

# Content

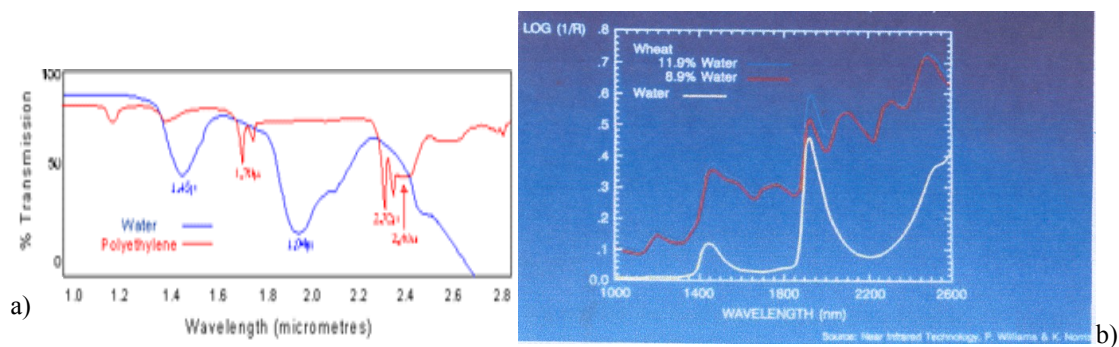
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## Introduction

### NIR definition

NIR stands for near-infrared and refers to the region of infrared light spectrum immediately adjacent to the visible region, falling between 750 and 2500 nm in wavelength, where most organic and also some inorganic compounds have excellent reflectance or transmittance properties, which means that they are able to highly absorb light at the NIR radiation.

It was in the nineteenth century when the first serious NIR measurement was performed, but only after World War II that the interest in NIR grew to quantitative measurements of water, some organic compounds and few studies in proteins (**figure 1a, 1b**).



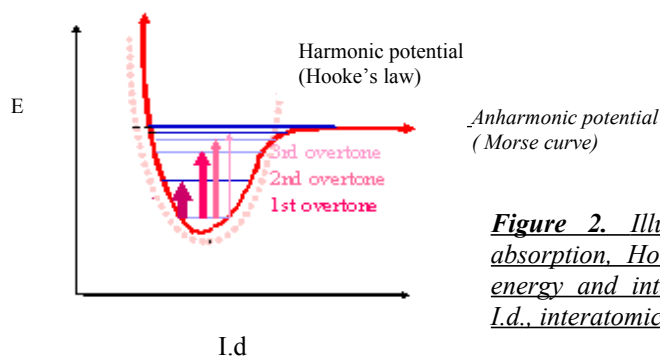
**Figure 1.** *a) NIR transmittance spectra of water and polyethylene; b) NIR reflectance spectra of pure water and wheat at two levels of moisture with constant protein content (12.4%).*

### NIR principles

The NIR spectroscopy theory is derived from quantum physics and molecular spectroscopy [1]. According to the principles of quantum physics, molecules may only assume discrete energy levels, from a fundamental frequency or wavelength (**figure 2**). In the figure 2 is illustrated the simplest theoretical treatment for the energy absorption behaviour of covalent bonds (e.g. O-H, C-H, and N-H). Where the energy (y axis) is calculated according to the formula:

$$E = hc\lambda^{-1} \quad (1)$$

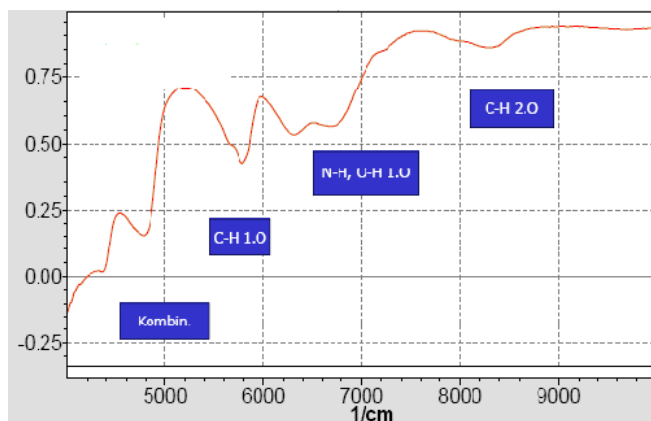
E is energy, h is Planck's constant, c is the velocity of light, and  $\lambda^{-1}$  is the wavelength in  $\text{cm}^{-1}$ .



**Figure 2.** *Illustration of the basic models for energy absorption, Hooke's law and Morse curve, as functions of energy and interatomic distance. Abbreviations: E, energy; I.d., interatomic distance*

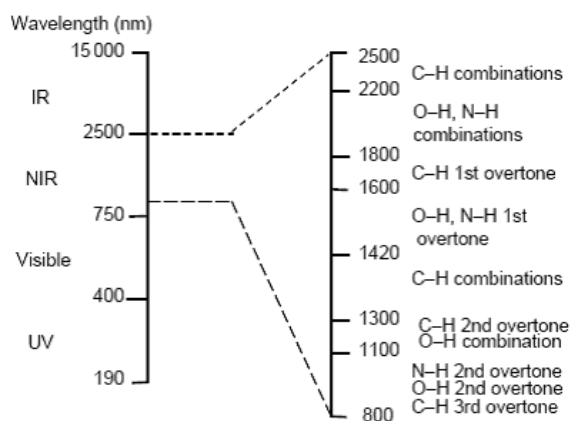
The Hooke's law curve (**figure 2**) corresponds to the dotted line which theory is based on the ideal diatomic harmonic oscillator (overtone), similarly to the vibrating string of a musical instrument. However, in practice the covalent bond vibrations are anharmonic

and follow the potential energies in the Morse curve (**figure 2**), which corresponds to the full line illustrating the decreasing distances at a slowly rate until approaches a constant level of energy (dissociation energy). It is the anharmonicity, which allows the harmonic motion (or overtones) to occur in the NIR region [2]. Another prominent feature of NIR is the combinations (**figure 4**).



**Figure 3.** *Spectrum with the main areas of absorption identification.*

Combinations arise by interaction of two or more vibrations taking place simultaneously. Thus, near-infrared spectroscopy is based on molecular overtone and combination vibrations (**figure 3 and figure 4**). Such transitions are forbidden [a] by the selection rules of quantum physics [a]. As a result, the molar absorptivity [a] in the near IR region is typically quite small, making the majority of NIR spectra to look rather uninteresting and complex due to overlapping peaks and valleys as it is showed in the **figures 1a, 1b and 3**. A NIR spectrum (**figures 1a, 1b, 3**) consists in a graph of absorption (y axis) plotted against wavelength (x axis) or equivalent scales (e.g.  $\text{cm}^{-1}$ , nm,  $\mu\text{m}$ ). On the NIR spectrum the absorption scale is marked by the basic modes of absorption. So when NIR radiation is passed through a non scattering organic medium, the intensity of absorption can be described in terms of transmittance (T), which can be represented by “ $\log 1/T$ ” or “% T”. This absorption mode is expressed by the linearity of the Lambert-Beer law (absorbance/ concentration relationship) [1]. In the case of sample, which produces diffuse reflectance (R) spectra, the linearity of the Lambert-Beer law is corrupted [1] and it can be expressed by the function “ $\log 1/R$ ”, where R is the reflection of the sample.



