Near-infrared spectroscopy: Comparison of techniques

M. Schilling

Near-infrared spectroscopy (NIRS) is a widely used analysis technique for identification of raw materials and quantification of substances in research and industrial applications. The aim of this white paper is to clarify differences and similarities between dispersive and Fourier transform analyzers.

Metrohm White paper

Introduction

The first commercial dispersive spectrometers emerged in the early 1940s for UV-Vis applications. This technology is based on the dispersion of light in dependence of its wavelengths. The dispersion of light is most commonly illustrated using a prism, although today, the prism is generally replaced by monochromator gratings. Dispersive spectroscopy is the method of choice for analysis in the UV-Vis range, but also for photoluminescence and near-infrared (NIR) applications. Commercial Fourier transform infrared (FT-IR) spectrometers first appeared in the 1960s. They were almost exclusively used in fundamental research fields because of their high cost. Technical improvements have made FT-IR spectrometers more affordable. They are mainly used in the mid-infrared (MIR) range for the identification of chemical substances and only recently became popular for applications in the near-infrared (NIR) range [2].

Since their first commercial appearance, both types of spectrometers were gradually improved. They are both state-of-the-art.

This white paper compares dispersive and Fourier transform technologies from an experimental point of view. The design and the physical principles underlying each spectrometer type will be explained and key aspects concerning NIR applications will be elucidated. Key aspects include the wavelength range, spectral resolution as well as wavelength accuracy and precision, data acquisition speed, and the signal-to-noise (S/N) ratio.

Technical overview
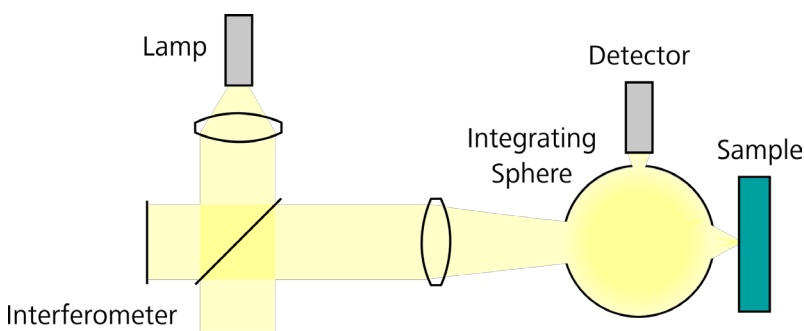
Dispersive spectrometers

Polychromatic light is emitted from a light source and diffracted on a grating. The diffraction depends on the incident angle, the width of the grooves of the monochromator grating, and the wavelength. In the reflected beam, the wavelengths composing the light are spatially distinguishable from one another. Through an exit slit, monochromatic light irradiates the sample. To enable scanning of different wavelengths, the monochromator grating is mounted on a motor, which changes its angular position. The motor is controlled by a digital encoder for a precise and repeatable variation of the angle. Thus, monochromatic light of different wavelengths sequentially passes through the exit slit to record the intensity spectrum (see Figure 1) [1].

FT technique

FT spectrometers contain an interferometer, which is composed of a beam splitter and two mirrors, one fixed while and one movable, whose distance to the beam splitter is variable (see Figure 2). Polychromatic light from the source is split into two beamlets, one reaching the fixed mirror while the other is reflected towards the moving mirror. The beamlets are combined again at the beam splitter. The resulting light intensity depends on the phase difference between the two beamlets, which is caused by the offset of the movable mirror. The detected intensity of the polychromatic light in function of the mirror offset is called interferogram. This is transformed mathematically to obtain a spectrum using the Fourier transform. The mirror offset of the moving mirror is determined by a laser [1, 2]. Using interferometry, light is not monochromatized and all wavelengths are measured simultaneously.
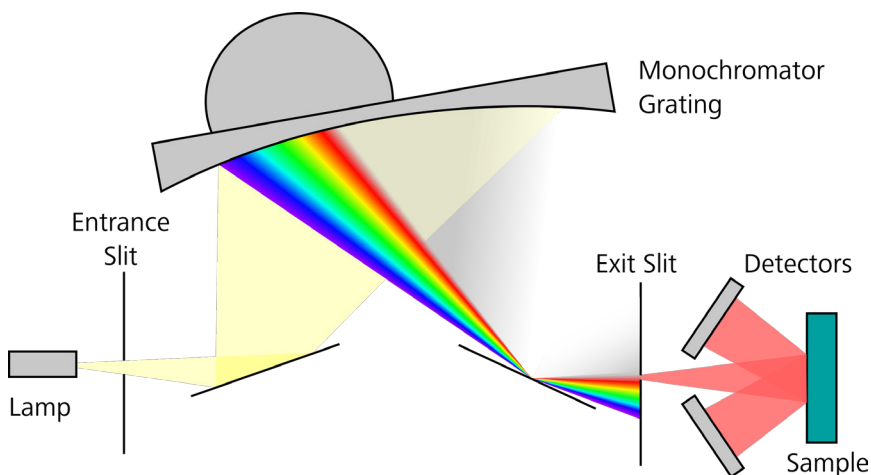
Figure 1. Illustration of the predispersive Metrohm XDS series and Metrohm DS2500 spectrometer in diffuse reflectance mode.

