Handbook of Near-Infrared Analysis

Emil W. Ciurczak, Benoît Igne, Jerome Workman, Donald A. Burns

NIR Instrument Sampling Configurations

Publication details
Jerome Workman
Published online on: 20 May 2021

How to cite: Jerome Workman. 20 May 2021, NIR Instrument Sampling Configurations from: Handbook of Near-Infrared Analysis CRC Press
Accessed on: 19 Sep 2023

Full terms and conditions of use: https://www.routledgehandbooks.com/legal-notices/terms

This Document PDF may be used for research, teaching and private study purposes. Any substantial or systematic reproductions, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The publisher shall not be liable for an loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.
8 NIR Instrument Sampling Configurations

Jerome Workman, Jr.*
MJH Life Sciences

CONTENTS

8.1 Introduction .......................................................................................................................... 145
8.2 General Considerations for Sampling ................................................................................... 146
8.3 Sample Type versus Sampling Method ................................................................................148
8.3.1 Liquids ......................................................................................................................148
8.3.2 Viscous Materials .....................................................................................................148
8.3.3 Pastes, Emulsions, and Slurries ................................................................................149
8.3.4 Solids ........................................................................................................................150
8.3.4.1 Sampling Powders ...................................................................................... 151
8.3.4.2 Sampling Amorphous Materials (Organic), Continuous Sheets, and Polymeric Film .................................................................................................................. 151
8.3.4.3 Sampling Lumps, Granules, or Pellets ...................................................... 151
8.3.4.4 Sampling Intractable Materials ..................................................................152
8.4 Sampling Method versus Sample Type ................................................................................152
8.4.1 Transmittance Windows ...........................................................................................152
8.4.2 Transmittance Cells (Liquid Handling) ....................................................................152
8.4.3 Gas Cells ...................................................................................................................152
8.4.4 Self-Supporting Films............................................................................................... 152
8.4.5 Specular Reflectance Measurements ........................................................................152
8.4.6 Diffuse Reflectance Measurements ..........................................................................153
8.4.7 Abrasion Measurement Techniques ..........................................................................155
8.4.8 Polyethylene Bag (1 mil Thickness) .........................................................................155
8.5 Optical Configurations for NIR Measurements ................................................................... 155
8.6 The Properties of Fiber Optics ............................................................................................ 159
8.6.1 Typical Fiber Optic Applications..............................................................................159
8.6.2 Materials for Optical Fibers....................................................................................159
8.6.3 Construction of Optical Fibers ..............................................................................159
8.6.4 Dimensions of Optical Fibers ..............................................................................160
8.6.5 Fiber Optic Connections .......................................................................................161
8.6.6 Properties of Optical Fibers...................................................................................161
8.6.6.1 Light Transmittance Losses in Fiber Optics (Attenuation)........................ 161
8.6.6.2 Determination of Signal-to-Noise for Single Fiber.................................... 162
References ......................................................................................................................................162

8.1 INTRODUCTION

The quality, repeatability, and reproducibility of near-infrared (NIR) spectra depend upon the consistency in sample preparation and the precise alignment of the optical interface between the sample and the spectrophotometer. A variety of sampling accessories have been offered...
commercially to optimize measurements of NIR spectral data. The most common NIR sampling techniques include reflectance measurements of powders, slurries, and liquids; transmittance of clear liquids; and fiber optic sampling for remote, quality control, hazardous, or multiple measurement head analysis.

There are no guarantees that a specific recommended sampling method will be efficacious as individual samples often present unique challenges. Issues include oil-in-water or water-in-oil emulsions, variance in particle size, high absorptivity, high crystallinity, high scattering material content, colorants or dye content, sample layering, low analyte concentration (i.e., below 0.5 wt%), small-range change in concentration, contaminants, and variable excipient quantities within a formulation. Other occasional problems with NIR measurement accuracy may include unusual reference tests that are not directly related to spectroscopic measurements, e.g., digestibility or calories; total oven volatiles used as a reference for moisture measurements; and where no direct signal exists for the selected analyte, e.g., sulfur in petroleum, or minerals in forages. In addition, one must remember that spectroscopy measures the molar concentration as weight per volume or moles per volume and not as weight percent.