**Figure 4.** *Principal types of NIR absorption bands and their locations.*

**NIR advantages  
and  
disadvantages**

Today, NIR spectroscopy takes its place along side with other major analytical technologies providing real time analysis that saves time and money. Moreover, it is in many ways unique, like for instance, requiring little or no sample preparation, performing non-destructive analysis of multiple parameters in less than a minute. However, the NIR technique presents also some disadvantages, like for instance the broad and overlapping absorption bands give to the NIR spectra more complexity and then the need for sophisticated chemometric techniques to extract meaningful information from the spectra, as well as statistical relationships between the spectral data and data from reference analyses designed by calibration models, and it is not a particularly sensitive technique because NIR radiation can typically penetrate much farther into a sample than MID infrared radiation [a]. Although the NIR technique is not perfect and can not measure everything, its power is demonstrated by the widespread applications in a host of industries, such as: food and beverage industry, agriculture, chemical, pharmaceuticals, textiles, polymers, cosmetics and medicine [2-4].

**NIR  
applications****NIR instrument**

Regarding the NIR instrumentation (**figure 5**), it contains the basic UV spectrometers components. In the modern commercial instruments (**figure 14**), it is integrated numerous technologies, such as Fourier transform, Software for developing calibrations utilising some types of classical and modern multivariate methods, in the hardware it can be usually be found diode emitters used for wavelength selection, detectors with high performance (semiconductors) and different processing modes [2].

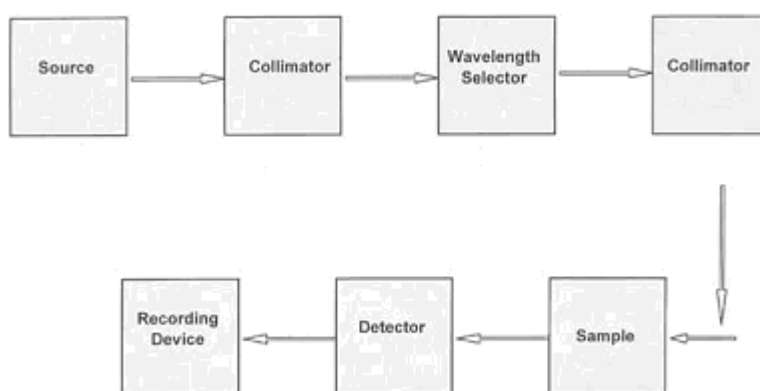
**Scope**

The scope of this literature is to approach the functionalities of a NIR instrument and the literature is organized in three main themes: “How it works”, “Applications and methods” and “NIR improvements”. In the first theme is described in detail the different parts constituents of a NIR instrument and it is also related to specific applications based on James B. Reeves tutorial [a]. In the “Applications and methods”, here is summarized the applications and two methods of NIR analysis. Finally, in the third theme is described some recent researches among the NIR applications.

## How it works

In general, the NIR spectrometer instrument is composed (**figure 5**) by a source of the radiation, a mean to select the specific wavelengths in the NIR region, a way to expose the sample to the selected radiation, a detector in order to detect the radiation emanating from the sample after expose and finally a recording device. Whereas, the type of wavelength selector, source of light and detector define the best instrument performance, the measurement capability is defined by the specific nature and configuration of optical components.

Spectrometer components



**Figure 5.** Basic scheme of a NIR spectrometer.

### NIR sources

Sources of NIR radiation for spectrometers consist in incandescent bulbs (tungsten lamps) and light emitting diodes (LEDs), but for each of these sources, there are wavelengths ranges over which they are effective.

In many cases, the incandescent bulbs are tungsten lamps. These lamps put out visible radiation and also some considerable NIR radiation (780-2500 nm). Due to emit dual radiation maybe will be necessary to use filters in order to eliminate, mainly, the visible radiation. On the other hand, the combination of filters and the light source is also for preventing unnecessary sample heating and potential heat damage, which it happens, particularly, with the incandescent lamps. However this source is cheap and it is readily available.

The light emitting diodes (LEDs) are a special type of semiconductor diode, which generate light at specific wavelengths, based on the chemical composition of the semiconducting material used. For near infrared light emission the semiconductor material used is the gallium arsenide (component used in laser diodes), which has a direct band gap with energy corresponding to near infrared. In semiconductor physics a direct band gap means that the minimum of conduction lies directly above the maximum of the valence band in momentum space [b]. However, due to both commercial production interest and material characteristics, they are not available at all wavelengths of interest, e.g. in upper NIR region there is a gap between 1700 and 2500 nm. This region is very useful and active to NIR. Despite this, their low power requirements are useful for portable spectrometers giving a very long life expectancy.

Incandescent bulbs

LEDs

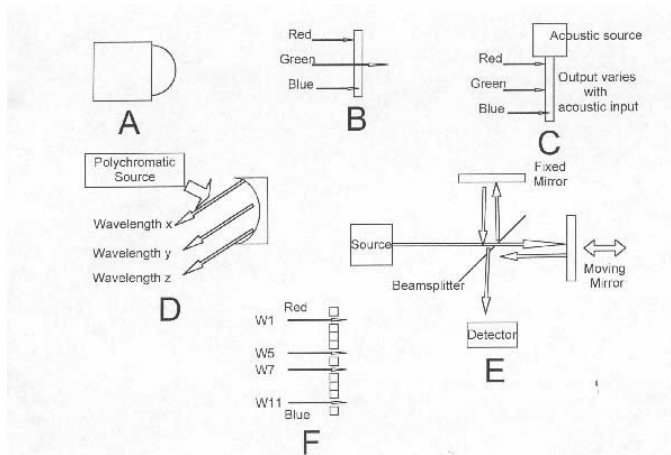
Moreover, increasing the voltage of the source as it is done with the incandescent lamps cannot increase their energy output.

For some applications where only one or two specific wavelengths are needed and at high energy levels, lasers (LEDs) have been used as a NIR source (*Faris et al.*), like for instance in monitoring changes in absorption of human tissues (e.g. cerebral blood) used specially in development of clinical studies.

### NIR wavelength selector

For the most applications it is desirable to either use only selected wavelengths or to be able to determine the response at many or all wavelengths available and therefore is used some methods of separating the source radiation into individual wavelengths (**figure 6**). The existing methods of wavelength selection are tending to determine the capability of current NIR instruments. Wavelength technologies include narrow passband (interference filter) fixed or variable filters, diffraction grating and interferometers.

The filter techniques, such as LEDs, are limited to measure limited wavelengths at a time, although tilting filters and acousto-optic tunable filter (AOTF) are used over a wide range of wavelength and also present the advantage of fast wavelength switching or sequential scanning. Similarly, the gratings are able to divide the incoming radiation into groups of wavelengths. Interferometers and Hadamard mask have the advantage of simultaneously to measure the entire wavelength range using multiplex techniques [2].



**Figure 6.** Different wavelength selectors: **A-** light diode array; **B-** filter; **C-** acousto-optical tunable filter; **D-** grating; **E-** interferometer; **F-** Hadamard mask.

