## INSTRUMENTATION

# Applying NIR to process control

*In the following article, William J. McShane of the Kraft Technology Center, Glenview, Illinois, explains the growing use of near-infrared spectrometers for process control not only off-line in laboratories but also on-line in the production process. McShane is Associate Editor for JAOCS News for Instrumentation.*

Near-infrared (NIR) instruments have been used for many years for the rapid off-line analysis of many types of analytes in an increasing array of materials. These applications have ranged from the oil content of corn, soybeans and oats (1) to fat, moisture and protein levels in semi-hard cheeses (2) and to particle size, moisture and protein in wheat flour (3). In many of these applications, the information generated was used for process control.

As industrial manufacturing moves toward ever-increasing levels of automation, faster line speeds, low-cost production and plant-wide integrated computer architecture, there is increasing pressure to provide real-time, accurate process analytical information to an expert system (human or computer) for process control. Even with rapid NIR spectroscopic measurements, off-line analyses in the classical quality control laboratory are still basically historical measurements. Any delays in providing process analytical information can rapidly add to the manufacturing costs of a food or packaged product. As a result, NIR spectroscopy is moving from the laboratory to the production lines.

NIR spectroscopy operates in the 800–1900 nm overtone region or the 1900–2500 nm combination region. A spectrometer will usually be equipped to operate in one of these regions; with accessories, it possibly can function in both regions. NIR spectroscopic instrumentation includes the spectrometer, sampling systems, detectors and data handling.

Commercial NIR spectrometers use a variety of wavelength differentiating techniques. These instruments, in their simplest form, use narrow band-pass filters to isolate different near-infrared spectral regions that correspond to known absorption bands of common constituents—such as water, fat and protein—and sometimes regions which do not exhibit absorption bands (for reference purposes). These systems sometimes use chopper wheels and reference standard disks to aid in ensuring photometric accuracy. The advantages of this type of system are its simplicity, low cost and ruggedness. Most quality control and industrial in-line analyzers have traditionally fallen into this category for those reasons. Due to their limited spectral coverage, however, they are rather inflexible in application, are sensitive to matrix changes and cannot be redeployed rapidly for new uses.

The next level of sophistication in wavelength generation was the use of tilting filters. The object was to use a set of narrow band-pass filters mounted on a vertically situated spinning wheel. The filters would allow a narrow band of light through; the tilting of the filter would then disperse this light over the band-pass, much like a prism spectrometer. This configuration produces a number of spectral windows with more information and allows more advanced signal processing, such as the performance of second derivative manipulations. Because it is relatively inexpensive and rugged, this type of system has been broadly applied and is now finding its way into on-line applications.

Lastly, top-end instruments are usually designed to scan the entire spectrum in a given region, usually 400–1200 nm or 1200–2500 nm; they sometimes have options for both. Early monochrometers were step-scanning units intended for research work rather than a plant environment. These units tend to be good research tools, but are large, slow, non-rugged and expensive. Newer units have rapid scanning capabili-

ties (claims of five scans per second are being made) and are more rugged. Some of the newer units are being placed in plants. In providing full spectral coverage, scanning instruments offer greater flexibility, less sensitivity to matrix changes and greater opportunities for the use of sophisticated signal processing and calibration algorithms than the previously discussed filter and tilting-filter designs.

Sampling in traditional off-line analyses has been accomplished by reflectance, transflectance and transmission. Solids and opaque fluids, such as pastes and slurries, are usually measured by diffuse reflectance. In reflectance measurements, the light energy strikes the sample surface orthogonally and the diffusely reflected energy (which contains the chemical information about the sample under interrogation) is collected by an off-set detector design. This type of design uses detector elements offset by some angle from the incident light beam's path and usually eliminates the directly reflected specular light, which does not contain chemical information. Integrating sphere designs are used frequently in this application. On-line reflectance measurements have been successfully carried out by placing a filter-based instrument over a conveyer belt.

