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Process Analytical Systems

Application Note:

Near IR Spectroscopy in Process Analysis

OUTLINE

1. CONCISE DEFINITION

Near-IR (NIR) is a spectroscopic method based upon the absorption of light in the wavelength region between 700 nm and 2,500 nm due to vibrations of molecular functional groups in the sample. These spectral features arise from overtones and combinations of the fundamental molecular vibrations of these groups that occur in the infrared (IR) at longer wavelengths. NIR is rich with features arising from vibrations of C-H, O-H and N-H [1].

NIR spectra are acquired by determining the absorbance, A, of light over a continuous range of wavelengths in spectrophotometers or at several specific wavelengths in fixed-filter photometers. Absorbance is defined as:

$$A = - \log (I/I_0)$$

where I is the signal from the sample relative to the signal from a reference, I_0. The reference can be an empty transmission sample cell for liquids, or it can be a broadband spectral reflector, such as a white ceramic, for reflectance measurements of solids.

Absorbance is usually linearly related to concentration, following Beer's Law:

$$A = \varepsilon\, Cl$$

where ε represents the molar extinction coefficient and C is the concentration of the species, and l is the optical path of light through the sample. For a particular species and fixed experimental setup, ε and l are constants. Letting a constant, $k = (\varepsilon l)^{-1}$, then

$$C = kA$$

A principal advantage of process NIR over IR is the ability to use fiber optics to transmit light between the instrument and the sample over considerable distance. This permits the instrument, a potential source of ignition, to be placed in safe areas where no flammable vapors exist. Only the fiber optic probe in contact with the sample and the optical fibers that connect to the instrument need be placed in the hazardous location. A disadvantage of process NIR is the characteristics of the spectra, which are typically comprised of broad, overlapping peaks in comparison to IR spectra. This often requires the use of sophisticated data analysis methods that place additional demands upon vendors to provide stable NIR instruments and upon manufacturers to have highly-trained staff, often at the Ph.D. level, for calibration model development, implementation and maintenance.

2. INTRODUCTION

NIR has been traditionally viewed by spectroscopists trained in laboratory methods as a less-than-useful spectral region that exists to fill the gap between the UV/VIS and IR regions. NIR peaks are broad, overlapped and much weaker than their IR counterparts. So, why has NIR become so widespread in process analysis?

Interest in NIR grew quickly in the 1980s due to the advent of fiber optics, bright light sources and sensitive detectors. NIR also solved some of the difficult sampling techniques characteristic of IR, because NIR optical paths through liquid samples may be millimeters or even centimeters, rather than microns. As a result, first commercial fiber optic spectrophotometers were introduced in the 1980's.

The importance of these developments lies in the ability to safely bring the sampling interface, a fiber optic probe, to the process while remotely placing the electronics (ignition sources) away from hazardous environments. This also meant that the traditional, time-consuming method of collecting ("grab") samples and bringing them back to the laboratory for analysis could be replaced by continuous "on-line" measurements without exposing workers to potentially dangerous chemicals.

Continuous on-line measurements, in turn, mean more responsive process control for better production yield, less rework of off-target material, improved product quality and enhanced worker safety. It began to change the paradigm by measuring chemistry directly, rather than inferring it from temperature, pressure, flow and fluid level.

For NIR to be accepted, it had to provide reliable instrumentation requiring minimal maintenance. Otherwise, there would be little advantage over the much more widespread, but more maintenance-intensive methods, such as process gas chromatography (GC). Thus, considerable advancements occurred over the next ten years or so to meet the requirement of instrument reliability.

As mentioned above, NIR peaks are generally overlapped. Gone is the isolated, narrow peak common in GC or IR analysis. As a result, mathematical methods using multivariate statistics were often required to analyze the subtle NIR spectral changes present among overlapped peaks. This field of multivariate statistical methods for chemical analysis is known as chemometrics [2]. Partial least-squares (PLS) is perhaps the most widely used chemometric method applied to NIR data [3]. These methods became widespread in the 1980s as computers improved.

Furthermore, as smaller NIR spectral changes were analyzed in regions with overlapping peaks using chemometrics, greater requirements were placed on the wavelength stability of the instrument. Changes of less than 0.050 absorbance units (AU) are typically analyzed in PLS models to predict chemical variables. A small shift in a NIR peak along the wavelength scale can produce such changes. Therefore, wavelength drift from the instrument could impair a PLS calibration model. Thus, considerable advancements in wavelength stability were made after the introduction of the first scanning fiber optic NIR instruments. This period also saw the introduction of newer technologies based upon different optical techniques, such as Fourier Transform Near-IR (FT-NIR), acousto-optical tunable filter (AOTF) and photodiode array (PDA) spectrophotometers.