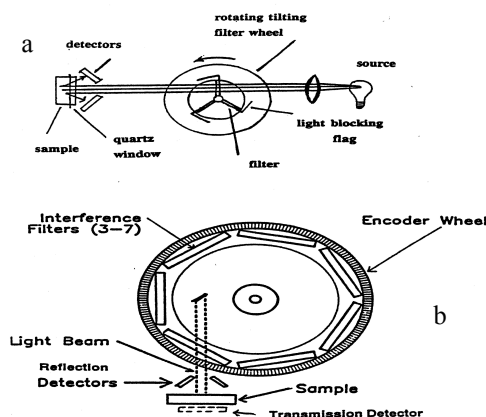
With LEDs (**figure 6A**) it is possible to select the wavelengths of interest, although it must be done using an auxiliary filter in order to obtain better resolution due to relatively broad energy emitted (near infrared, visible and near-ultraviolet light) by the diodes. LEDs combined with filters are efficient, rugged and inexpensive short wavelength sources making them ideal for portable and low cost instruments without moving parts (optic components).

LEDs  
with  
filter

Tilting filter

The first type of interference filter was designed tilting filter (**figure 7a**), which utilized wedge interference filter, i.e. a circular filter, that transmitted energy at varied wavelengths and bandpasses depending on the incident angle of the light passing through the interference filter. This filter was refined into the spinning filter systems in

which remains the same basic principle, but now the filters were mounted in an encoder wheel for greater positioning accuracy (wavelength reproducibility) and greater reliability (**figure 7b**) [2]. The use of tilting filters allows the instrument cover a wide range of wavelength, which can be useful for calibration development or for determining a wider range of constituents.



**Figure 7: Tilting filters instrument design**

AOTF

Another type of filter used for wavelength selection is the acoustic-optical tuneable filter (AOTF, **figure 6C**). The AOTF depends on the interaction of optical energy and a travelling acoustic wave in an anisotropic crystal (TeO<sub>2</sub> crystal). Here by vibrating the filter with acoustic energy at various frequencies various wavelengths are transmitted. Adapting this filter in an instrument it means that the sample can be scanned at a very high speed, which can be advantageous in a process where the product is flowing in a pipeline or on a conveyor belt. The only problem of this kind of filter is the thermal stability but new research and materials have been constantly followed in way to improve the problem.

In instruments where a wide range of wavelengths are of interest, such as for research and in developing calibrations, the primary means used to select wavelengths appear to fall into two categories: gratings (**figure 6D**) and interferometers (**figure 6E**). A grating consists in a metal or glass surface with many fine parallel lines engraved in the surface. The lines by diffraction divide the incoming radiation into various wavelengths prior to striking the sample and the detectors. Gratings come in variety of designs, which influence the wavelength range and the resolution of the instrument. One of the types of designs is the concave holographic grating, which is the basis of the most NIR dispersive instruments [2]. By adjusting the recording parameters in the generation of the grating, the spectral focus can be moved to a location near the astigmatic focus where the focal plane is nearly flat. This configuration is common in NIR instruments using flat diode-array detectors and an alternative standard deviation grating is the basis of most NIR scanning monochromators [2].

Gratings

Interferometer

In an interferometer the wavelength selection is accomplished by dividing a beam of light into two beams or paths. For one of the beams a path difference is introduced and the beams are then recombined producing interference patterns from which information at difference wavelengths can be extracted. Like grating based instruments, interferometers are designed to operate at specific wavelengths depending on the material used for the beam splitter, the source and detector. The Michelson interferometer is the basis of majority of interferometers systems. It is a rapid-scan interferometer that modulates the energy at a frequency proportional to the frequency of light, producing an interferogram that is converted in a spectrum by the Fourier

transform algorithm. In some applications, such as hyperspectral imaging, the mirror position is stepped slowly while images are collected and the interferogram is reconstructed and processed after data collection is completed. The interferometer technology, in the beginning, used white light sources, but nowadays researchers often use monochromatic light sources like lasers (e.g. tunable laser), which are used to calibrate the data and correct for the non-ideal behaviour of the mirrors either fixed or moveable.

Hadamard  
mask

Like the interferometer-based instruments, the Hadamard mask (**figure 7F**) instruments select the wavelength using an encoding process to distinguish the best enhancement of signal-noise ratio (SNR) for the reconstructed signals. However in the Hadamard mask is used the Hadamard transform instead of Fourier Transform. Hadamard instruments have the advantage of simultaneous measurement of the entire wavelength range, which is achieved by spatial light modulators (masks). This type of instrument it is not commercially available but it is well used in the NIR researches, more specifically in imaging studies [c].

### NIR Sample device

There is a different sample presentation technique available for any type of liquid, slurry, powdered or solid sample, and hence to this variety it possible that NIR analysis is applied widely. However, it is in the far infrared region that is possible having better absorption for crystal samples in inorganic compounds and in the skeletal bending mode of organic substances.

NIR  
transmission  
mode

When a sample is exposed to a source of radiation, the radiation can be absorbed, transmitted in part or whole through the sample, or reflected off the surface of the sample or sample holder. In the classical spectroscopy experiment, reflection is eliminated so that the proportion of radiation attenuated by the sample may be measured as transmittance. Lambert-Beer's law then defines proportionality between transmittance and the product concentration of the absorbing species and path length. For example, an experience with a clear transparent liquid sample such as beer, hot starch melts, wine or vegetable oil, the path length may be fixed by means of a static or flow-through sample cuvette or a pair of fiber-optic probes.

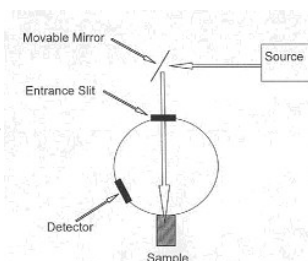
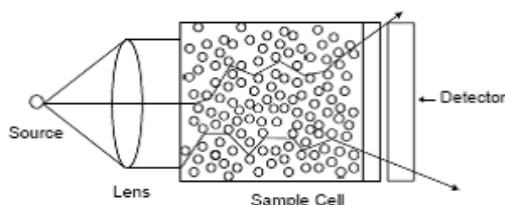
In the case of samples which produce scatter in transmission (**figure 8**) or diffuse reflectance spectra, a number of factors corrupt the linearity of the Lambert-Beer's law. Sample scattering results in an alteration of the proportion of absorbed and reflected radiation so that the pathlength becomes another unknown in the Lambert-Beer's law [2]. Particle size, particle shape, crystalline form, bulk density and the nature of the pore space (filled with air, water or oil) are all variables, which dictates the effective pathlength of the radiation. For example, in the figure 8 is illustrated an experience with a sample of milk where the fat globules scatter light and in the manner shown and invalidate Beer's law.

Diffuse transmittance (**figure 8**) and transmittance measurements are usually carried out in the 800–1100nm region of the spectrum where the weak absorptions enable useful data to be obtained using thicknesses of 1–2 cm of samples such as meat, cheese or whole grain and in liquid samples, such as milk. The near infrared transmittance (NIT) instruments, generally, are constituted with the detector directly opposite to the light source (i.e., at 180°) and with the sample in the centre. Alternately, the detector can be placed closer to the light source (at angles less than 180°), like it is present in the integrating sphere (**figure 9**). In this sampling geometry, the greatest advantage is that a detector placed at an exit port of the sphere that is not susceptible to energy fluctuations

Integrating  
sphere



from the incident beam caused by deflection (scattering), refraction, or diffraction of light when working in transmittance mode. Due to the purpose of the sphere is to scatter the radiation reflected from the sample, so it makes this sample presentation more useful when performing in diffuse reflectance (reflection mode) than in diffuse transmittance.