For analytical thoroughness in sampling, one should document the sample, as well as any unusual issues encountered during sample preparation. For NIR, most solid or opaque slurry samples are measured using a diffuse reflection measurement technique. A transflectance or transmission method is optimum for water clear liquids. NIR is useful for quantitative analysis, qualitative identification, or spectral matching, or for conformity or quality estimation screening for finished products or ingredients. Initially, the unprocessed spectral data is collected. These spectra may then be preprocessed using baseline or scatter correction, smoothing, derivatives, or normalization.

### 8.2 GENERAL CONSIDERATIONS FOR SAMPLING

Near-infrared is a form of electromagnetic radiation nominally extending from 780 to 2500 nm or even 2600 nm. This spectral region is designated as 0.78–2.5 µm, or 12,820–4000 cm⁻¹.

NIR measurements for powders may be made using reflection directly from the sample surface using a variety of powdered sample cups (Figures 8.1 and 8.2). A transflection measurement is made when energy passes through the sample, reflects from a diffuse reflecting background, and then passes through the sample again to the detector (Figure 8.3). Since the absorptivity for molecules in
the NIR region is much less than in the IR region, a larger pathlength is required to obtain a useful spectrum. For a transflectance cell, the pathlength may nominally be 0.30 mm, and for powdered materials, a sample pathlength may nominally be approximately 7 mm compressed to 5 mm. Note that the required pathlength for appropriate analyte signal, the specific application, and type of sample dictate which method should be used for measuring a spectrum.

For NIR measurements, the minimum wavelength measured is determined by the sampling method, the sample type, and the spectrophotometer optics. For the visible spectral region, the most common detector is silicon-based with a detectivity range of 300 to 1100 nm (0.30–1.1 µm). On the higher end of the NIR spectrum, the limitation is from Indium Gallium Arsenide (InGaAs) with a working maximum typically near 2750 nm for the extended types (i.e., 2.7 µm). Alternative detectors with a slower response include lead sulfide (PbS) with a maximum response wavelength near 2800 nm (2.8 µm). NIR as a technique has been treated separately (Burns and Ciurczak 2008). The NIR spectral region is composed of molecular absorptions as a result of vibrational overtones and combination absorption bands. The absorptivity associated with these bands is less, by one or more orders of magnitude, than the fundamental infrared absorptions. For example, the absorptivity of the first overtone of C-H stretching in the NIR is 100 times less than the fundamental; the second overtone is 1000 times less; and the third overtone is 10,000 times less than the infrared

FIGURE 8.2 Small powder cup for diffuse reflectance measurements.

FIGURE 8.3 Sample cup illustration for diffuse transflectance measurements.
fundamental absorptivity. As noted earlier, the magnitude of the absorption may be used to define the best procedure for pathlength and sampling. NIR tends to be less rigorous for sample preparation than infrared spectroscopy. Sampling for NIR analysis involves transmission or reflectance (normally diffuse reflectance) or a combination of both. For a general overview of the technique and its related sampling procedures, the reader is referred to a standard text on the subject (Burns and Ciurczak 2008).

In many cases, factors such as price, convenience of operation, optical performance/efficiency, and final application may be the final arbiter in the selection of a sampling method. The actual application can be an important deciding factor. Both NIR and mid-IR are used for factory-based measurements during manufacturing and processing of synthetic chemical materials and natural products. Sampling techniques may be manual or automated, at-line or “offline” for batch-oriented processes, or integrated on-line for continuous process monitoring. For additional reading, one is referred to references (Workman 2016, Chalmers and Griffiths 2002, Williams and Norris 1987, Roberts et al. 2004, Wiberg et al. 1990).