As can be seen from the evolution described above, considerable advancements have occurred from the introduction of the first process scanning spectrophotometers. All of these approaches assume that a complete spectrum is required to solve the analytical problem. Often, that is indeed the case, when many parameters need to be predicted from each spectrum, or when peaks appear in other regions of the NIR spectrum that should not be there (outlier detection). However, this assumption generally comes with a hefty price tag. Many of these process NIR spectrometers systems with probes and fibers cost well in excess of $100,000 USD. In addition, they require personnel with chemometrics expertise, not only in developing the calibration models, but also in maintaining them, as well.

In many instances, however, only a few wavelengths are required to provide an acceptable calibration. Moisture is one example where fixed filter NIR photometers have been commercially available for many years. Today these photometers are designed for use with optical fibers for the same reasons stated above. The method of multiple linear regression (MLR) can be used to select a few wavelengths from a complete spectrum analysis [4]. A photometer can then be configured with optical wavelength filters to match those wavelengths at 25 to 50% of the cost of its full spectrum counterpart, without the need for high-level internal expertise. The danger is that a contaminant will appear at a wavelength not analyzed by the photometer.

3. NEAR IR SPECTRA

Spectra of gasoline shown in Fig. 1 illustrate the characteristics of NIR spectra described above. These spectra represent transmission of light through a pathlength of 1 cm of gasoline. C-H overtones occur in the 1100 – 1200 nm region. Aromatic contributions give rise to the secondary peak near 1150 nm, with premium gasoline showing greater absorbance due to its greater aromatic content. The larger peak centered near 1200 nm arises from C-H, CH_2 and CH_3 groups. The region between 1300 and 1500 nm represents combinations from C-O-H. Note the small changes in absorbance and subtle changes in the shapes of the peaks throughout these regions. Nevertheless, PLS models of NIR spectra in this region are used to predict the octane number of gasoline on-line in real-time to better than 0.3 units at blending facilities. They can also predict many other components of gasoline at the same time that are important in refinery production, such as various additives.

NIR is commonly used to measure water (% and ppm) due to its relatively strong absorption. For example, NIR is commonly used to measure trace amounts of moisture near 1900 nm, as shown in the spectra of tetrahydrofuran in Fig. 2. These spectra show successive additions of 1,000 ppm water. The 1900 nm region is unique to molecular water, whereas the region the near 1450 nm can represent O-H from both water and hydroxyl. Note that contributions from water in Fig. 2 near 1450 nm are present, but are much weaker than the peak at 1900 nm.
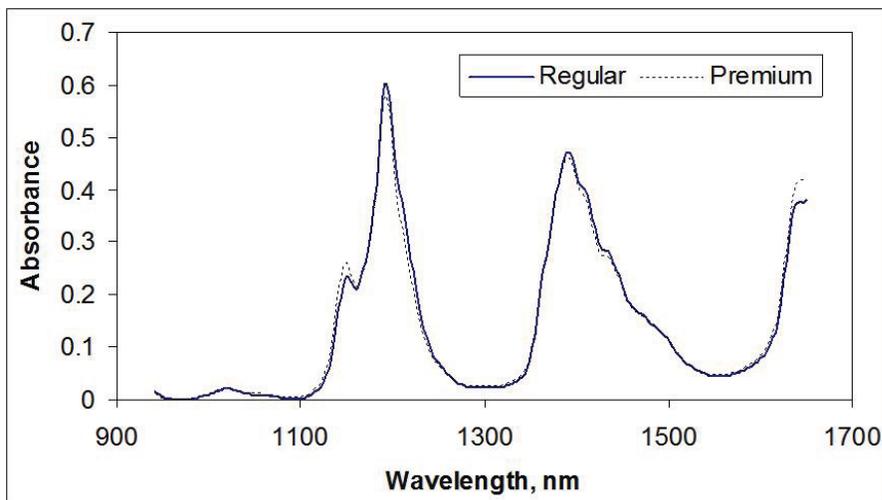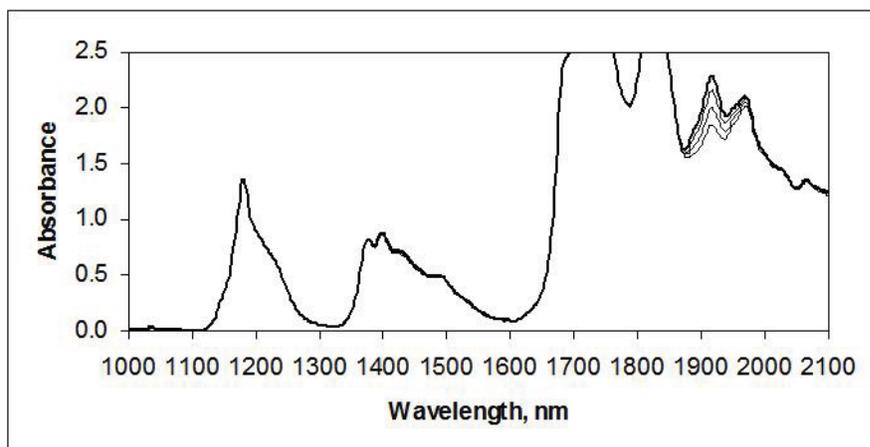