**Figure 8.** Diffuse transmittance spectroscopy **Figure 9.** Scheme of an integrating sphere.

In the 1100–2500nm region, the amount of scattering makes the path length so great that transmittance through 1 cm of most samples, such as wheat meal, flour or milk powder, is negligible. This situation is called diffuse reflectance because most of the incident radiation is reflected. A typical NIR diffuse reflectance experiment is shown in figure 10, in which a powdered sample is packed into a 1 cm-deep sample cell and covered with a quartz window. The sample cell is then placed into the instrument where it is illuminated with NIR radiation and the reflected radiation measured by a set of detectors set at 45°. This sampling geometry provides the illumination of the sample at 0° angle and the collection detectors, in number of two or four detectors, are at 45° for the reflected light. This configuration has been adapted for on-line measurement using a powder sampler for flour or milk powders. However, this sample geometry gives better measurements in transmittance mode than the integrating sphere [2].

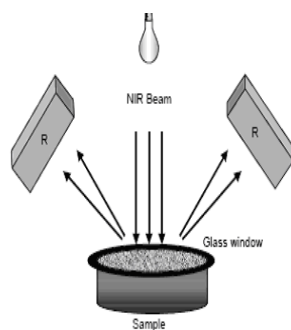
In sum, reflectance and transmittance modes have simple differences, but they are quite different when making measurements. Like for instance, both modes can measure ground samples, but, while the transmittance mode is applied to ground samples with large particles (e.g. whole grain), the reflectance mode is more suitable for ground samples with fine particles (e.g. wheat meal). This is possible because a ground sample with fine particles has a greater energy variation by scattering, refraction or diffraction of light than transmission of light through the sample, when a low frequency radiation (1100-2500 nm) penetrates the front surface. Whereas the ground samples with large particles need high frequency radiation (800-1100 nm) in order to get great depth penetration into the sample [3].

Moreover, in some samples more than one mode can occur, and in order to compensate this gap, both modes can be found in the modern instruments. Thus, we have a hybrid mode of transmittance and reflectance called transreflectance, where the radiation is transmitted through the sample reflected from a ceramic tile beneath the sample and then transmitted back through the sample before finally reaching the detector. This sample presentation is normally accomplished using a fiber-optic probe, in which one set of fiber-optic bundles carries the incident radiation and another carries the reflected radiation. This type of arrangement is particularly useful for large samples such as intact fruit.

NIR  
reflection  
mode

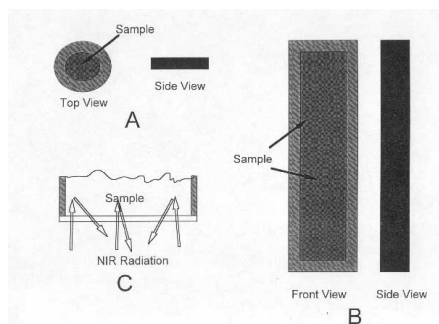
0-45  
sample  
geometry

Transflectanc



**Figure 10.** *Diffuse reflectance analysis of a powdered sample*

The method used to present a sample can also be very important in NIR spectrometer. With respect at this matter, the sample holders are also related in ways other than their sample capacity, spectrometer-processing mode or to the design of the spectrometer. For example, some instruments use round sample cups (**figure 11A**) for dry solid or grained samples. In order to scan the maximum amount of sample and to eliminate as much as possible the effects of irregularities or lack of sample homogeneity, these cups are often rotated. This requires that the instrument design's should be made to use the same sample cup and with an ample room for the rotation mechanism.



**Figure 11:** *Sample holders. A- round cup; B- transport cell; C- sample ring placed on top of horizontal window for scanning from below.*

Lack of sample homogeneity is always a problem when a sub-sample is being used to represent a larger sample. The larger the sub-sample size and the more homogeneous the sample from which it is taken, the greater the probability that it will accurately represent the original sample. In the figure 11B, one sample cell design for analysing bulk samples is shown. In this case, the cell is attached to a mechanism, which moves the cell vertically, while the scanning beam remains stationary. In a similar manner, samples on a conveyor belt or in a pipeline can be scanned using a stationary scanning beam, but without the need for any sample cell. Another way to scan a large sample is to use a wide angle-scanning beam and simply scan a very large sample area (**figure 11C**). Such design offers greater simplicity and avoids the need to fill and empty sample cells.

Cells constructed from quartz or glass, are often used in performing transmission mode with liquids, have varied sizes and designs, depending mainly on the design of the instrument.

#### NIR detector [d]

The detector is probably the part of an instrument that most users know and care the least about it. However, it is the most important part of any instrument, because lay on it the credibility of the analysis results. Thus, a poor quality detector (noisy, low

sensitivity, etc.) could result in poor data, regardless of the quality of the other system components.

In general, the choice of detectors is usually dictated by the wavelength range and other design parameters of the spectrometer, such as sample presentation. So the instrument manufacturers try to use the most appropriate detector available, and often do not offer the user a choice, except for top of the line research grade or custom built instruments, otherwise the user generally has little role in the decision of which detector to purchase. In addition to the above characteristics, the choice of detector it is also based on the following characteristics, which are of major importance owing to the detector performance: photo sensitivity (responsivity), noise equivalent power (NEP) and detectivity (D). The photosensitivity (responsivity) measures the photocurrent or voltage output per unit of incident radiant power at a particular wavelength and when the noise is not a consideration. The noise equivalent power (NEP) measures the quantity of light when the signal-to-noise ratio (S/N) is 1. Detectivity is a parameter used to compare the performance of different detector types and it is determined by the signal-to-noise ratio at a particular electrical frequency and in a 1Hz bandwidth when 1 watt of radiant power is incident on a 1cm square active area detector, which means the higher the signal of detectivity the better the detector.

The most common detectors used in NIR spectroscopy as well as in overall IR spectroscopy are: lead sulphide detectors (PbS) and lead selenide detectors (PbSe), silicon detectors, indium antimonide detectors InGaAs, InSb, InAs and the least common charged coupled device (CCD) (**table 1**). In general, these detectors offer high detection performance and fast response speed, although their photo sensitivity (responsivity) is dependent on wavelength, so due to this, they are called photon detectors. Normally, these types of detectors need to be cooled for accurate measurement, except when used in the NIR region.

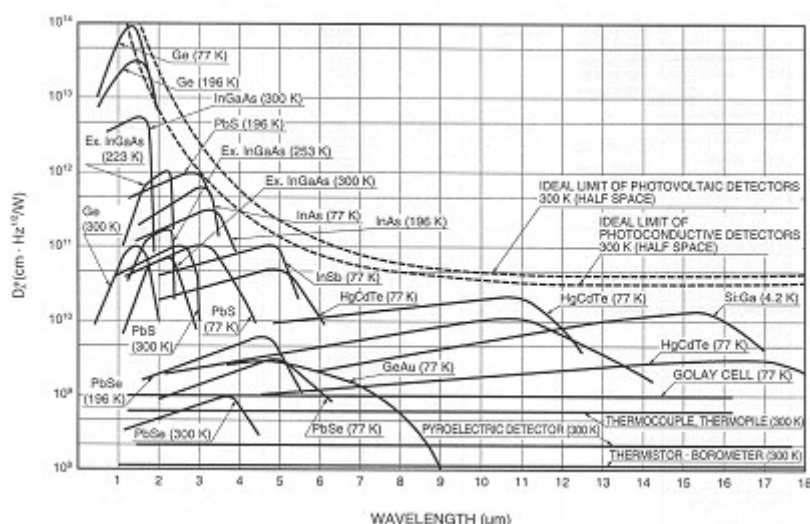
NIR  
detectors

The PbS and PbSe are lead salts semiconductors detectors used for the NIR region between 1100 and 5000. Compared with other detectors, such as InGaAs pin detectors, InAs and InSb, in the same wavelength region, the PbS and PbSe have superior features, such as higher detection capability, faster response speed, and unlike other semiconductors, the temperature characteristics of these detectors band gaps [b] have a negative coefficient. Due to the temperature sensitivity, the spectral response characteristics shift to the long wavelength region when cooled (**figure 12**).