8.3 SAMPLE TYPE VERSUS SAMPLING METHOD

NIR spectroscopy is most often applied to powdered samples and measured using diffuse reflectance. It is not particularly useful for gas phase or dark solids or slurries. It also gives inconsistent results to scattering slurries and variable layered materials with alternating scattering absorption layers. This is because diffuse reflection has limited capabilities of layered sample types. Fine, ground material is the optimum sample type for the NIR diffuse measurements. Slurries and liquids may be measured using transreflectance or diffuse reflectance. As will be mentioned throughout this text, it is essential that the analyst carefully document all experimental procedures, sampling methods, and conditions, and conscientiously note any abnormalities discovered during sample preparation. These should be recorded in appropriate lab analysis notebooks, either hard copy or electronic.

If the sample (solution or mixture) is known to contain water, then not only should this information be recorded but also extreme care must be taken to ensure that the sampling method is compatible with water being present. Comments are provided in Section 8.3.3 regarding the handling of samples containing emulsions and water that can interfere with proper analysis.

8.3.1 LIQUIDS

NIR is compatible with low-OH (i.e., low-water) quartz, glass, and silicate cell windows. NIR strongly absorbs water in glass near 1453 and 1938 nm. Other much less intense absorptions occur near 770, 847, 979, 1200, and 1780 nm (Workman and Weyer 2012). Traditionally, liquids have been considered to be relatively easy except for low-molecular-weight compounds, which often suffer from volatility problems and extremely high absorptivity that typically require extremely small optical pathlengths (most often 0.50–1.0 mm). The main method for liquids is transreflectance in a sealed transreflectance cell (Figure 8.3, as above). The transreflectance cell should have a temperature range from 10°C to 65°C for most sample types from volatile chemicals, aqueous solutions, or natural or synthetic oils. The temperature control for accurate multivariate calibrations should be ±0.1°C with a pathlength variation of no more than 3%–5% relative. For liquid analysis, the sample type and special characteristics, especially if a mixture, should also be noted.

8.3.2 VISCOS MATERIALS

A simple and convenient method for measuring viscous materials using NIR is to utilize an open slurry cup (or more simply a slurry cup). This cup is open and used in diffuse reflectance mode and has a depth so as to provide infinite optical thickness (Figure 8.4).
8.3.3 PASTES, EMULSIONS, AND SLURRIES

Depending on the constituents, pastes and slurries generally may be handled in a similar manner as proposed for viscous liquids (Figure 8.5). Always be aware of potential homogeneity problems. A slurry cup may be used for sample measurement, but if inhomogeneity is a problem, then the sample must be homogenized or carefully remixed to provide a more uniform suspension or emulsion (Figure 8.6). With multiple-phase emulsions or suspensions, be certain that separation does not occur if using a cup with an optical window. At the window interface, the polar nature of the optical material may cause segregation to occur. Common examples are emulsions, such as mayonnaise or margarine, and protein-containing materials; in this latter case, the protein may actually form a coating on the optical window. If an open cup is used, make certain that the separation of layers does not occur as the light layer will be measured and the heavy layer at the bottom of the cup will not be measured in proportion to the mixture composition. A disposable slurry cup may be used for rapid sample measurements when high numbers of samples must be measured and when measured samples are not retained (Figure 8.7).
Solids for NIR measurements may be solid blocks of material or are ground materials to pass a 1.0-mm screen (i.e., that are finer than 1.0 mm diameter particles). These samples may be measured “as-received” with high water concentration (above 30 vol%) or may be dried using microwave or forced air drying methods to near 0% water. The use of microwave drying carries with it the potential for damaging the sample due to high heat in various portions of the sample. Areas of particularly high heat occur due to the uneven field generation found in many commercial microwave heating systems. It also may occur due to bound or trapped water in microenvironments (i.e., pockets) of the sample. Note that traditional microwave ovens operate in a 1200 W field of 2450 MHz microwave energy. The purpose of the microwave field is to rotate the water molecules and cause surrounding molecules, based on the heat of friction, to rise in temperature. These molecules are rotating at 2450 million rotations per second to generate heat. In making spectroscopic measurements, one must attempt to mitigate spectral artifacts caused by refractive index, scattering, and polarization effects; and how to sample reproducibly and in a manner that is representative of the sample. Solid polymer samples of sufficient thickness may also be used for direct measurements using NIR. Typically, NIR will penetrate many polymer samples to 10 mm or more, and one should...
be aware that the NIR energy is penetrating the sample and the thickness will affect both shape and intensity of spectral bands.

