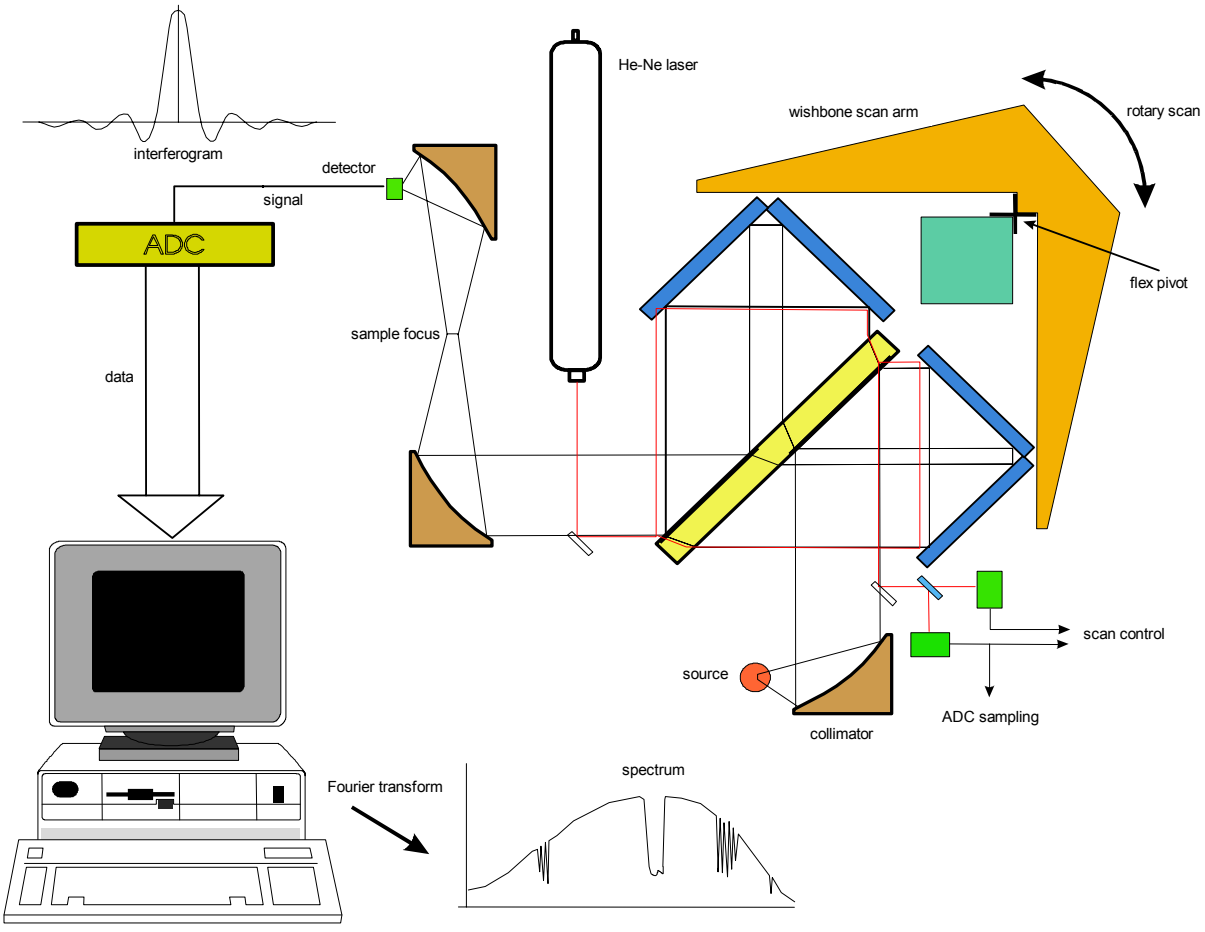
FT-IR
Reference Manual

This manual contains: *Information about the operation of ABB FT-IR spectrometers and useful information for ensuring optimum performance.*