Figure 2. Illustration of an FT spectrometer with Michelson interferometer in reflectance mode.

Dispersive spectrometer or FT?

There are several parameters that have to be taken into account when choosing the suitable technique. The most important ones i.e., the wavelength range, the resolution, the photometric accuracy and precision, the data acquisition speed as well as the signal-to-noise (S/N) ratio, are discussed here.

Wavelength range

The wavelength range of FT-NIR systems is limited as a result of the optics. It commonly ranges from 800 nm to 2'500 nm. Dispersive spectrometers enable data acquisition down to 400 nm and even below, thus including the visible spectral range (Vis). This enables applications in which the sample parameters of interest are mainly situated in the Vis-range, such as concentration and color strength measurements as well as the quantification of chromatic complexes, amongst others.

Resolution

The spectral resolution of a dispersive system can be fixed at a constant value by fixation of several instrument parameters such as the entrance and exit slit widths, the density of the grating steps, the quality of the encoder, the size of the spectrometer, etc.

In Metrohm NIRS XDS and DS2500 spectrometers, the resolution is fixed at 8.75 nm, which is more than sufficient for most applications. This becomes clear upon closer inspection of the natural bandwidth of the signals in NIR. Interferometers, on the other hand, allow the resolution to be defined by adjusting the maximum offset of the movable mirror (also called «Connes' advantage»). Thus, more highly resolved spectra can be acquired than with dispersive systems. Typically, spectra are recorded with resolutions of 8 cm^{-1} or 16 cm^{1}; higher resolutions are rarely used. At 2'500 nm, these resolutions correspond to ~ 10 nm and ~ 25 nm, respectively [3, 4].

There are two reasons for not using higher resolutions than the ones stated above. The first is that, harmonics and combination bands of pure substances in the NIR range have natural bandwidths larger than 10 nm. Therefore, a higher spectral resolution is not required. When measuring mixtures, spectral bands can get even broader, thus a higher resolution is not necessary for reliable results. Only a few minerals, rare earth oxides, and gaseous samples have bandwidths smaller than 8 nm.

Table 1. Examples of commonly analyzed substances and their bandwidths at the respective characteristic wavelengths.

Substance	State	Characteristic wavelength [nm]	Bandwidth [nm]
Polystyrene	Film	2188	9.5
Trichlorobenzene	Liquid	2154	15
Corn Oil	Liquid	2305	30.1
Water	Liquid	1928	110.4
Lactose	Crystal	2256	9.8
Soy protein	Powder	2053	37.5
Wheat Starch	Powder	2103	162
Sucrose	Crystal	2046	22.5

The second reason to not use resolutions higher than 8 cm^{-1} with FT-NIR systems is that an increase in resolution is always accompanied by an increase in spectral noise. To obtain a higher resolution, the maximum offset of the moving mirror and the mirror velocity have to be increased to obtain spectra within the same time as dispersive spectrometers. However, this raises the noise exponentially. To lower the noise level, either more spectra have to be co-added or the acquisition time has to be increased drastically [5]. The practical advantages of the higher resolution remain largely unexplored but could be beneficial in some applications [2].