Figure 1. NIR Spectra of Gasoline

Figure 2. Water in Tetrahydrofuran

Near IR Spectroscopy in Process Analysis

NIR reflectance measurements have been widely used for solids in food, agricultural, textile, pharmaceutical and other industries. Unlike the transmission of light through clear liquids described above, reflectance measurements are strongly influenced by particle size, uniformity and size distribution of the sample. Thus, much of the evolution of near IR reflectance has been directed toward mitigating these physical effects using larger areas of illumination, taking the average of many measurement points and using computational corrections. The NIR spectrum of wheat flour is shown in Fig. 3. The vertical axis is commonly reported as -log(1/R) in reflectance spectra, rather than absorbance, where R is reflectance. In the spectrum of wheat, moisture is again analyzed in the 1900 nm region, and protein is measured in the region near 2100 nm.
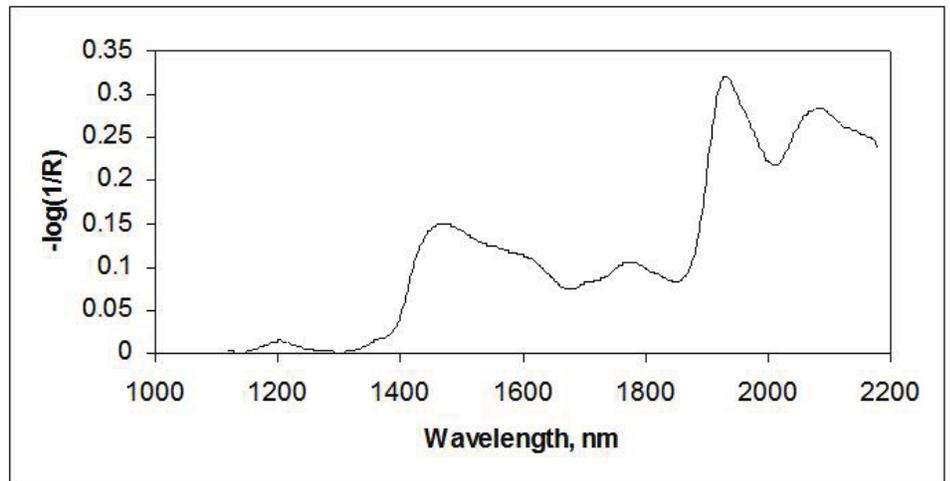

Figure 3. Reflectance Spectra of Flour

4. DATA ANALYSIS

4.1. Partial Least-Squares (PLS)

PLS is a powerful, multivariate quantitative method that is commonly used to predict properties from NIR spectra[2,3]. Mathematically, PLS uses eigenvectors and eigenvalues to perform a decomposition of the spectral and constituent concentration data simultaneously. The decomposition process is a systematic means to determine the most important variations in the data. PLS uses constituent concentration information during spectral decomposition, which weights spectra containing higher constituent concentrations more heavily. The term "factor" is used to describe a linear combination of spectral data. The first factor that is determined from the decomposition contains the most variation in the data.

This factor is then removed, and a second factor is then determined, which contains a smaller percentage of the overall variation, and so on, all guided by the constituent concentrations. When it is said that a particular solution is obtained with a "three factor" model, this means that the three most important factors explain a sufficient amount of the overall variation in the system, which results in an acceptable calibration. Each factor still contains information from each wavelength in the spectrum, some weighted more heavily than others. Thus, the dimensionality of the problem has been reduced from perhaps 1000 nm of data to three factors. By eliminating less significant factors, PLS is eliminating variations in the data that do not add useful information in establishing a calibration.

