The New Technologies Shaping **Near-Infrared Spectroscopy**

NIR spectroscopy has evolved from collecting data after the fact to gathering real-time sensor information in the field.

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Near-infrared (NIR) spectroscopy is the branch of vibrational spectroscopy related to the molecular absorption of light between ~750 to 2500 nm, which has a variety of industrial and medical applications. This region of the electromagnetic spectrum is unique in terms of its interactions with covalently bound molecules because the photon energies in this range are generally too large to correspond to the fundamental vibrational frequencies of a molecule, but too small to result in electronic absorption[1].

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Wilbur I. Kaye. Photo from the Beckman Historical Collection.

In 2003, Celio Pasquini demonstrated in his work on NIR spectroscopy that the simple harmonic oscillator model of a molecule does not allow for NIR light to induce molecular vibrations. But when using the more thorough anharmonic model, one can predict the existence of higher-order combination bands and overtones corresponding to NIR energy levels[1]. An investigation of the absorption properties of NIR light shows that the efficiency of the absorption band is directly related to the dipole moment. As a result, NIR absorption tends to be most active for bonds between hydrogen (H) and heavier atoms, such as the hydroxyl (OH) and amine (NH) functional groups. This makes NIR spectroscopy an ideal method for analyzing many organic compounds for properties such as moisture and protein concentration.

Historical overview

Fewer than 100 years after the discovery of IR light in 1800 by astronomer William Herschel, scientists began using NIR spectroscopy for chemical analysis[2]. However, it was not until the 1950s that the first commercial NIR spectrophotometers became readily available. Most review articles on this subject[3,4] credit this sudden boom in NIR spectrometer technology with Wilbur I. Kaye's groundbreaking work at Beckman Instruments Inc. during that period[5,6]. As a result, not only did Beckman introduce a commercial NIR spectrophotometer during this

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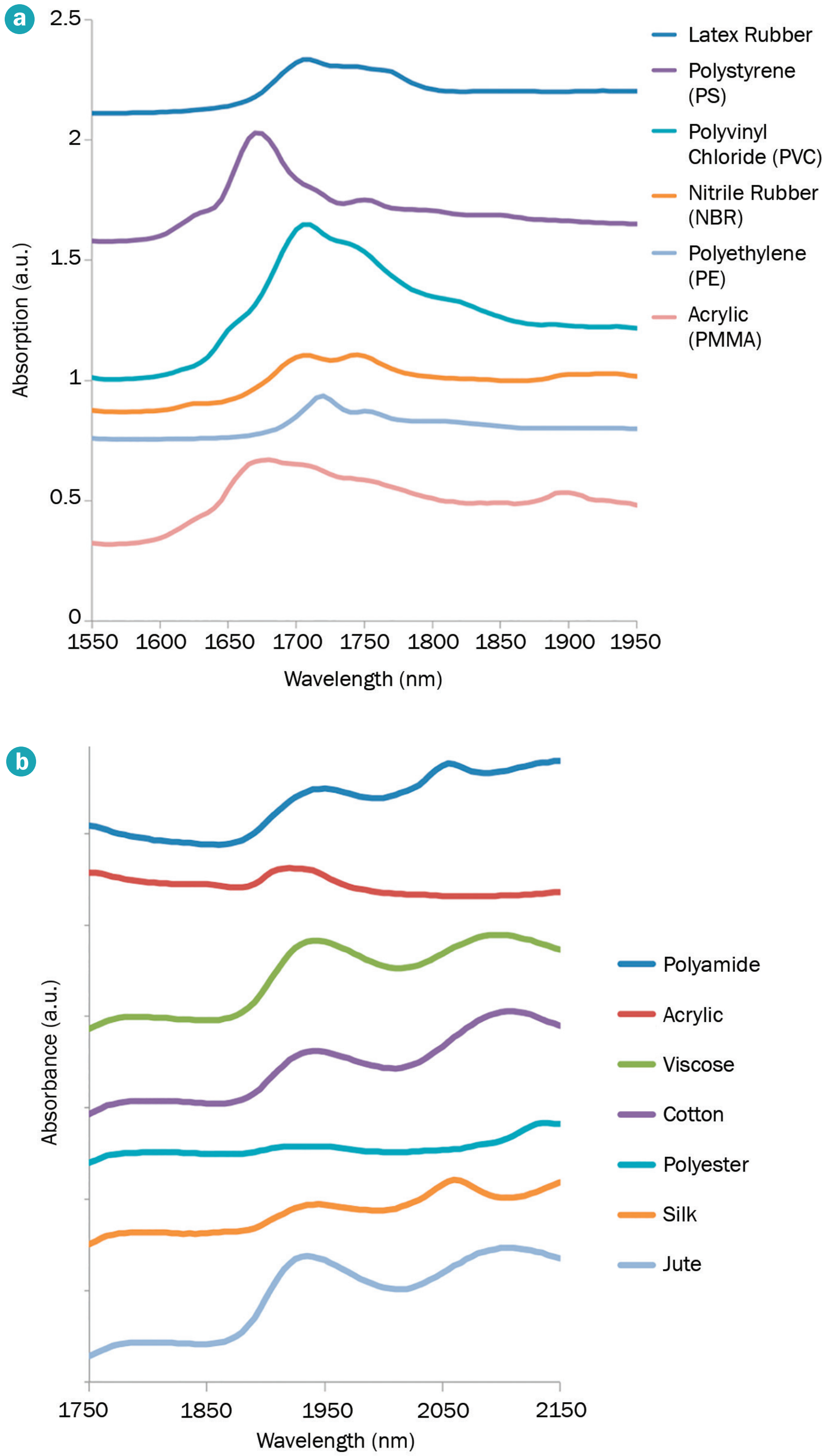
Spectral Engines