Photometric precision and wavelength accuracy

FT spectrometers are calibrated by collecting a high-resolution spectrum of water vapor, ensuring an accurate and precise recording of the wavelength response. Modern NIR monochromators, such as those used in the Metrohm NIRS XDS and DS series, are controlled by an extremely accurate digital encoder to assure maximum repeatability.

The spectrometers are calibrated using internal and external standards containing rare earth oxides. This calibration concept (standardization of bandwidths, response wavelength, and photometric response) with certified reference standards allows direct transfer of spectra and chemometric models.

Data acquisition speed

The data acquisition speed of both spectrometer types, dispersive and FT, are comparable. Both technologies can acquire two scans within a second [6]. Some of the main benefits of dispersive spectrometers are the wide wavelength coverage, the very low noise level, which results in a very high S/N ratio. According to Shaw and Mantsch (1999), «there are a wide variety of applications that require this combination of speed and accuracy.» [2]

Table 2. Comparison of the specifications of FT-NIR and predispersive spectrometers [6].

| Attribute	FT-NIR	Predispersive
Source	High intensity	High intensity
Wavelength selection	Interferometer	Grating before sample
Detector	Semiconductor	Semiconductor
Scan time	< 1 s	< 1 s
Resolution	1-64 cm^{-1}	~ 8 nm (12 cm^{-1} @ 2500 nm)
Resistance to vibration	Medium	Good
Accessories	Powder, solid, liquid	Powder, solid, liquid
Wavelength precision	~ 0.01 nm	~ 0.005 nm
Wavelength accuracy	~ 0.05–0.2 nm	~ 0.05 nm

Signal-to-noise (S/N) ratio

In NIR spectroscopy, the most important parameter in the acquisition of spectra is generally not the resolution, accuracy, or repeatability, but the signal to noise (S/N) ratio.

In UV-Vis and NIR spectroscopy, the main source of spectral noise does not derive from the very sensitive detectors (PbS or InGaAs used for NIR spectrometers are 1'000 times less noisy than the detectors used in the MIR [6]) but from the light intensity: the noise is directly proportional to the light intensity and inversely proportional to the wavelength.

In FT-NIR instrumentation, photon noise is superimposed in the interferogram and the Fourier transform cannot reassign these individual contributions to the corresponding spectral ranges. This disadvantage of distributed noise in FT-NIR can be problematic, e.g., when information of interest is in low-intensity regions at high noise [7, 8]. By contrast, dispersive systems sequentially scan all wavelengths, so that each absorbance measurement is independent and the noise is directly associated with it. With dispersive systems, it is possible to adjust the optical path for an ideal signal amplitude, regardless of areas with higher noise levels.

The new Metrohm NIRS monochromators are based on the patented XDS (off-axis digital synchronous) and DS technologies, which ensure an ideal focus of the monochromatic beam thanks to the precise setting of the angular position by the encoder.

These innovations yield an unrivaled, nearly constant noise level over the entire Vis-NIR spectral range from 400 to 2500 nm, whereas the noise level of FT systems increases dramatically towards the spectral limits because of the optics (see Figure 3). In addition, the S/N-ratio of dispersive systems is 2–60 times greater than those of FT systems[1].
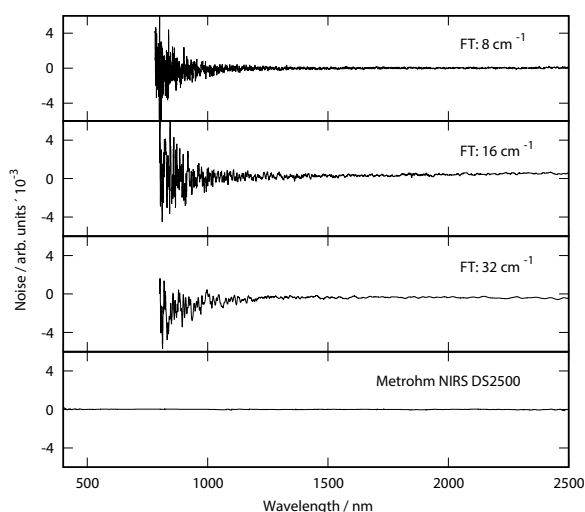
Figure 3. Noise spectra acquired with the Metrohm NIRS DS2500 and an FT-NIR instrument in reflection mode using a reference material with an absorbance between 0.25 and 0.4. On the FT system, the scanning speed was adjusted to match the same data acquisition time of the Metrohm NIRS DS2500 (~ 20 s) with FT data acquisition parameters: double-sided bi-directional interferogram; phase resolution twice as high as set spectral resolution; scanning speed: 5 kHz to 10 kHz; Blackman-Harris 3-term apodization window; Mertz phase correction.