PLS reconstructs a spectrum that represents the predicted constituent value. This predicted spectrum is subtracted from the actual spectrum to determine spectral residuals. Spectral residuals are important in outlier detection to ascertain whether the model prediction is believable, i.e., whether the spectrum of the unknown fits within the calibration set used to construct the model.

Disadvantages include the high level of expertise needed to understand and use PLS programs - expertise that many companies lack. Outlier detection may become too sensitive, arising from other factors, such as probe fouling, particles present in the sample and temperature variations in the sample. These problems may lead to spectroscopic anomalies not accounted for in the calibration model. On the other hand, learning of these problems will likely lead to better on-line measurements.

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4.2. Multiple Linear Regression (MLR)

MLR attempts to select a set of wavelengths from the calibration samples that minimizes the sum of the squares of the residuals between the predicted and actual concentrations. All possible combinations of wavelengths are quickly examined with the computational power found in most personal computers today to find the best set. Tests can be used to determine if adding additional wavelengths to the model are statistically significant [4].

One of the tendencies in using MLR is to simply find the set of wavelengths that produce the "best" fit. This may not be the best strategy, because it may be strongly influenced by noise in that particular data set. User guidance is important in arriving at a robust solution. For example, restricting the wavelength search to regions in which a particular species is known to absorb may prevent the computer from finding a wavelength in a less important region, such as an absorbance valley, or in a region with an extremely small absorbance variation. A leave-one-out approach can also help to determine the robustness of an MLR calibration model. A variety of other statistical parameters can help determine the quality of an MLR model. The shape and pattern of residual plots (actual vs. predicted values) may aid in removing outliers from calibration models.

In addition to the wavelengths selected by the MLR model, more wavelengths can be added to a process photometer to help determine if a sample is an outlier. For example, if several wavelength are required in the 2000 to 2100 nm region to measure the hydroxyl number in a particular resin, perhaps an additional wavelength can be added at 1150 or 1200 nm where the C-H peaks should be relatively constant.

The presence of a contaminant elsewhere in the spectrum not analyzed by the photometer may change the absorbance of these C-H peaks outside their normal absorbance range, which could signify an outlier.

4.3. Calibration Transfer Between Instruments

Many manufacturers have multiple processes at each plant site and multiple plant sites around the world. As such, they will typically use more than one instrument to measure the same chemistry, presumably using the same model. The problem is that no two instruments are identical. Perhaps the most important difference among instruments is along the wavelength scale. This could involve a small shift of all wavelengths or a change in the wavelength spacing signifying a change in wavelength resolution. As pointed out above, spectral residuals in PLS models can increase quickly even with small absorbance changes over a broad wavelength range that can result from such changes. It becomes impractical to calibrate each new instrument with all of the original calibration samples, which sometimes number in the hundreds. Therefore, calibration transfer methodologies have been developed to help install and adjust models in new instruments without having to rerun all calibration samples. Many commercial PLS software packages now include a calibration transfer module for this purpose. However, their success is apparently quite variable, and it is quite common to hear that calibration samples have been re-run on new instruments.

5. FIBER OPTIC INSTRUMENTATION AND REQUIREMENTS

5.1. Scanning Spectrophotometers

Scanning process instruments rely upon projecting light from an optical fiber or a bundle of optical fibers onto a diffraction grating. The grating disperses the light into its constituent wavelengths. It is mechanically rotated such that a narrow group of wavelengths is sequentially allowed to pass through a narrow slit. In pre-dispersed instruments, monochromatic light passing through this slit is sent to the sample through a fiber optic cable. The light returning from the sample is then directed to an optical detector. Conversely, in post-dispersed instruments, light is sent directly to the sample and the returning light from the fiber optic cable is directed to the grating where it is dispersed, and passes through a slit placed before the optical detector. Various means are used to relate the position of the grating to the expected wavelength that corresponds to a given signal in constructing a NIR spectrum. The need for faster collection times places a significant burden upon moving the grating quickly and knowing which wavelength corresponds to a particular signal. This is particularly important because PLS models generally require sub-nanometer wavelength stability over time.