Figure 1. The NIRONE sensor weighs 15 g, and incorporates a MEMS Fabry-Pérot interferometer, an InGaAs photodetector, two tungsten lamps, and all of the control, processing, and communication electronics into one 2.5- × 2.5- × 1.75-cm box.

time, but so, too, did Perkin-Elmer Inc. and Applied Physics Corp[3].

The 1950s were followed by another decade of advancements in NIR technology; but with the introduction of gas chromatography, NIR spectroscopy fell out of favor in the 1970s[3]. Nothing exemplifies this dormancy period in NIR spectroscopy better than David L. Wetzel's 1983 scholarly review in *Analytical Chemistry* titled "Near-Infrared Reflectance Analysis: Sleeper Among Spectroscopic Techniques"[4]. As computer and electronics technology blossomed in the late 1980s and early 1990s, NIR spectrophotometers went through a second renaissance, as detailed in T. Davies' aptly titled 1998 review, "The history of near-infrared spectroscopic analysis: Past, present, and future — 'From sleeping technique to the morning star of spectroscopy'"[7].

Over the next 20 years, NIR spectroscopy technology continued to advance, and it has matured into one of the most widely deployed techniques. Today, NIR spectroscopy is regularly used in applications from agricultural product testing to biomedical diagnostics[8,9]. To facilitate deployment over such a wide range of applications, NIR spectrophotometers are commercially available in an equally wide range of system configurations. Today's options for NIR spectrometers include laboratory spectrophotometers,



Spectral Engines

Figure 2. An example NIR spectra of plastics **(a)** and textiles **(b)**, used for the development of material identification libraries with the aid of the NIRONE sensor.

industrial process control systems, portable/hand-held spectrophotometers, and modular NIR spectrometers, just to name a few.

At this point, it is illustrative to review the current state of NIR spectrometer technology by examining three case studies: first, how MEMS technology has facilitated NIR spectrometer ultraminiaturization, which is fueling the next generation of hand-held technology; next, the critical role that modular fiber-coupled spectrometers have played in advancing NIR spectrophotometers; and finally, the embedded NIR solutions used in industry to maintain optimal quality during the production process.

Ultracompact

While there are multiple methods for miniaturizing spectrometers, the most efficient way to produce quality spectral data in the smallest form factor is through the use of microelectromechanical systems (MEMS). In these microspectrometers, MEMS technology is typically used to produce an active interferometer through extremely small mirror movements inside the device. This allows for the creation of millimeter-scale Fourier transform and Fabry-Pérot interferometers, which can be used with single-element detectors to produce high-quality spectra. These MEMS-based spectrometers can be integrated with compact tungsten vacuum lamps or NIR LEDs to produce an ultracompact NIR spectrophotometer. One example is the NIRONE sensor from Helsinki (Figure 1).

The extreme compactness of MEMS-based NIR spectrometers has facilitated the advancement of a wide range of portable and hand-held applications. A full list of the use cases of mobile systems using MEMS-based NIR spectrometers is beyond the scope of this review, but some of the most common applications include material identification, verification, and sorting. Several example spectra from the plastics and textile industries are shown in Figure 2.

Additionally, these MEMS spectrometers can be coupled with modern wireless communications technologies. This creates distributed networks scalable up to thousands of NIR sensors in an intelligent cloud for fast data collection and analysis. These networks can be distributed throughout an industrial processing facility to enable the next generation of process analytical technologies, or used in widespread consumer testing applications where each device can be connected to a machine learning database to improve performance with each scan.