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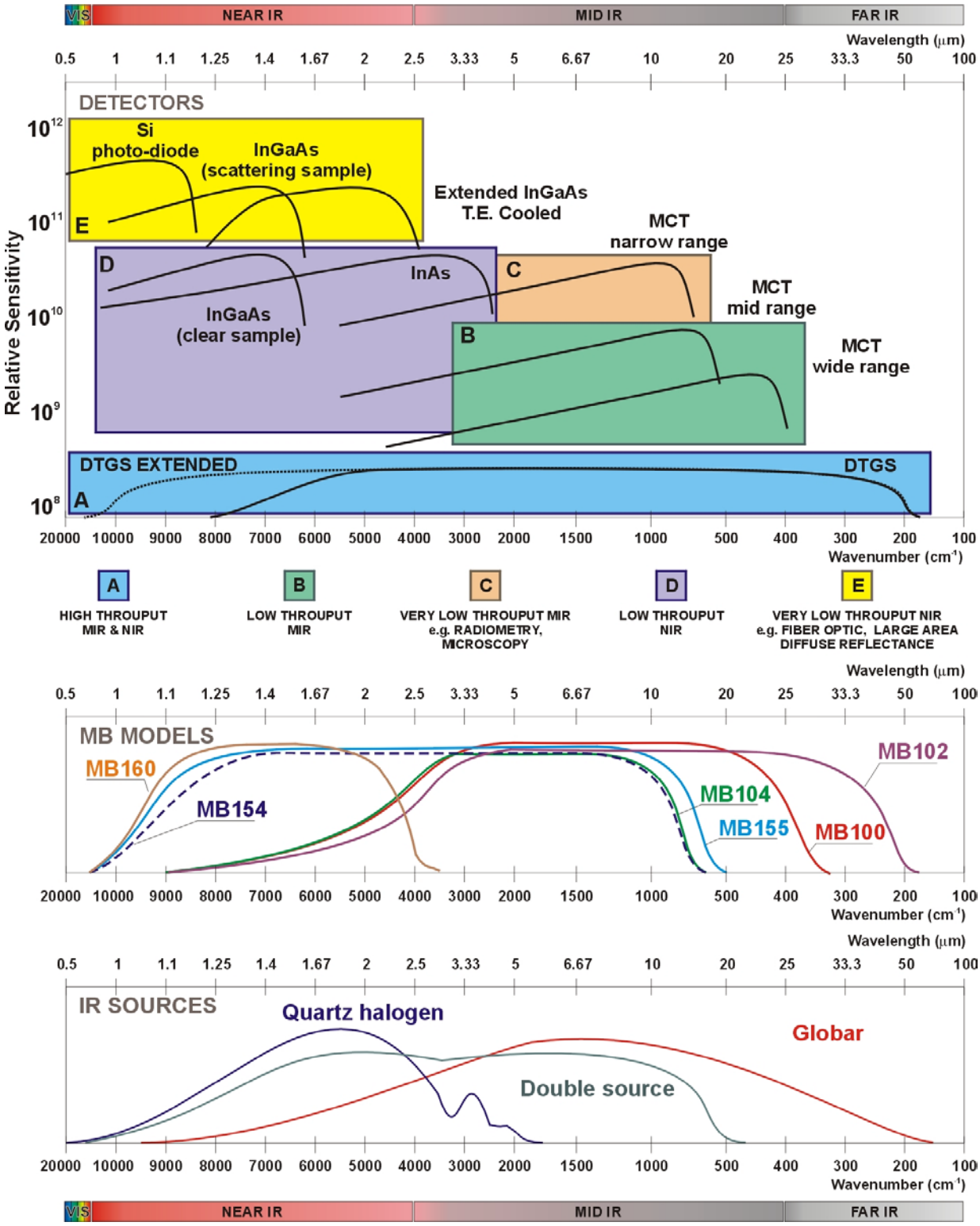
VIS
NEAR IR
MID IR
FAR IR
Wavelength (µm)
0.5 1 1.1 1.25 1.4 1.67 2 2.5 3.33 5 6.67 10 20 25 33.3 50 100
DETECTORS
Relative Sensitivity
10^12
10^11
10^10
10^9
10^8
Si photo-diode
InGaAs (scattering sample)
E
Extended InGaAs T.E. Cooled
MCT narrow range
D
InAs
C
MCT mid range
InGaAs (clear sample)
B
MCT wide range
DTGS EXTENDED
DTGS
A
20000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1500 1000 500 400 300 200 100
Wavenumber (cm-1)
A HIGH THROUPUT MIR & NIR
B LOW THROUPUT MIR
C VERY LOW THROUPUT MIR e.g. RADIOMETRY, MICROSCOPY
D LOW THROUPUT NIR
E VERY LOW THROUPUT NIR e.g. FIBER OPTIC, LARGE AREA DIFFUSE REFLECTANCE
Wavelength (µm)
0.5 1 1.1 1.25 1.4 1.67 2 2.5 3.33 5 6.67 10 20 25 33.3 50 100
MB MODELS
MB160
MB154
MB102
MB104
MB155
MB100
20000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1500 1000 500 400 300 200 100
Wavenumber (cm-1)
Wavelength (µm)
0.5 1 1.1 1.25 1.4 1.67 2 2.5 3.33 5 6.67 10 20 25 33.3 50 100
IR SOURCES
Quartz halogen
Globar
Double source
20000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1500 1000 500 400 300 200 100
Wavenumber (cm-1)
VIS
NEAR IR
MID IR
FAR IR

WARNING! **All servicing of the equipment is to be performed by Qualified Service Personnel only.**

No user/operator adjustments inside the equipment are necessary or recommended by the manufacturer.