8.3.4.1 Sampling Powders

Unlike the many methods used to prepare powders for measurement using infrared spectra, for NIR measurements the samples are generally dried and milled using a cyclone mill with a 1.0-mm screen, to make particles less than 1 mm in diameter. The powdered samples are placed in a variety of sample cups specifically designed for dried and ground material. Such cups include the locking powder cup (Figures 8.1 and 8.2) and open powder cups (Figure 8.5). There are a myriad of variations of this theme of presenting an infinite thickness of powdered material for the NIR measurement. Sample thickness for these cups may vary from 5 to 30 mm or more. The typical active window of the sample for measurement using different cup types is from 35 mm up to 5 inches or approximately 125 mm. When the measurement beam size is far less than the sample cup diameter, the sample may be rotated off-axis to measure multiple replicates of the sample during a single rotation.

8.3.4.2 Sampling Amorphous Materials (Organic), Continuous Sheets, and Polymeric Film

Polymer sheets may be measured in transmittance geometry or in diffuse reflectance geometry. A film holder may be used for transmittance (Figure 8.8). For diffuse reflectance, a standard reflectance cup with a diffuse back reflector may be used. For this application, a piece of the sheet or film is cut to the size of the sample cup and a diffuse reflectance measurement is made. It is important to remember that for a sample with limited thickness, the effective pathlength of a measurement is more than twice the physical pathlength of the sample. If the film sample has a metalized coating, it will act as an etalon and give interference fringes in addition to the molecular spectrum. These fringes are due to multiple reflections in the film and have a periodicity proportional to the film thickness. See film thickness measurement in the index of this set of volumes. Other methods for handling polymers and films may be used from infrared sampling techniques. The reader is referred to the index on thin films and polymer sampling as well as the chapter within the infrared text volume on the subject of sample preparation.

8.3.4.3 Sampling Lumps, Granules, or Pellets

This class of solids is an extension of the sample types already discussed, and many of the procedures already highlighted may be used here. These materials may be used in various diffuse reflectance cups in bulk form or ground and mixed for sample presentation using powder cups.

FIGURE 8.8 Film holder for transmittance measurements of films.
8.3.4.4 Sampling Intractable Materials
Sample with high absorbance (or less than 1% reflectance) may not provide enough signal for many commercial NIR spectrometers. If such samples must be measured routinely, one may try a spectrometer with much higher dynamic range. The measuring instrument must have at least one absorbance unity higher dynamic range than the typical samples measured.

8.4 SAMPLING METHOD VERSUS SAMPLE TYPE
This section provides similar information and cross-referenced information to those of the previous section, but in this case, it is more procedure-oriented. Hints and tips are provided for the actual method rather than focusing on the sample and its properties.

8.4.1 Transmittance Windows
The most basic sampling device for NIR includes a sampling system with a NIR transmissive window; low O-H-containing special glasses should transmit more than 90% of energy across the entire NIR region.

8.4.2 Transmittance Cells (Liquid Handling)
Liquids are generally measured using a fixed transfectance geometry with many commercial NIR instruments (Figure 8.3). Some instruments enable configuring either reflectance or transmittance geometry, and so transmittance measurements are permitted. Typical transmittance cells may be rounded (cylindrical) or rectangular, as illustrated in Figure 8.9. Rectangular cuvets may be square-shaped or be described as having an elongated rectangular cross section with a thin pathlength (of approximately 1.0 mm) and a width several (i.e., 5–10) times the pathlength. These are designed for ease of handling or when the beam size has a relatively large cross section.

8.4.3 Gas Cells
Gas cells are considered a form of transmission cells. Infrared is a technique often used for measuring gases due to the requirements for high resolution and high sensitivity. NIR is 100–1000 times less sensitive than infrared to the same functional groups, and thus, NIR is generally not considered to be adequate as a laboratory or process gas measurement technique. It could be applied to the identification or quantification of high-pressure gases if there is a simple matrix and high resolution is not a requirement.