---

[1] To obtain these results, the measuring parameters of FT systems where adapted to ensure that data acquisition times were the same as those of a NIRS DS2500 spectrometer for better comparability. An external standard was used and a band was evaluated at 975 nm. The same FT data acquisition and processing parameters were used as described in Figure 3.

For qualitative and quantitative applications, the S/N ratio is critical. To detect non-compliant products, e.g., pills that lack active ingredient, it is necessary to have a high-quality signal because the absorption coefficients are small in NIR spectroscopy. The spectral deviation caused by low constituent concentrations can be confused with noise. In this case, noncompliance would not be detected. Finally, while noise criteria are less important for identification methods based on spectral correlation, noise nevertheless impacts the number of samples required to build up a library. With dispersive systems, it is possible to build more robust spectral libraries.

Because high noise levels lead to high spectral variation, more robust qualitative and quantitative models can be developed using dispersive systems [9]. As the very near infrared range (800 to 1100 nm) is detected at a constantly low noise level, models with enhanced analytical figures of merit are possible with dispersive Vis-NIR systems [6, 10].

Other technical considerations
Currently used monochromators realize a rapid scanning of the whole spectrum (~ 0.5 s). The acquisition time is comparable to that observed with interferometry with comparable resolution.

In FT instruments, the sample is illuminated by the entire spectral range of the strong light source used at once. The resulting high beam power density can heat up the samples. This is a disadvantage when dealing with photosensitive samples, which might deteriorate under such conditions, but also when dealing with biological samples whose overheating can cause accelerated bacterial growth or denaturation of sensitive proteins. With predispersive systems, light is monochromatized before scanning the sample; therefore, the sample is exposed to a much lower beam power density, preventing damage.

Interferometry requires the use of a laser for the precise measurement of the position of the movable mirror. This laser can be considered an expensive consumable because its service life is limited. FT-NIR systems are generally considered to be less robust than monochromators and are less suitable for at-line, online, and inline process applications, where strong vibrations can occur, generating potential misalignment of the moving parts and thereby leading to distortions [6].

Because of the optical material used in FT-NIR spectrometers, almost all available spectrometers use desiccants to control the humidity of the system to avoid aging. These desiccants have to be regenerated on a regular basis, which can lead to downtime of the spectrometers. The robust optics used in the Metrohm NIRS XDS and DS2500 spectrometers do not require desiccants. Several maintenance steps can be eliminated.

The use of dispersive systems is straightforward compared to the use of FT systems, where many parameters can be modified, heavily influencing spectra. Even though the mechanics for the positioning of the moving mirror are quite elaborate and its position is determined by a reference laser, phase errors can occur, which have a large impact on the spectra. To get rid of them, several phase corrections can be applied (such as Power spectrum, Mertz correction …). However, this requires an experienced user who is acquainted with these methods.

Metrohm White paper

Conclusions

Dispersive spectrometers are commonly used in UV/Vis and Vis-NIR instruments. FT instruments were initially developed for the MIR range to optimize the measurement quality, because MIR spectroscopy users are confronted with low intensity light sources, strong absorptions, and noisy detectors. FT instrumentation has indisputable advantages in the MIR range (2'500–25'000 nm; 4'000 to 400 cm^{-1}) compared to dispersive techniques (Felgeltt's, Jacquinot's and Connes' advantages). Many manufacturers of spectrometers apply the FT technique for the NIR range as well, but the advantages do not have the same impact in low-wavelength ranges (800 to 2'500 nm; 12'500 to 4'000 cm^{-1}). The nature of NIR spectroscopy is different from MIR spectroscopy. For NIR, there are strong sources, weaker absorptions, and quieter detectors. Advantages perceived in FT-MIR are not necessarily applicable to FT-NIR. Additionally, gratings are very reproducible and amenable for information transfer between instruments.