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Important: Please be prepared to provide the serial numbers of all units.

You can also consult ABB's web site at **www.abb.com/analytical**

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ABOUT THIS MANUAL

Purpose

This manual provides reference information that applies to all ABB FT-IR analyzers and spectrometers.

Audience

This manual is intended for personnel responsible for ensuring optimum performance of the analyzer or spectrometer, and for those who wish to learn more about the system.

References

Appendix B contains a list of reference documents. You may also find further information and links to other sources of information on our web site:

www.abb.com/analytical

Conventions used in this manual

This symbol refers you to another manual or document.

Note: *Supplemental information to help the reader.*

Important: *Information that is important, but which does not concern the safe use of the equipment.*

This symbol shows that Caution is required. Follow the instructions carefully to avoid damage to the equipment.

WARNING! Failure to comply with these instructions can result in serious injury or loss of life.

CHAPTER 1

INTRODUCTION

1.1 ABB spectrometers and analyzers

ABB Fourier Transform Infrared (FT-IR) spectrometers and spectrometer-based analyzers are reliable instruments designed for a wide range of analyzes applications in a variety of environments, including factories, quality control laboratories, research laboratories and educational institutions.

Thanks to permanent factory alignment of the optics, these instruments provide exceptional repeatability and stability over time. They have high sensitivity and photometric linearity. Each spectrometer is manufactured to exacting standards such that the absorbance of a stable sample is the same to within close tolerance from spectrometer to spectrometer. As a result, all ABB FT-IRs have identical absorbance response. The high degree of reproducibility is easily maintained and is verified by means of a simple validation protocol.[a]

[a] *Refer to Chapter 5* Calibration Transfer *for information on ensuring accuracy in quantitative analyzes.*

The spectrometers and analyzers are controlled by acquisition software which resides in an external Personal Computer[b] (PC) and uses the Microsoft Windows® or Windows® 2000 operating system. In the case of automated industrial analyzers, all aspects of system operation including sample system control functions as well as communication with external devices are controlled by the software.

[b] *ABB can supply the instrument with or without a computer.*

The spectrometers are used with various sampling accessories which may be supplied by accessory vendors. In some cases ABB has developed sampling accessories for specific applications (see Chapter 8 *Sampling* Accessories). Sampling accessories are supplied with their own user manuals.

1.2 Design features

ABB spectrometers and analyzers are designed to provide outstanding performance. Some of the design features are:

- Unique permanently aligned Michelson interferometer. The interferometer does not require any alignment in use. It always provides optimum performance.
- Rotary-scan motion with a long-life frictionless flex pivot on the interferometer scan arm. The flex pivot does not wear out and insures constant performance over long time.
- The scan arm has 2 cube-corner mirrors that introduce a varying optical path difference. When one cube corner advances towards the beamsplitter, the other one moves away from the beamsplitter. The optical path difference equals 4× the mirror displacement.

- The use of cube corners and the unique constraint of the scan arm insures that modulation efficiency is inherently constant over the full mirror scan. This insures highly consistent line shape functions.
- Single substrate self-compensating beamsplitter. Different parts of the substrate are used for beam splitting, beam recombination, laser modulation, and zero path difference white light detection. Interferograms are inherently symmetric and therefore require minimal phase correction. This results in superior spectral fidelity.
- He-Ne laser for metrology with quadrature detection.
- A built-in white light channel is used for scan initialization at start-up. The white light is turned off after start-up and scan synchronization is maintained by bi-directional fringe counting.
- Aluminum casting technology providing rigid optical and mechanical supports.

Figure 1-1 shows a simplified optical representation of the spectrometer design. It illustrates how the infrared beam travels from the source to the detector.