8.4.4 Self-Supporting Films
Measuring thin polymer films has been previously mentioned. Adequate sample for NIR measurement of polymers generally requires a 1 mm thickness of material. Thin films of less than a few hundred microns in thickness are generally measured using infrared spectroscopy due to the increased sensitivity of infrared and the higher resolution available in most commercial infrared spectrometers.

8.4.5 Specular Reflectance Measurements
Specular reflectance (or mirror reflectance) represents an elastic photon reflection where only the direction of the incoming photon is changed; therefore, the original energy (i.e., frequency or wavelength) is identical after the reflection. The most common applications of specular reflectance are for the direct measurement of surfaces for contaminants or for the measurement of optical properties of
materials in the NIR spectral region – e.g., certain optical mirror or lens materials, paints, or coatings. For the NIR region, these measurements are referred to as transflectance or reflection/absorption (Figure 8.3, as above). As may be observed in Figure 8.10, for specular reflection measurements, the incident angle and reflection measurement angle are the same. If the incident angle and the reflection measurement angle are different, other reflective interactions will be measured, such as diffuse reflection, interactance, or transflectance. In these types of measurements, an inelastic photon interaction occurs and an absorbance due to interaction with the sample is the most likely result.

8.4.6 **Diffuse Reflectance Measurements**

Diffuse reflectance is the most common of all measurement techniques using the NIR spectroscopy. The method is used when a Lambertian (or light-diffusing material), such as a fine powder, is measured. Optical effects which primarily occur on the surface of the sample, such as specular
reflection, Mie or Rayleigh scattering, and diffuse reflection (Figure 8.11), can impact the quality and characteristics of the final measured spectrum. A conventional sampling cup and measurement geometry for systems designed for diffuse reflectance measurements are shown in Figures 8.3, 8.13, and 8.14.

For the NIR measurements, uniform particle size is critical. Reducing the particle size by grinding will often improve the quality of the final spectrum. Also, a uniform particle size or a narrow particle size distribution is beneficial. Nonpowdered samples can be studied directly from the sample surface as long as the surface is irregular (granular or diffuse) and not polished. This chapter covering infrared diffuse reflection measurements contains several useful recommendations for dilution with KBr.

The spectrum produced from a diffuse reflectance measurement does not bear a direct numerical relationship between peak intensity and composition, in contrast to traditional transmission measurements in which the absorbance form of the data is directly proportional to concentration. With diffuse reflectance, spectral distortions are generated by a constantly varying effective pathlength, which is defined by the depth of penetration of the beam into the sample. This is dependent on the absorptivity of the sample at each particular wavelength (frequency), and the measured intensity throughout the spectrum varies accordingly. A correction that can be applied to the diffuse reflectance spectrum, which can help linearize the data, is the Kubelka–Munk function (Equation 8.1):

$$f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty}, \quad (8.1)$$

where $f(R_\infty)$ is the corrected spectrum and $R_\infty$ is the ratio of the sample diffuse reflectance spectrum to a nonabsorbent reference (normally KBr or KCl), both measured at infinite depth. In the mid-IR region, infinite depth corresponds to approximately 3 mm.
The consequence of the $1 - R_e$ is to invert the spectrum and provide an absorbance-like format. It will be noted from the previous expressions that this corrected function can be correlated with concentration. Note that this function is normally only applied to undiluted (or concentrated) powdered samples.

### 8.4.7 Abrasion Measurement Techniques

Very hard surfaces can be studied by the abrasion of the surface with a sheet of abrasive material, such as silicon carbide or carborundum paper. At this point, a number of different methods may be used to analyze the abraded material. Following a roughening of the surface, diffuse reflectance may be used to measure the material (Figure 8.12).