5.2. Fourier Transform Spectrophotometers (FT-NIR)

The process FT-NIR spectrophotometer is an amplitude division interferometer. It is based upon the original Michelson interferometer or one of its derivatives. In all cases, a beamsplitter is used to separate the incoming light beam into two beams, which are later recombined, focused into an optical fiber and sent to the sample [5]. One optical path in the interferometer

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is kept constant and the other is varied by some mechanical means. An interferogram is produced upon recombining the beams, which contains all the wavelengths in the spectra. Applying a Fourier transformation to the interferogram results in a frequency spectrum (wavenumbers, cm^{-1}), which is readily converted into a wavelength spectrum (nm = 10^7/cm^{-1}). There are a variety of ways by which one optical path is varied, including a moving mirror, moving optical wedges, and moving both reflectors in tandem. These developments focused upon issues present in the process environment in contrast to the laboratory, such as the effects of mechanical vibration and large temperature fluctuations. FT-NIR have a "multiplex" advantage over scanning instruments, as well as greater wavelength resolution. The "multiplex" advantage, like the PDA discussed below, means that all wavelengths are analyzed at the same time. The greater wavelength resolution is useful in some applications, but is not particularly required for the generally broad peaks found in the NIR. For hot process samples, blackbody radiation is generally eliminated when taking the interferogram. However, FT-NIR technology has a moving part and can still be prone to vibrations in spite of the design advancements.

5.3. Acousto-Optic Tunable Filters (AOTF)

In contrast to scanning instruments, AOTF does not require a moving part. Rather, light is directed into a crystal of TeO$_2$. A high-frequency acoustic wave in the radio frequency range is coupled into the crystal by the use of a piezoelectric material bonded to the crystal. These acoustic waves quickly propagate through the crystal, interact with the broadband light and generate two monochromatic beams of light, each polarized in a different direction. In essence,

the crystal is being made to act as a transmission grating controlled by changes in atomic spacing due to acoustic wave propagation. Either of these monochromatic beams can be used as a source of NIR light, coupled into an optical fiber and sent to the sample. Wavelength switching is very fast compared with scanning instruments, and because the AOTF can be programmed to select any sequence of wavelengths. Hence, more time can be spent on specific peaks or in regions of interest, and less time need be spent in spectral regions containing little or no useful information.

5.4. Photodiode Array Spectrophotometers (PDA)

The PDA is perhaps the most intuitively obvious way of acquiring NIR spectra. A compact, linear array of detectors is placed at an appropriate distance from a diffraction grating to analyze the complete sequence of wavelengths. Thus, light in a narrow spectral region continuously impinges on its own detector element is the array. The integration time, akin to the exposure time on a camera, is easily adjusted to optimize signal-to-noise. PDA has been the latest technology to develop due to the more recent availability of NIR detector material. Although Silicon (Si) PDAs have been commercially available for some time, they can only be used below about 1000 nm. This region is comprised of even weaker, more overlapped vibrational peaks from higher order overtones than those shown in the previous section. Weaker NIR peaks, in turn, require longer optical paths for liquids and are not particularly practical for reflectance from solids other than for color. The more recent availability of Indium-Gallium-Arsenide (InGaAs) detector material makes the PDA more useful for NIR analysis. InGaAs PDAs currently cover the range from 900 – 2200 nm. The PDA detector is sealed in an optical enclosure and cooled thermo-

electrically. Each photodiode detector in the array is multiplexed and amplified electronically. As with AOTF, PDA is extremely fast, and is able to collect and average a large number of complete spectra in a fraction of a second without moving parts. Another advantage over lead-sulfide (PbS) detectors traditionally used in the NIR is the superb low-light sensitivity of InGaAs for highly absorbing liquids or reflectance from solids. Their disadvantage at present is the high price of the detector, although they have decreased since 1990.

5.5. Fixed Filter Photometers

Traditionally, fixed filter photometers capable of analyzing multiple NIR wavelengths worked by passing light through a sample cell within the instrument. The sample is continuously extracted from the process and pumped through this cell. Light is then passed through a rotating wheel containing a number of optical interference filters. Interference filters allow light only within a narrow wavelength range, typically 10 – 20 nm wide to pass. Different wavelengths are selected in this way and rotated in front of a NIR detector. Thus, traditional photometers had a moving part and still extracted the sample from the process to the instrument. More recently, fiber optics have been integrated into photometers to gain the advantages described above. Also, by using beamsplitters and multiple detectors rather than moving filter wheels, some process photometers have eliminated all moving parts and allow all detectors to analyze their wavelengths simultaneously, as in the PDA. This is a subtle, but important point. In process analysis, the sample continuously moves past the fiber optic probe. By analyzing all wavelengths on the same volume of sample at the same time as it moves through the fiber optic probe, potential "process noise" can be eliminated. By adding a microprocessor, process NIR

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photometers can use multiple wavelengths and MLR to monitor a broad range of applications.