Avantes

Figure 3. The AvaSpec-Mini-NIR symmetrical Czerny-Turner spectrometer.

Modular, fiber-coupled

While ultracompact spectrometers have many advantages and are rapidly facilitating the growth of portable NIR spectroscopy, for many applications traditional Czerny-Turner dispersive spectrographs are still preferred. Even though some instrumentation manufacturers still prefer to build their own spectrographs, these days most companies have found it more advantageous to use modular spectrometers instead.

Since the invention of these spectrometers in the 1990s, modular fiber-coupled spectrometer technology has evolved into a well-established field, with standardized drop-in spectroscopy solutions for OEMs. This has given instrumentation designers the freedom to focus on system-level performance, applications, and user interfacing without having to design their own spectrometer. Having a fiber-coupled entrance slit also provides NIR spectrophotometer designers the ability to spatially decouple the spectrometer from the sample. For example, the integrator can use a wide variety of fiber optic probes, including reflection and transflection probes, which can be tens to hundreds of meters long, allowing for a sample to be measured in a harsh environment, far away from the sensitive electronics of the spectrophotometer itself.

Figure 3 shows one such drop-in OEM NIR spectrometer module. These modular instruments can be configured with a wide variety of entrance-slit widths and diffraction gratings, providing systems integrators with the ability to choose their preferred balance between spectral range, resolution, and throughput. For example, if the specific application requires excellent resolution, the system can be configured with a 25-µm slit providing spectral resolution as fine as 1.5 nm. However, if spectral resolution is not a high priority, but total light throughput is critical, a slit width as wide as 500 µm can be installed, providing extremely high throughput at far courser spectral resolutions.

The design of such spectrometer modules also enables systems integrators to choose between various linear array detectors to measure the range from 900 to 2500 nm — for example, 256 versus 512 elements — with or without embedded thermal electric cooling. Also, with such modules, designers have the freedom to choose between creating their own custom electronics to run the spectrometer, or using off-the-shelf control electronics provided by the vendor. For these reasons and more, the fixed grating Czerny-Turner spectrometer modules have become the industry standard for OEM systems engineers in both process and laboratory applications.

Embedded, fit-for-purpose solutions

It is also important to discuss the recent trend of viewing spectroscopy as a sensor solution, not just as a spectrometer. Over the past decade, as technology has become more user-friendly and intuitive, many users are no longer satisfied with purchasing instruments that merely measure spectra. They are looking for a complete, application-specific solution that provides process-relevant analytical data directly. As a result, companies such as tec5 AG in Germany have made a reputation combining available spectrometer technologies with customized optical, mechanical, electronic, and embedded software capabilities to provide the end user with fit-for-purpose NIR sensor solutions.

One example where embedded NIR sensors are being used for quantitative online analysis is in the measurement of copper (Cu) and iron (Fe) in electrochemical plating machines, an application on which tec5 is working with Atotech

GmbH in Germany (Figure 4). Similar fit-for-purpose NIR sensors have been embedded in various industrial applications, including the monitoring of the thickness of tablet coatings and the concentration of active pharmaceutical ingredients for incoming goods inspections and end-product quality control in the food processing industry.

At the core of these new generations of fit-for-purpose sensor solutions is their embedded data processing capability, which allows for the implementation of essential spectral processing algorithms to be calculated in the onboard controller, including multivariate data analysis. These types of NIR sensors calculate measurement or test results within the electronics for direct use by a process control system, providing a ready-to-use solution that can work without a PC. Besides the elimination of the need for PC-based software, this sensor concept enables the user to directly receive go/no-go readings and all other process-relevant feedback automatically via various industrial interfaces, making this technique also accessible to nontechnical operators.

Atotech, Germany

Figure 4. Cu and Fe online analysis, integrated in an electrochemical plating machine.

Looking ahead

Over the past 70 years, NIR spectrometers have evolved from large laboratory devices, which took a team of trained scientists to operate, to ultracompact distributed sensors that can integrate into a process so seamlessly that most operators do not know of the device's existence. These technological advancements have opened up several new application spaces for NIR spectroscopy. While it is impossible to predict precisely what the next 70 years of technological advancements will bring, it is a safe assumption that the trends toward compactness, modularity, and fit-for-purpose solutions are here to stay. This is part of the reason that the molecular spectroscopy market in which NIR analyzers are included is projected to continue to grow at a compound annual growth rate of 7%[10] for the foreseeable future.

Meet the author

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