### 8.4.8 Polyethylene Bag (1 mil Thickness)

Samples may be placed in thin but strong 1-mil-thick polyethylene bags for disposable sampling. These bags will leave a small, generally insignificant spectral signature, which must be included during the calibration phase to eliminate the bias in predicted values caused by the positive photometric offset and additional bands. The difference between reflectance spectra measured using the bag and standard window solid cup is minimal.

### 8.5 Optical Configurations for NIR Measurements

Most NIR instruments either exhibit a $0/45^\circ$ geometry or use an integrating sphere detector. The look-up and look-down configurations are illustrated in Figures 8.13 and 8.14, respectively (Wendlandt and Hecht 1966, Kortüm 2012).

The integrating sphere provides a more uniform sampling of the reflection from samples, whereas the detector plane tolerances in non-integrating sphere measurements cause greater variation between instruments. They may be compensated for by precisely adjusting the height and the angle of detectors with respect to the sample measurement plane.

The integrating sphere is most often coated with barium sulfate or halon coating, or is machined from Spectralon™ or Fluorilon to provide a highly uniform and reflective light integration chamber (Figure 8.15).
The advantages of an integrating sphere become obvious when it is realized that the image pattern at the detector varies with the characteristics of the samples presented to the instrument. When the beam angle is scattered or refracted off-axis, or is diverted from normal angle, the beam image area can vary and a normal 0/45° detector will lose some of the energy not captured. The integrating sphere is able to capture such diverging beam energy and direct it toward the detector surface. A standard measurement configuration for reference reflectance standards is referred to as the d/8° measurement geometry. This configuration is used to calibrate the reflectance of photometric reference material standards (Figure 8.16).
**FIGURE 8.15** Illustration of standard integrating sphere reflectance measurement configuration.

**FIGURE 8.16** Illustration of d/8° integrating sphere reflectance measurement configuration.
The various specialized reflectance or transmittance measurements are used to determine the precise sample characteristics desired. Specular reflection and diffuse reflection represent the major reflectance techniques using an integrating sphere. Specular reflection is mirror reflection and consists in elastic collisions of light photons from the immediate surface of the sample. Specular reflected light energy contains only information related to the surface characteristics of the sample. Specular reflection allows surface properties such as refractive index and thin film thickness to be determined. The technique also permits the measurement of atomic or molecular surface structure for film monolayers.

The use of linearly polarized light in specular reflectance is provided by the Glan–Taylor prism polarizer or similar polarizing elements. The linearly polarized light is required to provide calculations for the most optical constants. The use of polarized light makes these measurements possible due to the requirement that the quantity of reflected light from a sample depends upon the state of polarization of the incident light. These relationships are explained by the Snell and Fresnel law equations.

Grating spectrophotometers always produce partially polarized light, which can become a disadvantage for quantitative specular reflectance measurements. The nature of reflectance spectra depends upon the angle of incoming light as well as the polarization properties of this light. Diffusely reflected light is light that has penetrated into a sample where it is exposed to the absorption properties of the sample. Thus, the light is attenuated based upon the atomic or molecular interaction of the sample with the incident light. If a sample absorbs no energy, such as in elastic collisions, total reflection occurs. If a sample absorbs all of the incident energy, such as in the case of a light trap, no reflection occurs. Most real diffuse samples reflect some measureable quantity of light. The light that interacts with the sample in an inelastic manner yields chemical information about that sample.

Both transmittance and reflectance data are used for qualitative or quantitative work. In quantitative analysis work, both transmittance and reflectance data are related to concentration with the assumption that Beer’s law applies to both cases. In transmittance ($T$) measurements, we relate concentration directly to absorbance as:

$$\text{Absorbance} = -\log_{10} T.$$  \hspace{1cm} (8.2)

In reflectance ($R$) measurements, we relate concentration directly to absorbance using:

$$\text{Absorbance} = -\log_{10} R.$$  \hspace{1cm} (8.3)

On occasion, we see Kubelka–Munk transformed data also used to relate concentration to reflectance measurements as:

$$\text{Kubelka-Munk Reflectance} = \frac{(1 - R)^2}{2 \cdot R}.$$  \hspace{1cm} (8.4)

The Kubelka–Munk and absorbance equations for reflectance require a near-infinite thickness for the sample; this requirement is met if the sample thickness is sufficient to absorb or reflect all the impinging energy.