The silicon detector also known as "PIN" photodiode [e] has the speed, sensitivity and low cost. This type of detector is optimized for the visible (VIS) and near infrared (NIR) spectral regions with typical response maximum between 859 and 950nm. The response can also be enhanced for operation at 1100nm or even in the long wavelength (**figure 12**) when it is combined with gallium (Ga).

Similarly to the silicon detectors, the indium antimonide detectors InGaAs, InAs and InSb are also denominated PIN photodiodes detectors. The InGaAs detectors have a small energy gap, and due to this they have sensitivity in the long wavelength range. The energy gap of InGaAs detectors varies, and depends on the composition of In and Ga so it is possible to manufacture these detectors with various spectral responses. The figure 12 illustrates the various spectral responses, the standard detector has a wavelength cut-off at 1.7  $\mu\text{m}$ , and varying the temperature it has another wavelength cut-offs at 1.9  $\mu\text{m}$ , 2.1  $\mu\text{m}$ , 2.6  $\mu\text{m}$ .

The InAs and InSb detectors have spectral response ranges (**figure 12**) correspond to those of the PbS and PbSe detectors, although they are used in different applications, e.g. laser detectors.



**Figure 12.** Spectral response characteristics of various infrared detectors

The charged coupled device (CCD) was primarily used in UV-VIS spectroscopy, but because the silicon used in these devices cannot provide photosensitivity beyond 1.1  $\mu\text{m}$  a different material is required for work in the NIR. A CCD is a solid-state device in which electric charge is generated and accumulated when impacted by light. This device can be used in linear arrays, as well in diode arrays, to detect the light coming from a stationary grating. Also like diode array detectors, there are limitations to their use due to their present availability for only the visible and some NIR regions. The table 1 resume the detectors used in NIR instruments and some their specifications.

Detector	Wavelength range (nm)	Region	*Responsivity/**detectivity	Remark
PbS	1100-2500 400-2600 1100-4500	NIR UV-NIR NIR-MIR	Intermediate/intermediate	PbS 'sandwiched' with silicon photodiodes, are often used for VIS-NIR
PbSe	1100-5000	NIR-MIR	Fast/ high	The detector must be cooled with liquid nitrogen
InGaAs	700-1700	NIR NIR Raman	Fast/very high	Linear arrays high sensitivity, dynamic range, signal-to-noise performance and stability FT-NIR Diode arrays spectrometers
InSb/InAs	1000-5500	NIR MIR IR	Fast/ very high	High quality detector Detector photodiodes
CCD	800-2200	NIR	Fast/high	High performance detector Applied in cameras Diode arrays spectrometers

**Table1.** NIR detectors. \*Responsivity a measure of detector performance, which measures the detector photocurrent per unit incident radiant power at particular wavelength. \*\* Detectivity is the signal-to-noise ratio at a particular electrical frequency and in a 1Hz bandwidth when 1 Watt of radiant power is incident on a 1cm<sup>2</sup> active area detector. The higher detectivity the better the detector.

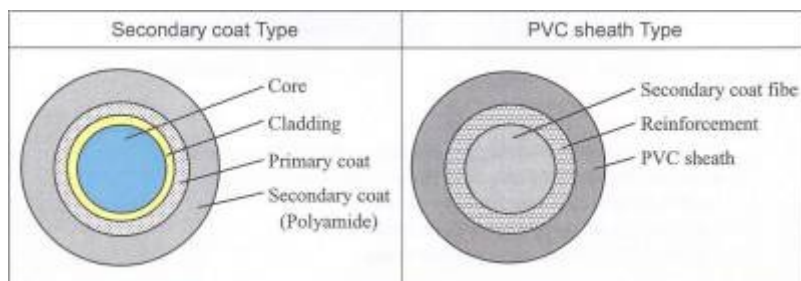
## NIR optical accessories

In this category of accessories reside the optical components, which are needed to focus, collimate, or redirect the NIR light. The focusing and collimating optics are either mirrors or lens. The mirrors present parabolic, ellipsoidal or even aspheric forms and they are often front surface, either aluminium or gold are used. On the other hand, lens may also be able to be used as optical elements such as CaF<sub>2</sub>, quartz or borosilicate glass.

The redirection is typically accomplished using flat front surfaced mirrors. Aluminium is typically used because of its relatively low cost. Gold can also be used since it has higher reflectance in the NIR, but drops off, as it gets closer to the visible.

Other optical components such as wheels and flippers that contain calibration or qualification standards have also been placed in FTNIR instruments in order to reduce the energy for highly transmitting samples.

Modern NIR instruments come with fibre optics [f]. The fibre optics (**figure 13**) has a central transparent core surrounded by a cladding with a lower refractive index and an external buffer. Their function is to guide the input optical energy down the central core by total internal reflection at the core-cladding interface. The maximum acceptance angle of the fibre optic depends on the index of refraction of the core and cladding materials. This sample interface optic is useful for transmission, diffuse reflection and transmittance modes instruments. For example, in case of in-line transmission measurements across a pipe, sometimes, only a single point entry is desirable, the fibre optics probes can provide a double pass through the sample using a reflector to redirect the energy back towards the incident direction.



**Figure 13.** *Cross sectional view of large core fibre.*

## NIR data storage

Once the signal is produced, the results need to be stored or at least output in an easy form to be able to use. A wide range of options are available for doing this, and their form is largely determined by the function of the instrumentation in question. In general, output can be divided into two forms either a raw spectrum of the sample is produced, which the user applies various programs to build a calibration, or it is obtained a value for a measure of interest, e.g., octane value for gasoline. The first case is applied to general purpose spectrometers and the second to meters designed to determine specific analyte, where in this case all the mathematics involved in converting spectral data to a value, such as the octane value for gasoline, is built into the meter itself, because someone has previously determined the wavelengths to use and how they are related to the octane number or other parameter of interest. In the case of the general purpose spectrometer, it is up to the user to find the relationship between the spectra and parameter of interest.

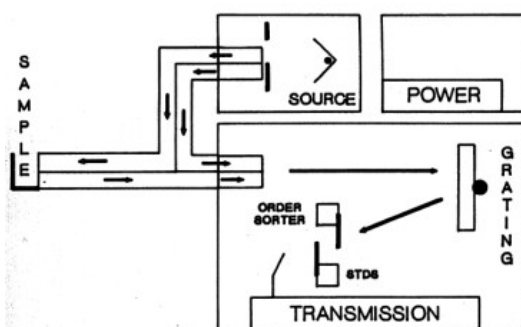
Finally, while in the past, many instruments came with proprietary computer hardware and software, today, many if not most of the general purpose instrumentation uses the personal computer, with data conversion being available to allow the use of other programs for data manipulation, storage, plotting, etc. Thus, the software sold with the spectrometer may only provide for data collection or for collection and manipulation, i.e. spectral subtraction, derivatization, conversion to other data formats, calibration development, etc.