Transflectance is a cross between reflectance and transmission. This sampling technique is used for transparent and translucent liquids and works by passing light through a cell window, reflecting off a mirrored surface and passing through the cell window again to the collector optics. Both diffusely reflected and transmitted light are measured. Transmission measurements are carried out in much the same way as in uv-visible spectroscopy and with many of the same constraints.

Recent advances in fiber optic technology now make multiplexing possible, i.e., using one spectrometer to interrogate multiple sampling points. It also permits placement of the spectrometer in a remote, benign environment. Fiber optic use should provide significant gains in the extension and enhancement of spectrometer life and performance over technologies which require the on-site presence of a spectrometer.

Detector selection is decided by the wavelength region chosen. Silicon photodiodes and photomultiplier tubes are effective from 400-1000 nm. Germanium photodiodes may be used if the 800-1800 nm region is of interest. Lead sulfide can be used from the 400-2500 nm. However, due to the superior sensitivity of silicon photodiodes and photomultipliers out to 1000 nm, lead sulfide is most frequently applied to the 1000-2500 nm range. Lead sulfide also exhibits much greater thermal sensitivity than silicon and must be thermoelectrically cooled.

Given the large quantity of data and the complex regression mathematics used for most NIR calibrations, it is not surprising that this technique did not gain popularity until laboratory microcomputers became widely available and affordable. Most instrumental computers are now PC-compatible and are
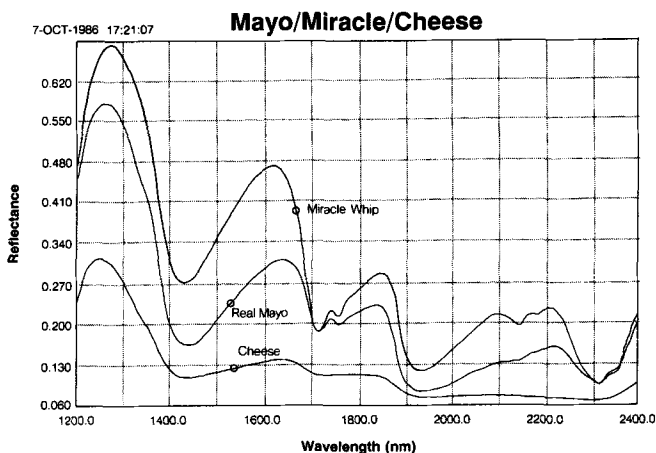


FIG. 1. The NIR reflectance spectra in the 1200–1400 nm region of a viscous salad dressing (Miracle Whip), mayonnaise (Real Mayo) and cheese (unpublished data).

moving rapidly into the minicomputer performance range. Actual capabilities are dependent upon the instrument vendor's applications software, although good sophisticated aftermarket spectroscopic software can now be obtained. Some of the spectral manipulation techniques commonly used are derivative, smoothing, baseline correction and Fourier self-deconvolution. Commonly used calibration methods include multiple variant linear regression, principle component analysis, discriminant analysis, partial least squares and variations of Beer's Law. Computer communications, once a major stumbling block, are now commonplace and essential for feedforward-feedback closed loop process control operations.

As mentioned earlier, NIR spectroscopy has been applied to a wide range of food products. In additional applications, various ingredient components can be observed in the near-infrared spectra of viscous salad dressings (Miracle Whip), mayonnaise (Real Mayo) and cheese, as shown in Figure 1. The major water bands can be assigned to the 1440 and 1930 nm regions (2). The fat and protein bands can be observed at 1730 and 1760 nm. The fat bands also can be observed at 2310 nm. In some cases, carbohydrate and acidic O-H absorption bands, as in the Miracle Whip spectrum, can be observed at about 2140 nm. NIR spectroscopic measurements on peanut butter revealed a linear spectral correlation for sucrose at 1450 nm, as shown in the second derivative spectra in Figure 2 and the regression curve in Figure 3. This sharp band, arising in the general region of the strong 1440 nm water band, has been assigned to crystalline sucrose having a single OH group which is nonhydrogen-bonded due to crystal structure conformation (4).