The refractive index of materials changes the angle of refraction for light impinging upon a sample surface. This angle of refraction from the front surface of a sample follows Snell’s law as:

$$n_1 \cdot \sin(\phi_1) = n_2 \cdot \sin(\phi_2),$$  \hspace{1cm} (8.5)

where $n_1$ is the refractive index of the initial medium the light is passing through, $n_2$ is the refractive index of the second medium, $\phi_1$ is the incident angle of the light, and $\phi_2$ is the angle of refraction of the light.
The amount of reflection from the surface of a material for different polarizations of light is computed using the following formulas. Snell’s law is used to compute the angle of refraction from the angle of incidence of light reflection from a surface as light as it passes through two materials of differing refractive indices. The reflection of s-polarized (i.e., $R_s$, parallel ($R_\parallel$) or $0^\circ$ polarized light) is computed using the following:

$$R_s = \frac{\sin^2(\phi_1 - \phi_2)}{\sin^2(\phi_1 + \phi_2)}. \quad (8.6)$$

The symbols are those as used in the Snell’s law example, where $n_1$ is the refractive index of the initial medium the light is passing through, $n_2$ is the refractive index of the second medium, $\phi_1$ is the incident angle of the light, and $\phi_2$ is the angle of refraction of the light.

Furthermore, the reflection of p-polarized (i.e., $R_p$, perpendicular ($R_\perp$) or $90^\circ$ polarized light) is computed using the following:

$$R_p = \frac{\tan^2(\phi_1 - \phi_2)}{\tan^2(\phi_1 + \phi_2)}. \quad (8.7)$$

### 8.6 THE PROPERTIES OF FIBER OPTICS

#### 8.6.1 Typical Fiber Optic Applications

Optical fibers are useful for remote or process measurements using optical spectroscopy, particularly NIR, visible, and the higher-frequency infrared (typically above 1000 cm$^{-1}$). The basic properties of fiber optics include materials, construction, dimensions, and overall optical properties (Newport Corp. 2018, Ganz et al. 1995, Fiberguide Industries 2018).

NIR fiber optic materials consist of low-OH silica (SiO$_2$) with minimal inclusions, like entrapped air. A fiber bundle consists in cladding layer(s) and a coating layer for protection.

#### 8.6.2 Materials for Optical Fibers

A variety of materials are used for the construction of fiber optics. Although many more materials are useful for communication-grade fibers, fibers used for spectroscopy require low attenuation or high transmission of energy over the wavelength or frequency of interest. The main materials used for spectroscopic fibers include low-OH silica (visible and NIR up to 2.5 $\mu$m), fluoride fiber (long-wavelength NIR into the infrared region to 4 $\mu$m), and chalcogenide (for the infrared region above extending to above 10 $\mu$m).

#### 8.6.3 Construction of Optical Fibers

The basic components of spectroscopic-grade fiber optic cables and standard cable connectors are shown in Figure 8.17; they include several key elements as follows. The core, composed of low-hydroxyl-containing glass or plastic, is the light-transmitting portion of the optical fiber. The larger the core diameter, the greater the light transmitted, which is determined by the area function of $A = \pi \cdot r^2$. Surrounding the core is the cladding. The cladding is the boundary zone for the light transmitted down the core. Its purpose is to provide an interface of material at a different refractive index to cause reflection of the light within the core so that the light waves are transmitted down the fiber; the cladding is of lower refractive index than the core. The coating surrounds both the core and the cladding. Coatings are for protection of the basic optical cable and are generally multilayers of plastic meant to absorb some mechanical shock and preserve the
fiber. The coatings are either mechanically or chemically strippable. Tables 8.1 and 8.2 show the typical characteristics of NIR fibers.

