharmaceutical, and chemical industries.

Polytec's NIR real-time PAS spectrometers provide an ideal solution for NIR process analytics. Based on a transmission grating design with diode-array detector, flexible fiber-coupled measurement probes and available chemometrics software, they ensure fast and precise data acquisition.



Read on for a brief introduction to the basic principles of NIR spectroscopy, its chemical analysis capabilities and its many applications across a variety of industries.

Introduction to near infrared spectroscopy

When you are near a campfire, you can “feel“ the heat emitted by the flames, but what is happening to warm you up? Thanks to scientists, we now know that hot gases and burning wood emit both visible light and IR radiation. Furthermore, water molecules in your skin absorb some of the IR radiation. This process raises the temperature of the water and the temperature in the surrounding tissue. Nerves in your skin sense the rise in temperature and let you know it is getting hot well before the temperature rise poses a threat to your skin.

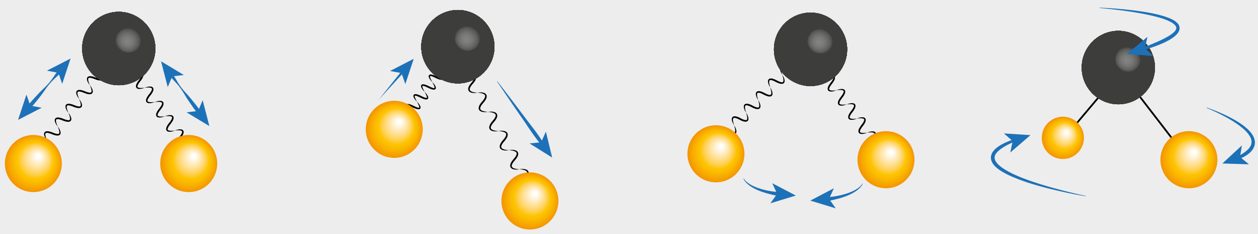
The theory

Spectroscopy is an analytical technique that measures a sample's interaction with optical energy by detecting the light transmitted through or reflected from the sample. The initial data acquired is called a spectrum, which is a plot of detected light intensity versus the wavelength of the light.

In IR spectroscopy, molecules absorb specific frequencies of optical energy (photons) elevating the molecules into excited states from their “ground state” by stimulating vibrations and rotations of the molecular bonds. This excitation is “allowed” for transitions in which the dipole momentum of the molecule changes. The infrared range of the spectrum (0.78 µm - 1000 µm) consists of the near-infrared (NIR) (780 - 3000 nm), the mid-inrared (MIR) (3 - 50 µm) and the far-infrared (FIR) (50 - 1000 µm)*. At NIR wavelengths, molecular overtones and combination vibrations show in the measured spectra.

*according to ISO 20473

Shown in the figure below are some typical vibrations detectable in the NIR range:



Symmetrical stretching *Asymmetrical stretching* *Bending* *Rocking*

Typically, NIR spectra will show broader bands which consist of the overlapping overtones and combination-vibrations found in more complex molecules. Bonds that can usually be “seen” in NIR spectra are H-C, H-O, H-S, and H-N. Organic materials commonly contain these molecular H-bonds. Because of this fact, biological and organic materials are widely analyzed using NIR spectroscopy.

In addition to the chemical structure of a sample, several physical parameters can influence the NIR spectrum and can be measured. For example, the band position of the water absorbance shifts with temperature. Besides temperature, additional parameters that can be measured in the NIR spectral region include particle size and layer thickness.

NIR vs. MIR

For mid-infrared (MIR) spectroscopy, the detected bands are primarily due to fundamental molecular vibrations as opposed to the overtone and combination bands measured in NIR spectroscopy.

While MIR is also used to detect the chemical structure of a sample, NIR has several significant advantages. For instance, many materials have a lower absorption coefficient in the NIR spectral range. This property allows relatively deep penetration of the radiation in the sample and provides measurements of both surface and volume parameters. Therefore, the sample's characterization is simplified and requires less preparation. Also, the field-of-view (FOV) is more extensive for NIR, making it better suited to manufacturing processes. Significantly, NIR spectroscopy permits using fiber optics and sapphire windows advantageously for process control applications. Optical assemblies utilizing these elements are cost-effective and robust. For example, a rugged and compact optical assembly can function as a probe in a harsh and crowded environment. Optical fibers can relay the information from the probe to the spectrometer far away from the hazards. Thus, numerous fiber probes can monitor multiple sites safely by multiplexing the optical signals into a single spectrometer, eliminating the need and expense of a spectrometer for each probe. In summary, NIR spectroscopy has many advantages over MIR and is a cost-effective and useful measurement tool for process control and automation.