### NIR types of instruments

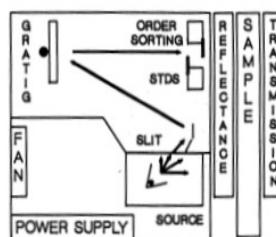
The NIR instruments can be characterized in several ways, i.e. they can be distinguished by their hardware characteristics [1] such as, wavelength selectors, type of detectors, and sampling mode. Thus, there are many types of designation of NIR infrared, e.g. fibre optic probe and moving grating NIR instrument (FOG) and non-contact reflectance diode array NIR instrument (NCDA).

However, until the 80's there were only two basic types of NIR instruments (monochromators), those employing discrete wavelength filters and wavelength scanning instruments using holographic gratings. Both types employ high-intensity white light sources (e.g. tungsten-halogen source lamp) and one or two types of detector depending upon the wavelength range being used. For NIR region (1100-2500 nm) a lead sulphide detector provides appropriate sensitivity [1, 2]. The modern design monochromators are shown in figure 14 A and B. This type of instrument design is not complex, but the good control of the grating mechanical motion over the instrument life is critical to the reproducible wavelength performance ensuring thereby the stability of calibrations.

A



B



**Figure 14:** Designs of NIR reflectance /transmittance. *A-post-dispersive, fast-scanning, grating spectrometer; B- pre-dispersive, fast-scanning, grating spectrometer*

These instrument designs differ in that figure 14B shows a typical pre-dispersive monochromators based instrument where the light is dispersed prior to striking the sample. In figure 14A, the port dispersive design allows the transmission of more energy into either a single fibre optic strand or a fibre optic bundle [1]. The white light is piped through the fibre optic where it strikes the sample, and returns to the dispersive element (grating). After striking the grating, the light is separated into the various wavelengths prior to striking the detectors [2]. This type of instrument design is not complex, but very good control of the grating mechanical motion over the instrument

life is critical to the reproducible wavelength performance ensuring thereby the stability of calibrations.

The future instrument designs include more modern advances such as, diode arrays, which can have fibre optic with high sensitive silicon CCD array detectors or can use concave holographic gratings with silicon or InGaAs photodiode array detectors, and interferometers with no moving parts or tuneable laser sources. Further, it will be describe the Fourier transform NIR instrument as an example that how an NIR instrument works.

FTNIR

An FTNIR spectrometer utilizes an interferometer to modulate the NIR signal and a computer to obtain the spectra of materials and it is what distinguishes a FTNIR from most other spectrometers. A simplified system of FTNIR is showed by the figure 15.

NIR  
light  
source

The NIR energy is supplied by halogen bulbs, with 5-50 watts, which extend their lifetime. The energy of the source is collimate and directed into an interferometer where is modulated. Each wavelength has a distinct modulation frequency in the range of kHz, which can then be transformed by the computer into its actual electromagnetic frequency.

FTNIR spectrometer uses a beam splitter in order to reflect the NIR energy onto a fixed mirror and transmits the remaining to the moving mirror. The beam splitter is layered coatings placed in a substrate, such as: quartz, CaF<sub>2</sub>, and KBr. The resulting interference between the beams (reflected and transmitted) depends on the optical path difference or retardation. When the fixing and moving mirrors are equidistant from the beam splitter, the retardation is zero. So at this point all the source of energy reaches the detector and the variation in intensity as the moving mirror is translated contains the spectral information retrieved by the Fourier transform. Before achieving the detector the path length of source energy is controlled by a laser (HeNe laser), which control the moving mirror movement, ensure of the alignment of interferometer and provide wavelength selection. The NIR signal is delivered to the sample, which selectively absorbs and reflects or transmits the remainder to the detector. Since the FTNIR are considered to scan rapidly, detectors that can respond quickly are also required, such as: InSb, InGaAs. Other optical components are needed to focus, collimate, or redirect the NIR energy. In order to redirect the NIR energy is typically used aluminium, gold and for focusing or collimate optics are either mirrors or lens. In mirrors are used as a front surface gold and aluminium and in lens are the CaF<sub>2</sub>, quartz and borosilicate glass typically used as optical elements. And also may exist in a FTNIR spectrometer other optical components that will perform as attenuators for high transmitting samples. Wheels or flippers that contain calibration or quantification standards have also placed inside the FTNIR spectrometer.

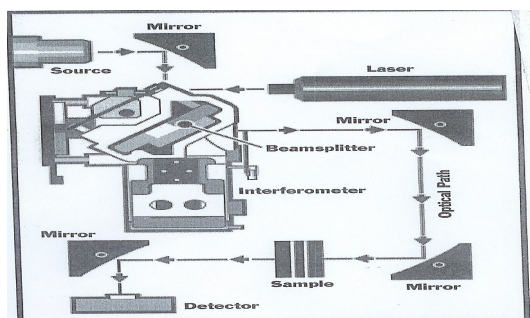
Optical  
configuration

Detectors

Optical  
components

Due to his ability to reproduce accurate and reproducible spectra for identification, the FTNIR is particularly used in Pharmaceutical, petrochemical and chemical applications assuring the quality of the applications.

Applications



**Figure 15.** Scheme of FT-NIR instrument [2].



## NIR commercial instruments

Table 2 highlights some instruments companies, types of instruments, wavelength and applications coverage of models manufactured. The type of designation of the instrument is considered by the manufacturer to be a dedicated NIR instrument or whether the instrument is optimized for a different wavelength region. However, only the instruments specifically optimized in the NIR region are useful for serious quantitative work, such as the NIR units design for the grain or flour industry.

Manufacturer	Instrument Type	Wavelength (nm)	Application	Comments
<b>Perten Instruments AB</b> P.O.Box 5101 SE 14105 Huddinge H.Q. Stockholm Sweden Tel: +46 8 880 990 Fax: +46 8 888 210 E-mail: info@perten.com www.perten.com	Diode array NIR	950-1650	Food Grains, meals, pasta  Measure moisture, protein, oil, starch, fibre	immediate results(6 sec), high capacity gold coated ruled stationary grating Semiconductors as detectors quality analysis off-line
<b>Perkin Elmer</b> 761 Main Ave. Norwalk CT 06859-0012 USA Fax: +1 203 761 2882 Email: info@perkinelmer.com www.perkinelmer.com	FT-NIR IR-NIR	700-2500 680-4800	Pharmaceutical tablet, powder	high sensitivity sampling speed quantitative and qualitative analysis off-line
<b>LT industries</b> 811 Russell Ave Gaithersburg MD 20879 USA Tel: +1 301 990 4050 Fax: +1 301 990 7525 E-mail: info@ltindustries.com www.ltindustries.com	NIR FT-NIR	700-2500	Pharmaceutical petroleum chemical textiles food beverage wood	fibre optics high capacity in-line at-line on-line quality control

**Table 2:** Commercially available NIR instrumentation. Abbreviations: NIR -near infrared; FT-NIR – Fourier transform Near infrared transmittance; IR-NIR – Infrared/ Near infrared; FT-NIR – Fourier Transform Near infrared.