5.6. Fiber Optic Multiplexing

Fiber optic multiplexing is another important technological advancement for process analysis. It permits several fiber optic probes to be sequentially analyzed with one instrument, thereby decreasing the cost per point of analysis. One means to accomplish this is to use a pair of angled reflectors at opposite ends of a rotating shaft inside the multiplexer. Light is brought into the center of one side toward the axis of the shaft, reflected up along a rotating arm and back out the same side into another fiber optic cable connected to the first probe. Thus, there is a central fiber optic connection and several connections around the periphery of a circle. Light returning from the probe is connected to the opposite side of the multiplexer at a similar position on the periphery of the circle, reflected down to the shaft and reflected again into the central connector and out toward the detector. Rotating the to next position on the circle examines the next probe, and so on.

One fiber optic cable can be routed from one side to the other of the multiplexer bypassing a fiber optic probe. This can be used to measure changes in the instrument over time, such as the aging of the light source, and correct the spectrum from each probe accordingly. This is particularly important if such changes have different magnitudes in different spectral regions. This procedure is commonly referred to as "internal" referencing. It is generally needed in process systems because the reference spectrum is taken with an empty transmission probe or a reflectance standard with a reflectance probe. It is stored in the computer and used for many months. Therefore, the internal reference is used to make corrections when process probes cannot

be removed frequently from the process and re-referenced.

5.7. Enclosures for the Process Environment

The presence of process NIR spectrophotometers and photometers in the production environment can pose fire or explosion hazards if flammable vapors exist. Therefore, NIR process equipment will likely require special enclosures to reduce or eliminate such risks to personnel and equipment. Hazardous area classifications for North America are divided into Class, Division and Group under the NFPA 496:1993 standard. Common classifications for NIR analyzers are defined below [6]:

5.7.1. Class 1, Division 1, Groups B-D

Areas where flammable gases and vapors are likely to be present continuously, intermittently or periodically in quantities sufficient to produce explosive or ignitable mixtures, including most chemical vapors (other than acetylene, Group A). Enclosures for these environments can be bolted and sealed, or may have a pressurized purge systems that will turn off the instrument if pressurization is not maintained. European Zones 0 and 1 correspond to Division 1.

5.7.2. Class 1, Division 2, Groups, B-D

Areas where flammable gases and vapors are likely to be present to produce explosive or ignitable mixtures only in the case of accidental rupture or breakdown of equipment, including most chemical vapors (other than acetylene, Group A). Enclosures for these environments generally have pressurized purge systems in which the instument will continue to function, even if pressurization is lost.

Loss of pressurization can be detected electronically by process control computers systems, although such connections require intrinsic safety barriers. Cenelec Zone 2 corresponds to Division 2.

5.7.3. General Purpose, NEMA 4

Although there are variety of NEMA classifications, NEMA 4 is a commonly used enclosure, where 4 represents a watertight (weatherproof) enclosure. A comparable Cenelec designation would be IP65.

6. FIBER OPTICS AND FIBER OPTIC PROBES

The advancements in NIR instrumentation described above would required concomitant advancements in fiber optic probe technology. The most stable spectrometer would be useless if the fiber optic probe to which it is attached falls apart in the process. Process probes have to withstand the rigors of the manufacturing environment, including high temperatures, high pressures, aggressive chemicals, mechanical vibrations, and often, combinations of the above.

6.6. Transmission Probes

6.1.1. Insertion

Insertion probes are typically long metal rods, ¾ - 1 in. (18 – 25 mm) in diameter and commonly 6 – 36in. (9 - 91 cm) long that are designed to be inserted through valves into the side of a reactor or into a large pipe. These probes generally transmit a collimated beam of light through the sample only once between sapphire windows placed in a cutout along the side of the probe near the tip. Collimated light is used to eliminate the potential effect on the spectrum due to changes in the refractive index of the liquid sample. Light is coupled into and