Many scientific articles demonstrate equivalent performance of dispersive and FT systems for routine analysis [11–13]. Some studies show better predictive capabilities with monochromators, i.e., dispersive systems, and suggest this type of technology for offline use in laboratories [6, 14].

The choice of NIR instrument has to be assessed according to many technical and economical characteristics of the application: sampling mode, spectral range, resolution versus signal-to-noise ratio, robustness of the spectrometer, versatility of the instrument, control software and chemometric tools, support and supplier responsiveness, as well as cost of the instrument and its maintenance and repair [5, 6].

Summary

While dispersive spectrometers are mainly used for quantitative applications in UV-Vis (200–800 nm), spectroscopy using Fourier transform (FT) techniques is mostly applied for identification and line analysis in the mid-infrared (MIR) region (3'000–50'000 nm). For the near-infrared (NIR), the spectral range between the visible (Vis) and MIR range, both dispersive and FT technologies are used. Because of continuous technological advancements, both spectroscopic technologies are comparable in performance. The decision between dispersive and FT-NIR spectrometers cannot be made a priori, but rather depends strongly on the application.

Sources

[1] D. Bertrand et al., La spectroscopie infrarouge et ses applications analytiques, Tec&Doc, 2000.

[2] R. A. Shaw and H. H. Mantsch, «Near-IR Spectrometers», in Encyclopedia of Spectroscopy and Spectrometry, Academic Press, 1999, pp. 1451–1461.

[3] T. Meyer et al., «Suppression of mechanical noise and the selection of optimal resolution in FT-NIR spectroscopy», NIR news, 17 (8), pp. 12-14, 2006.

[4] O. Kolomiets et al., «The influence of spectral resolution on the quantitative near infrared spectroscopic determination of an active ingredient in a solid drug formulation», Journal of Near Infrared Spectroscopy, 12 (5), pp. 271–277, 2004.

[5] FOSS, NIR Spectrometer Technology Comparison, White paper from FOSS, 2013.

[6] E. Ciurczak et al., «Examination of NIR Spectrometers: Dispersive vs. Interferometric Types», Amer. Pharm. Rev., 11 (4), pp. 3-5, 2008.

[7] E. Voigtman, «The Multiplex Disadvantage and Excess Low-Frequency Noise», Applied Spectroscopy, 41 (7) pp. 1182-1184, 1987.

[8] F. Grandmont, «Développement d'un spectromètre imageur à transformée de Fourier pour l'astronomie», Doctoral Dissertation, Université Laval, 2006.

[9] J. B. I. Reeves and C. M. Zapf, «Discriminant analysis of selected food ingredients by near infrared diffuse reflectance spectroscopy», J. Near Infrared Spectroscopy, (5), pp. 209–221, 1997.

[10] D. Cozzolino et al., «The use of visible and near-infrared reflectance spectroscopy to predict colour on both intact and homogenised pork muscle», LWT - Food Science and Technology, 2003.

[11] P. R. Armstrong et al., «Comparison of Dispersive and Fourier-Transform NIR Instruments for Measuring Grain and Flour Attributes», Applied Engineering in Agriculture, 22 (3), pp. 453-457, 2006.

[12] A. Kazeminy et al., «A comparison of near infrared method development approaches using a drug product on different spectrophotometers and chemometric software algorithms», Journal of Near Infrared Spectroscopy, 17 (5), pp. 233–245, 2009.

[13] A. Mouazen, «Near infrared spectroscopy for agricultural materials an instrument comparison», Journal of Near Infrared Spectroscopy, 13 (2), pp. 87–98, 2005.

[14] P. Chalus et al., «Comparaison de spectromètres proche infrarouge pour la détermination de principes actifs dans des comprimés», Spectra Analyse, 247, pp. 44–49, 2005.

Contact: Mathias Schilling, mathias.schilling@metrohm.com

Ω Metrohm