The criteria for instrument selectivity should be that the photometric (energy measurement) and the spectral (wavelength selection) performance be adequate for the application of interest. Better performance than that required for the applications may result in a more costly than necessary instrument. Other important criteria may include: reproducibility, speed, ruggedness, functionality, cost, photometric specifications, instrument noise, stability, photometric linearity and stray light, dynamic range, spectral performance [3].

The statement in this topic was based on the information found in the diverse sources, such as, the reference [2, 3, a] and website references [g, h, i, j].

## NIR Applications and methods

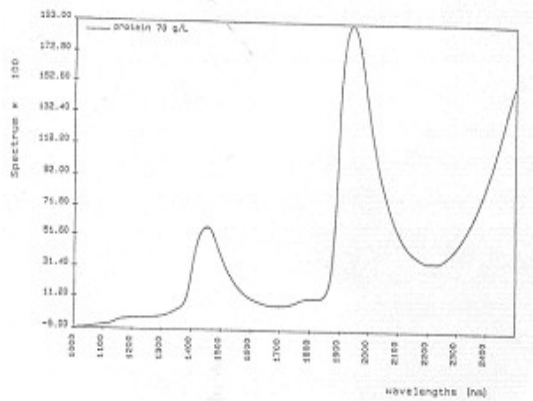
The applications of NIR technology [4] have become, over the course of the last decade, a widely used analytical method in many areas. Typical applications are in quality control analysis for food, beverage, agriculture, pharmacy and petrol-chemistry industries and in performing medical diagnostics (e.g. blood sugar).

In the food and beverage industry measurements of protein, moisture, fat, fibre, caffeine content, or of alcohol concentration use NIR technology as routine analyse, performing them in off-line and on-line processes (**table 2**). Also, in the agriculture NIR off- and on-line instruments have application in analysis of quality control, such as measurements of protein content and moisture (grains), hardness and baking quality (flour), caffeine content (coffee, green tea), sugars in fruit, fat content in fish.

Since 30's, the petrochemicals have been developed a range of NIR calibrations to monitor chemical and physical properties, such as octane number, benzene, methanol content, methyl group analysis, density, sulphur for petroleum and its refining products. In other chemical industries the NIR technology has been used to monitor the water, detergent solids and glycerol in shampoo, naphtha composition and ethylene polymerization, and to analyse moisture and lubricant levels on polymer films. In the cotton industry NIR technology is employed in cotton blending, mercerization and fibre maturity measurements using off-line instruments, which provides a rapid process. For quality control of the dyeing procedure for carpet yarn and measurement of yarn diameter, on-line NIR analysis has been developed [4].

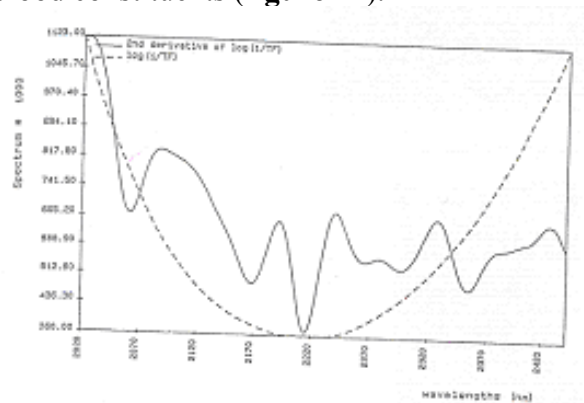
In pharmaceuticals the NIR methods have been accepted by the Food and Drug Administration (FDA) and now they are used in measurement of salicylic acid content in the aspirin, in checking incoming raw materials for drug production and sample identification can be achieved by at-line NIR fibre optic systems.

Supremely, the significant research in NIR technology was in medical field with the study of rapid routinely analysis of blood serum and the whole blood substances [5], which describe that Nir blood analyses were comparable with the normal routine laboratory techniques, due to the capacity of many of biological constituents has absorption peaks in NIR region (700-2500nm). Moreover, this region has the advantage over other types of spectroscopic measurements because the body fluids and soft tissues are relatively transparent at these wavelengths. The experiment was carried with blood and serum samples, from healthy patients and hospitalized patients. While the blood sample was drawn into sodium heparin containing collection tubes, mixed and measure in NIR spectrometer at ambient temperature, the serum was obtained by centrifugation of the blood during 60 minutes at room temperature and before measure the serum was storage at -20 degrees Celsius. The instrument was a diffuse transreflectance spectrometer (1000-2500nm) with four lead sulphide detectors, transreflectance holder sample (cuvette) and the illumination was carried by a 20mm diameter beam perpendicularly to the quartz window. The samples were measured three times and by having three spectra from a single specimen it was able to reduce the error by averaging the measurements and also by some pre-treatment drying the sample on a glass fibre filter it was possible to reduce the water influence in the spectra. The result average spectrum shows a typical log (1/R) curve in the 1000-2500 nm of a blood serum (**figure 16**) and it is observed that the amplitudes of the two strong absorption bands of water at approximately 1450nm and 1930nm exceed many times those of other constituents, thus these bands exert a masking effect on the compounds of interest (protein and lipids). Therefore, for qualitative detection of constituents only those regions between or flanking the bands of water can be used and along with the mathematical models was



**Figure 16.** The log (1/R) spectrum of a blood serum specimen (1000-2500 nm) [5].

Therefore, for qualitative detection of constituents only those regions between or flanking the bands of water can be used and along with the mathematical models was possible to conclude that was possible to distinguish the absorptions curves of different blood constituents (**figure 17**).



**Figure 17.** The log (1/R) spectrum( broken line) and its second derivative (full line) of blood serum sample in the wavelength region 2020-2500 nm for the protein.

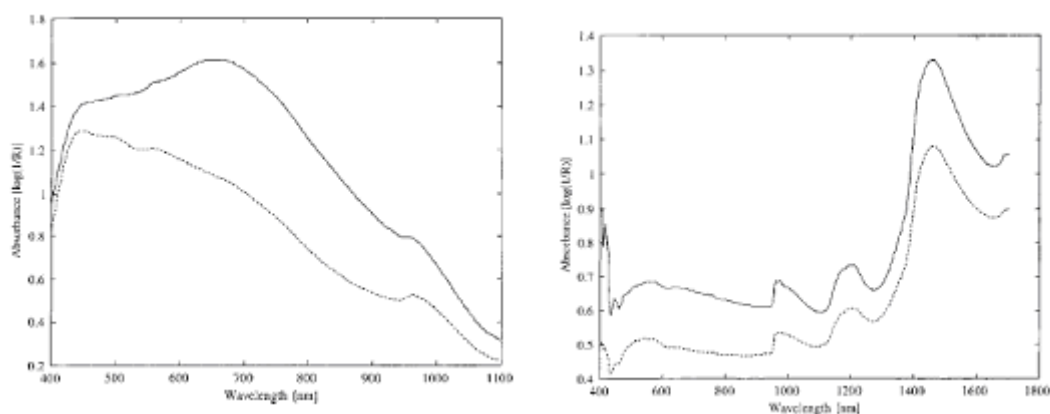
Another example of research in NIR methods is applied to food/agriculture industry, where non-destructive near-infrared (NIR) measurements were performed on 100 live salmon [6]. The experience is carried by two different NIR instruments: a grating monochromator instrument equipped with a fibre optic interactance probe, and a diode array instrument measuring diffuse reflectance in a non-contact mode with goal of determining the crude fat content using partial least squares (PLS) regression and full cross-validation was used to evaluate the performance of the calibration models, expressed as the root mean square error of prediction (RMSEP).