### 8.6.4 Dimensions of Optical Fibers

Fiber size for spectroscopic use varies from 200 to 600 µm, with 600 µm the most common. Fiber types include single mode, graded index, and step index. Single-mode fibers are generally 5–10 µm in diameter and are used exclusively for video or telecommunications. The single-mode fiber allows only one mode or light ray to be transmitted down the core. Graded index fibers consist of a core surrounded by a number of glass cladding material layers, each with a successively smaller refractive index as you move away from the center of the fiber. Most graded index fibers are used for communications and are typically found in 50, 62.5, 85, and 100 µm sizes. Step index fiber consists of a core surrounded by a single cladding layer of lower refractive index. The step index fiber is most common in spectroscopy, and it is found in the 200–600 µm sizes.
8.6.5 Fiber Optic Connections

Figure 8.17 demonstrates the typical fiber connector type, often referred to as the SMA connector. This connector provides both strain protection and a fast-locking system for rapid locking and unlocking of the fiber connections. The fiber connector terminates the fiber as it is connected to a transmittance device, a source lamp, a spectrometer, or a detector. The connectors allow a quick connect/disconnect and align the core elements of the fiber ends to minimize attenuation. The alternative to the use of connectors is to splice the fibers, both time-consuming and inaccurate. In addition to the quick connect/disconnect SMA connectors, there are many threaded types which rely on a screwing mechanism for connection and disconnect. There are dozens of different connector types commercially available.

8.6.6 Properties of Optical Fibers

8.6.6.1 Light Transmittance Losses in Fiber Optics (Attenuation)

Losses in fiber optic transmitted light are due to absorption, reflection, scattering, misalignment, and microbending; the losses can vary with temperature, wavelength, and fiber condition. The greatest causes of attenuation include OH absorption at 960 and 1950 nm – and some attenuation from 1800 to 2500 nm – and Raleigh scattering in the 200–600 nm range. The quantity of optical loss is expressed as an attenuation rate in decibels (dB) of optical power per kilometer (km). Typical losses result from launch optics, temperature variations, fiber couplings in optical path, aging (solarization), optical alignment, preparation at exposed surfaces, normal attenuation due to fiber length, coupling at detector, and repairs/splices.

The losses in energy transmitted through a fiber can be calculated by using Beer’s law. Beer’s law states that the irradiance of energy through an absorbing medium falls exponentially with the distance of transmission following the relationship:

\[ I_d = I_0 \cdot 10^{-\alpha d/10}, \]  

(8.8)

where \( I_d \) is the irradiance at distance \( d \) from the source, \( I_0 \) is the source irradiance at \( d = 0 \), \( \alpha \) is the attenuation (absorption) coefficient in units of dB/unit length (e.g., meters or kilometers), and \( d \) is the fiber length in unit length (meters or kilometers).
Attenuation losses are wavelength dependent; thus, the value for $\alpha$ is a function of the incident wavelength ($\lambda$) (Table 4.8). During fiber manufacture, thermal variations are present when the glass is in a molten state; the result is a refractive index variation throughout the fiber. As light passes through these variations, a phenomenon termed Rayleigh scattering occurs; this scattering reduces the fiber throughput and is proportional to $\lambda^{-4}$, where $\lambda$ is the wavelength of the incident light. At longer wavelengths, the O-H present as an impurity in the SiO$_2$ (glass) causes absorption losses at 950, 1250, 1380, 1920, and above 2200 nm. The overall quality of a fiber is sometimes standardized to the Rayleigh scattering limit of 0.17 dB km$^{-1}$ at 1550 nm.

8.6.6.2 Determination of Signal-to-Noise for Single Fiber

The theoretical total signal (SN) from an optical system (fiber) can be given by

$$SN = R_S \cdot B_\lambda \cdot \theta \cdot \tau \cdot Q, \quad (8.9)$$

where $R_S$ is the source spectral radiance, $B_\lambda$ is the spectral bandwidth, $\theta$ is the etendue (throughput), $\tau$ is the transmittance loss, and $Q$ is the quantum efficiency (electrons per second).

The measured signal-to-noise can be calculated as the full transmitted signal divided by the RMS noise (in transmittance units).

REFERENCES