NIR spectroscopy also has been applied to the analysis of cis-unsaturation in lipid components, hydrogenated oils, refined oils and finished shortenings (5,6); and the degree of unsaturation, solid fat index and mean carbon number in triglycerides (7).

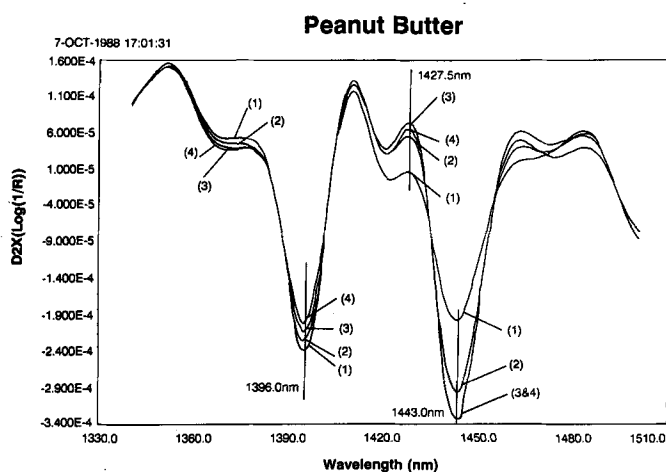Future developments in NIR instrumentation

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**Peanut Butter**



FIG. 2. The second derivative of Log (1/R) spectra in the 1330–1510 nm region of selected peanut butter samples. The sucrose levels, as determined by HPLC, are: 1 = 5.6%; 2 = 8.7%; 3 =10.3%; 4 = 10.4% (unpublished data).
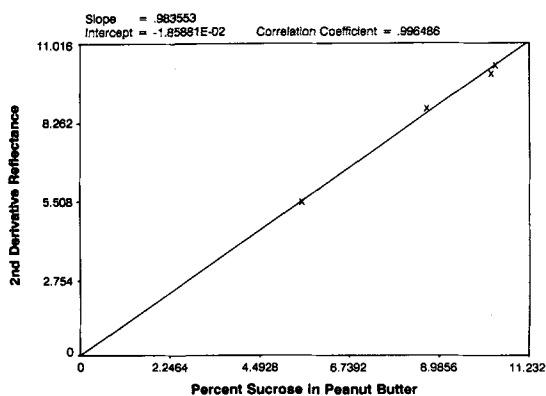


FIG. 3. The regression plot of the second derivative of Log (1/R) absolute net intensities versus sucrose concentration. All data are given in Figure 2. The regression produced an intercept of —0.0186 and a correlation coefficient of 0.996.

likely will focus on greater reliability and speed, full spectral coverage "on-the-fly," and more sophisticated acquisition techniques. Due to recent developments in liquid crystal technology, the problems of mechanical masking elements, which plagued and stalled Hadamard Transform spectroscopy in the late 1960s, have largely been circumvented. A working Hadamard Transform NIR spectrometer has been constructed and commercial development will be only a matter of time (8).
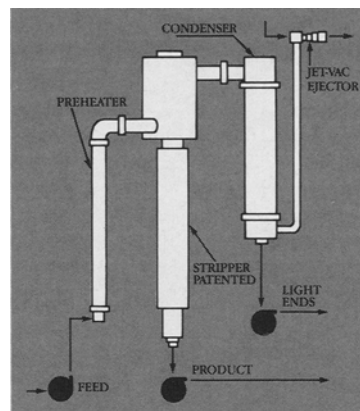
Meanwhile, Infrared Fiber Systems in late 1988 announced the prototype development of an acousto-optical tunable filter-based near-to-mid-infrared spectrometer. A photodiode array NIR spectrometer also has been developed (9). The introduction of multi-spectral region Fourier Transform spectrometers several years ago by a number of FTIR manufacturers has introduced Fourier Transform NIR spectroscopy.

All of these technologies offer rapid full spectral acquisition; simple, rugged designs; and no moving parts (with the exception of FT-NIR). Couple these spectroscopic technologies with advanced sampling techniques—such as evanescent wave techniques—and the future of NIR holds great promise for quality control and process analytical chemistry.

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