What can you measure?

There are two general questions that NIR spectroscopy can answer about a sample: (1) What is it? and (2) How much is in there? Unknown substance identification can reveal the identity of a contaminant in the material while comparative analysis can check the material's consistency compared with the previously manufactured product. Spectra, properly analyzed, can be used to measure and track the amount of a specific substance in a sample (quantitative analysis).

A wide range of industries including food and feed, agricultural and seed, dairy, pharmaceutical, and chemical, are using NIR spectroscopy. The driving force for NIR process control is often compliance with product specifications or regulatory requirements. NIR's flexible integration allows measurement positions to be anywhere in the production chain – from incoming goods inspection, production steps, or final goods inspection. The often slow and complex wet-chemical off-line tests can be replaced by NIR spectroscopy. Fast and accurate on-line NIR process-spectroscopy can typically measure product-relevant parameters including moisture, protein, fat and starch content or compliance with required specifications.

Instrumentation and calibration

To successfully implement NIR spectroscopy, it is essential to both employ the right instrument and pay the utmost attention to the calibration. Another major influencing factor is the sample presentation – the way the sample and light are brought together in a reproducible and standardized way.

A calibration contains the essential information needed to relate changes of the desired measured parameter to the changes observed in the NIR spectrum. Usually, in creating the calibration, samples are measured with NIR, then separately analyzed with a conventional, absolute method (e.g., wet-chemical) for this desired parameter. Obtaining a valid calibration is essential. The better the calibration, the more precise and robust the results will be.

Fourier Transform (FT) NIR spectrometers

A Fourier Transform (FT) NIR spectrometer has a broadband light source directed via an interferometer through the sample to a single element detector. A scanning mirror moves in the interferometer modulating the output through the sample to the detector. An interferogram of the signal intensity from the detector as a function of mirror displacement contains the spectral information. A mathematical technique called a Fourier transform is used to obtain the NIR spectrum from the interferogram.

Since FTIR spectroscopy measures the absorption of a multispectral beam of light, the absorption rates are inferred for each wavelength of light. Consequently, FTIR spectroscopy cannot be completely accurate about the absorption rate of any wavelength within the beam. In contrast, dispersive spectroscopy (e.g., volume phase holographic (VPH) transmission gratings) measures each wavelength individually and is entirely accurate.

FT spectrometers offer high resolution and high signal-to-noise ratios. However, they contain moving parts which can cause sensitivity to vibration and they are slower, typically taking over a second to acquire a spectrum.

Dispersive spectrometers with detector arrays

Like with FT spectrometers, dispersive spectrometers use broadband light sources for illumination. Collection optics followed by a dispersive element (grating) that splits the received light according to wavelength is followed by a linear detector (pixel) array where each pixel corresponds to a wavelength simultaneously detected with all of the other wavelengths.

Dispersive spectrometers are fast (milliseconds per spectrum) and rugged because of a simple design with no moving parts. Given the limited number of detector pixels and limits in the width of the entrance slit, these instruments usually offer a lower resolution or limited spectral range.

Calibration and chemometrics

By calibrating a NIR spectrometer against a fixed reference, it will inherit the variability of that reference method. It is essential to recognize that all analytical methods do have variability. Generally, analytical methods that are primarily manual have higher variability than highly automated methods.

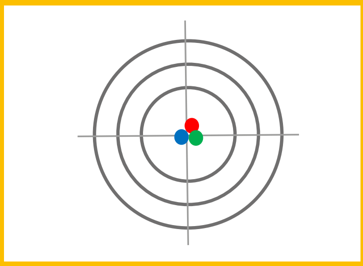
It is critically important that we recognize the difference between two commonly used terms: accuracy and precision.

Accuracy concerns itself with minimizing the deviation of a measured value to a standard value or known amount. For a substance with a well-known spectral wavelength, the closeness of the measured wavelength to the known wavelength is a gauge of the spectrometer‘s accuracy.