For the fibre optic instrument (FOG) the wavelength range from 800 to 1098 nm and for the diode array instrument (NCDA) using the wavelength range from 900 to 1700nm. The measurement times were 21 and 3s respectively. The performance results of each instruments was performed by calibrations methods and with it was possible to predict the fat content of live salmon using a post-rigor calibration model (**table 3**) from the article).

Instrument	Status	Number of PCs	Correlation coefficient	RMSEP ( $\text{g kg}^{-1}$ )
FOG	Live	9	0.90	14.1
NCDA	Live	7	0.90	13.9
FOG	Post-rigor	7	0.91	12.9
NCDA	Post-rigor	6	0.88	15.0
FOG	Live+post-rigor	7	0.91	12.9
NCDA	Live+post-rigor	10	0.90	14.0

**Table 3.** Predictive performance of FOG (800-1098 nm) and NCDA (900-1700 nm) instruments.[6]

The figure 16 shows the average absorbance spectra taken with the FOG instrument for the live salmon and for the same salmon post-rigor (left). The same is also seen for the corresponding spectra taken with the NCDA instrument (right). The NIR analyses were repeated three times on the NCDA instrument. The variation in the predicted values was  $\pm 1 \text{ g kg}^{-1}$  fat [6].



**Figure 18.** (left) average spectra of live (full curve) and post-rigor(broken curve) salmon measured by the fiber optic interactance probe and moving grating NIR instrument (FOG). (right) average spectra of live (full curve) and post-rigor (broken curve) salmon measurement by the non contact reflectance diode array NIR instrument.[6]

In conclusion of both methods above described, it can be said that it is difficult to assign specific features to specific chemical components. Thus, multivariate (multiple wavelength) calibration techniques (e.g., principal components analysis or partial least squares) are often used in order to extract the desired chemical information. Moreover, careful development of a set of calibration samples and application of multivariate calibration techniques is essential for near infrared analytical methods, making possible to say that NIR is an accurate method.

## NIR New improvements [3]

New NIR techniques development has been done in several distinct application areas of NIR spectroscopy. However, it is the pharmaceutical industry the most important and expanding fields for NIR [3], where the NIR technology is used to identify and monitor incoming materials, analyse for active ingredients, measure dissolution properties and mechanical performance of tablets and also in optimising a (pre)processing method (e.g. principal component regression (PCR) and partial squares regression (PLS)), such as the new indicator signal-to-error (SE) [7], which is considered to be able to correct the problem of spectral variations caused by varying particle size and varying compression (e.g. powders) recorded in reflectance mode. Though, considerable research is going on the medical field, particularly in non-invasive testing procedures and monitoring of patients during surgery. Investigations have also continuing on non-invasive blood tests, such as glucose, which has been the “philosopher’s stone” for NIR for many years, but is not yet within reach.

Recently, in the agriculture, the major development of NIR technology is done in the quality assessment of intact fruit, whereby on-line process sorting of fruit is possible to determinate the soluble solids (mainly sugars), starch, acidity, detection of internal defects and sensory properties. Nevertheless, soil analysis by NIR, particularly for carbon, nitrogen and anions is becoming more common, and NIR soil mapping have also been attempted. Interest is also growing in in-field pasture monitoring, with a potential role for portable NIR instruments. Grass and crop on-site analysis for dry matter and nutrients, particularly in breeding trials, is a major new field of NIR research, with NIR sensors mounted on forage or grain harvesters. Prediction of nitrogen fertiliser requirements of crops, particularly rice and wheat, via NIR leaf tissues analysis, presents an important advance in cost-efficient application of fertiliser and has environmental benefits. Quality assessment and process management of organic fertilisers and compost by NIR is also gaining interest. Environmental applications in general, involving the sampling and testing of manure, slurries, sewage, lake sediments and other bio-soils for nitrogen, other nutrients and even metals are an important new field for NIR.

Because NIR applications are so varied, the instruments technology has growth in parallel with them. In order to express NIR advantages, numerous technologies have been integrated in NIR modern instruments providing all tributes to the strength and viability of this spectroscopy technique. Like for instance, the on-line near infrared (NIR) analysers are used widely for quantitative composition measurements in real-time process control systems. The accuracy and repeatability of the measurements are amongst the detector characteristics the most important factors when evaluating the total performance of these analysers, but the lower detection limit is often limited by noise in the measurement signal. The reducing noise in an optical analyser can be done by digital filtering technique [8]. In the measurement capability (wavelength selectors) of the Nir instrument, the hyperspectral imaging technique provides additional new measurement possibilities, such as simultaneous individualize spectral measurements of many different areas of complex heterogeneous samples [k].

To conclude, I would like to comment that the analytical technique of NIR spectroscopy has a bright future, owing to its widespread applications and the development of its instrumentation technology.

## Summary

### General uses

- Quality control analysis
- Quantitative determination of compounds in mixtures
- Identification of samples

### Common applications

- Determination of protein, moisture, hardness and baking quality in grain and flour.
- Measurement of salicylic acid content in the aspirin checking incoming raw materials for drug production and sample identification.
- Checking incoming raw materials for drug production and sample identification.
- Monitor of the whole blood substances and blood serum.
- Determination of fat in salmon fish.

### Samples

- **State:** any solid, liquid samples can be analysing.
- **Amount:** the amount of sample is variable due to many different types of sample holders and cells available.
- **Preparation:** Little or no sample preparation is required.

### Analysis time

- High-speed quantitative and qualitative analysis without consumption or destruction of the sample.

### Instrumentation

- **Sources:** LEDs, tungsten lamps.
- **Detectors:** PbS, PbSe, Silicon, InGaAs, InSb, and CCD.
- **Wavelength selection:** LEDs, tilting filter, AOTF, gratings, Interferometers, Hadamard mask
- **Sample holders:** Round sample cups, Cells, integrating sphere, 0-45 sample presentation
- **Radiation modes:** Transmittance, Diffuse transmittance. Reflectance, Diffuse reflectance, Transflectance.
- **Optical components:** fibre optics, mirrors, lens.

### Limitations

- **General:** NIR spectroscopy it is not a stand-alone technology; the use of separate calibrations for each constituent or parameter and a portion of unknown samples must periodically be analyzed by the reference method to ensure that calibrations remain reliable and it may be necessary repeat several times. Despite the intuitive disadvantage of broad and overlapping absorption bands sophisticated chemometric techniques can extract meaningful information from the complex NIR spectrum and use also statistical relationships between the spectral data and data from reference analyses designed by calibration models.
- **Sensitivity and detection limits:** high sensitivity and detectivity depending on the detector
- **Complementary techniques:**

- UV visible spectrometer and coupled with fibre optic devices for remote analysis.
- IR and MIR spectrometer in identification analysis using Fourier transform.
- HPLC coupled with FT-IR operating in MIR and NIR regions, for quality control analysis.

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