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out of the probe with fiber optic connectors. Light propagates within the probe along one side either using a fiber optic cable or a hollow reflective tube. It is reflected back up the other side of the probe using a retroreflector placed inside the probe at the tip. Light passes through a collimating lens and through the sample between the windows and then out of the probe to the analyzer. The windows are generally brazed into the probe and the braze material may be subject to chemical attack. There always seems to be one application in which the chemistry attacks the braze material. Some use primary o-ring seals for the windows selected for specific chemical compatibility rather than using a braze. Insertion probes must be removed for cleaning and re-referencing. These probes can typically withstand temperatures up to 250 °C and 1000 psi (7 Mpa). They are more expensive than flow probes by 50 – 100%, but they are often the only way to continuously monitor reactions in a reactor. Typical optical paths range from 1 to 20 mm for transmission probes in the NIR.

6.1.2 Flow

These probes are designed for slip (side) streams, which are fast bypass liquid streams with smaller diameter piping. Liquid is often pumped through side streams. Flow probes are placed between pipes anywhere from ¼ - 1 inch. (6 – 25 mm) in diameter in which the liquid flow passes through the body of the probe. Most rugged flow probes have sapphire windows and primary o-ring seals. Collimated light passes across the liquid moving through the probe perpendicular to the direction of flow. These probes generally have a removable clean port. The side stream can be closed off and drained using valves and sample ports, and the clean port on the probe can be removed for easy cleaning of the optics. Thus, the probe does not

have to be removed from the process piping. This is important because in hazardous environment, optical fibers are contained in conduits attached directly to the probe making frequent removal difficult. The sample can be also be conditioned in side streams by heat-tracing to control sample temperature and by filtering to remove light scattering particles or bubbles that would adversely impact spectroscopic measurement. Side streams allow samples to be readily taken for laboratory analysis in order to adjust the calibration of the instrument over time.

6.2. Reflectance Probes

Reflectance probes are used similar to the insertion probes described above. They generally use multiple fibers to provide larger areas of illumination and greater intensity for collection of light reflected from the sample. Many configurations are commercially available. The simplest involves placing multiple optical fibers around one central fiber within the probe. The multiple outer fibers are bundled into one optical fiber generally connected to the light source, and single fiber is connected to the detector. The fibers in the probe are generally placed in a ¼ in. (6 mm) diameter metal tube containing a sapphire window at the tip. Various techniques are used to minimize the specular component of the diffuse reflectance from the sample and to minimize stray light inside the probe. Other designs utilize larger diameters and have reflective tubes inside, thereby eliminating the presence of fibers within the probe. This permits higher temperature operation. Reflectance probes can be inserted directly into light scattering liquids or into moving streams of powder. Sample presentation at the probe tip for solids is critical. Variations in packing efficiency of the powder against the probe will strongly impact the quality of spectral data. Using fiber optic reflec-

on-line becomes more difficult for larger solids, such as pellets, simply because the optical fibers limit the image spot size relative to the larger size of pellets. Illuminating larger areas of solids from a distance have been done for moisture for many years. However, these methods do not rely on fiber optics.

6.3. Internal Reflectance Probes

Attenuated total internal reflectance (ATR) is used to measure the liquid phase in multiphase samples containing light scattering centers, such as particles in slurries and bubbles in foams. This method has been used successfully in the IR and the UV where the absorption from vibrations and electronic transitions, respectively, are intense. This is not the case in the NIR. ATR operates by propagating light within an internal reflectance element. In the IR, this is usually a cylindrical rod or flat plate. Light internally reflects off the surface of the element in contact with the sample and "senses" the sample only within a micron or so into the sample, even though the propagated beam is contained within the rod or flat plate. Only a few reflections are required in the IR to acquire good quality spectra. The peaks in the NIR are much weaker and require thousands of reflections to produce acceptable spectra. One way has been found to accomplish this in the NIR, and that is to shrink the thickness of the internal reflectance element to less than one micron and propagate light through this thin film. This thin film is deposited on a glass surface at the end of a fiber optic insertion probe that is placed in contact with the liquid sample. Thousands of internal reflections occur resulting in a spectrum of the liquid phase in the slurry approximately equivalent to a transmission cell with a path of 3 – 4 mm. The danger in using ATR in the process is that surfaces can become coated and prevent the ATR probe from sensing changes in bulk chemistry.