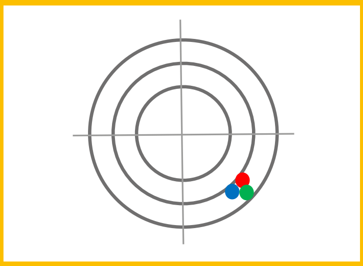
Precision (or repeatability) refers to the closeness of two or more measurements to each other. For example, if the spectrum is recorded many times, the differences between the first, second, and third spectrum gauge the precision of the spectrometer.

The manufacturing quality of the spectrometer‘s overall optical system determines both the accuracy and precision of the instrument. Also, this same manufacturing quality strongly influences the transferability of calibrations from one spectrometer to another.

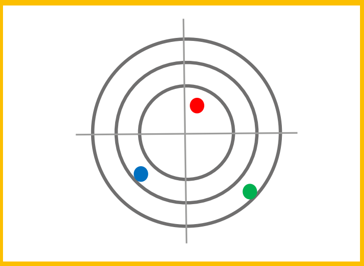
Chemometrics is the combination of mathematics, statistics, and computer science used to extract useful information from chemical data. In all cases, the aim is the chemical interpretation of the data.



high precision
high accuracy



high precision
low accuracy



low precision
low accuracy

Vibrational spectroscopy is an indirect method for the quantitative analysis of chemical mixtures. To use vibrational spectra for quantitative analysis, one must find a relationship between the measured data and the concentrations of those particular chemicals in a mixture. Models, based on these relationships, are calculated by appropriate chemometrics software and are often termed calibration curves. They relate the concentration of the analyte to the response of the spectrometer using a linear regression model, which is an iterative process. After constructing the model, it is necessary to assess its quality through observation of the model parameters and to validate the model with independent data.

The chemical information of vibrational spectra is hidden in the band positions, the band intensities and also in the bandwidths. The band positions give information about the appearance of certain chemical compounds in a mixture. The strengths of the bands are related to the quantitative content of these compounds via the Beer-Lambert Law. The bandwidths can give information about the thermodynamics and kinetics of chemical molecules. The easiest way to determine the content of a chemical compound is to measure the change of the intensity of a well-resolved band tied directly to this compound. But this case is infrequent.

It is mandatory to carry out a careful and extensive calibration to obtain a proper quantitative analysis. This calibration is frequently considered to be complicated and time-consuming. However, only a proper calibration, which is reliable and robust, guarantees the long-term stability of a process control system.

Applications

NIR spectroscopy is an essential tool for the modern agricultural sector and is used to characterize crops, animal feed, and raw biomaterials. NIR spectroscopy generates vital quality metrics for dry matter, protein, moisture, oil, particle size, ash, starch, water absorption, and selective chemical bonds. It can also analyze the ingredients of food (meat and meat products, dairy, beverages, oils, baking products, etc.) during processing or through final product samples. Measurable parameters include moisture, protein, fat, free fatty acids, ethanol, density, solids, organic acids, carbohydrate profile, and other constituents.

NIR spectroscopy is also suitable for chemists developing new compounds and as an inline quality assurance tool for production. It can measure the mixing efficacy or the internal structure of a solid sample, such as pills. It also analyzes materials used in the non-food sector, including bioenergy, pulp and paper, forestry, building, and textiles. NIR methods also work where the light passes through interfering substances, such as glass or plastic containers.

Business and process advantages include monitoring the progress of a process, reducing waste, saving energy, stopping a process in time, and increasing yield.

High performance
Polytec PAS NIR spectrometer systems

Polytec NIR real-time PAS spectrometers provide an ideal solution for NIR process analytics applications in food, agricultural, chemistry, pharmaceuticals, bioenergy, pulp and paper, forestry, building, textiles, and more. Based on a transmission grating design with a diode array detector, the PAS NIR spectrometer ensures fast and precise data acquisition. Flexible combinations with fiber-coupled components allow for integration in many measurement scenarios according to the user's requirements. Highly standardized components provide reliability, precision, and user-friendliness.

Software packages for data acquisition, in-lab analysis, process control, and monitoring are available. Software packages from renowned providers for multivariate data analysis are also available, including:

- Qualitative and quantitative compositional analyses to determine the concentration of products, additives and by-products, and to identify process-specific substances
- Physical parameters in both the reactor and the reaction mixture, such as the humidity level
- Layer thickness measurement

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Advantages of NIR process spectroscopy:

- Real-time process monitoring and control
- Non-destructive, non-invasive
- No sample preparation and wastage
- No chemicals
- Lower energy consumption and maintenance costs
- Quantification of several product-specific parameters

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2022/10 - Technical specifications are subject to change without notice