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6.4. Fiber Optics

The optical fibers available for NIR are multi-mode with diameters generally ranging from 200 to 600 microns. They have a silica core with a doped silica cladding, and a polyamide protective coating. There are two types of fibers used with process analyzers, referred to as low-OH and high-OH. High-OH fibers are used in the UV/VIS because they are less prone to solarization (darkening) upon exposure to UV light. Their higher OH content precludes their use for most NIR applications. Low-OH fibers are used in the NIR to minimize absorption due to the fiber itself in the important O-H regions near 1450 nm and above 1900 nm. A lens is used to inject light into the optical fiber to match its typical acceptance angle of 22°. Light follows a variety of paths through the fiber and is only attenuated slightly over long distances. For example, a typical low-OH fiber at 1600 nm only absorbs about 0.08 AU over 100 m, which means that about 83% of the light is transmitted in each direction to the fiber optic probe, or 69% round trip. Assuming that the fiber optic probe itself transmits 40% of the light and the sample in the probe, in turn, transmits 40% of the light, that leaves 69% times 40% times 40%, or about 11%, which is easily measured with most NIR detectors. Fibers are jacketed by a variety of protective materials that may also be reinforced by metal coils. Fibers are typically epoxied into metal connectors with their ends exposed and highly polished. Single fibers are generally used over longer distances due to cost, whereas fiber bundles are used over short distances. Fiber bundles may have tens or even hundreds of fibers contained within the cable. Fiber cables are generally secured in manufacturing facilities within conduits or in cable trays. Care must be taken not to bend fibers too sharply. Typically a minimum 6 in. (9 cm) bend radius is specified.

7. Organizational Issues

Although this article has focused upon the technologies involved in process NIR, it may not be obvious to many readers that successful implementation is more dependent upon corporate organizational issues than upon the instrumentation itself. This is a bold statement.

Process analytical chemistry is highly multi-disciplinary (7). It involves process engineers and chemists who know what they want to measure and where it can be measured, instrumentation technicians who will maintain the instrument, technology gatekeepers who look for new instrumentation, analytical chemists who perform the laboratory chemical analyses upon which the NIR calibration is based, and researchers who likely perform the initial feasibility studies. There are also specialists in data communication, safety and others. Therefore, the person who identifies the instrument may not be the same person who calibrates it, or who is the eventual "owner" of the equipment. The person who develops the NIR calibration may not be responsible for its maintenance over time.

Companies that establish the means for this "internal technology transfer" among their various groups will have the greatest likelihood of achieving the benefits of on-line NIR technology described above. A fundamental requirement for such success is visible and consistent upper management support of process analytical chemistry. Without this, workers will be less inclined to "stick their neck out" and try a new technology that may help their organization to improve product quality more efficiently. This is difficult in an era of corporate downsizing where concern for job security does not inspire workers to take such risks. This is also made difficult in most instances because these instruments are often installed in existing, profitable processes. Their benefit is not "all or nothing", but rather incremental, which is harder to justify. Sometimes, catching a major process upset early pays for the entire cost of the instrument. In other words, if everything worked perfectly there would be no need for NIR instrumentation in the first place. Lastly, for companies just beginning to consider such on-line measurement technology, it is important to build advocacy with early success by judicious selection of the first application. Selecting a pricey nine-probe NIR spectrophotometer and developing the world's most sophisticated PLS model for the first on-line NIR application is probably not the best approach to build this advocacy. With diligence and a consistent focus, NIR process instruments can help manufacturers achieve the objectives of improved product quality, reduced manufacturing costs and enhanced worker safety.

Near IR Spectroscopy in Process Analysis

ABBREVIATIONS

NIR	Near-infrared
IR	Infrared
Mid-IR	Mid-Infrared
UV	Ultraviolet
VIS	Visible
PLS	Partial Least-Squares
MLR	Multiple Linear Regression
AOTF	Accousto-optic Tunable Filter
FT-NIR	Fourier Transform Near Infrared
PDA	Photodiode Array
AU	Absorbance Unit
GC	Gas Chromatography
Nm	Nanometer
cm^{-1}	Wavenumber (=107/nm)
A	Absorbance
I	Sample signal (Intensity)
I$_0$	Reference signal
C	Concentration
e	Molar extinction coefficient
L	Optical path length
Si	Silicon
InGaAs	Indium-Gallium-Arsenide
Psi	Pounds per square inch
Mpa	Mega Pascal
ATR	Attenuated Total Internal Reflectance

Guided Wave Model 412 NIR Spectrometer

Guided Wave Assorted Probes and Flow Cells

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Zpurge Unit
Class I, Division 2

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Class I, Division 1

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