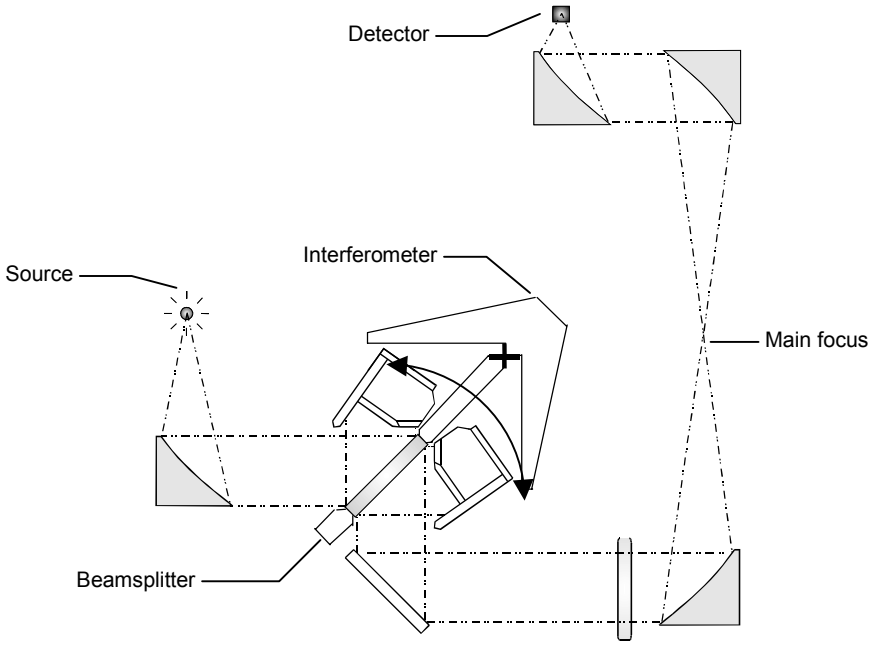


Figure 1-1. Schematic diagram of ABB spectrometers

Figure 1-2 shows the various optical beams as they go through the Michelson interferometer.

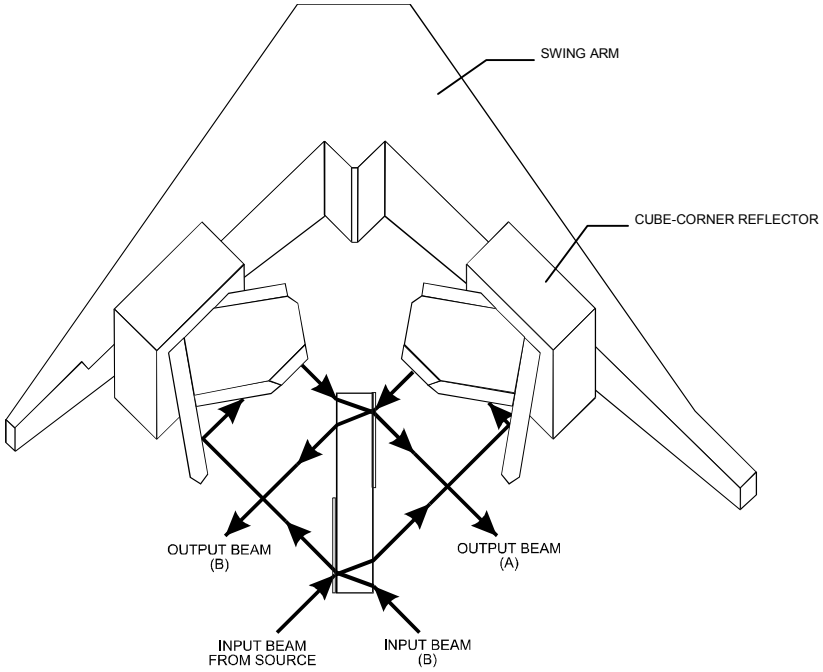


Figure 1-2. Michelson interferometer

CHAPTER 2

SAFETY POLICIES

All ABB spectrometers and analyzers receive the following safety certifications:

- CSA (Canadian Standards Association)
- CE (ce-test European Community)
- UL (Underwriters Laboratories Inc.)

Under normal operating conditions, all ABB spectrometers and analyzers are completely safe to operate. However, since each spectrometer contains a low power He-Ne laser and uses high voltages, refer to the spectrometer and analyzer User's Guides supplied with your system for specific safety instructions.

WARNING! **Failing to comply with any of the instructions, precautions or warnings contained in the spectrometer and analyzer User's Guides is in direct violation of the standards of design, manufacture, and intended use of the equipment.**

ABB assumes no liability for the user's failure to comply with any of the safety requirements presented in the spectrometer and analyzer User's Guides.

CHAPTER 3

INTRODUCTION TO FT-IR SPECTROMETRY

The FT-IR (Fourier transform infrared) spectrometers manufactured by ABB are precise and stable analytical instruments which perform chemical analyzes using infrared light. Measuring the absorption of infrared light by the sample over a range of wavelengths yields a spectrum. This spectrum contains information about various properties of the sample, such as the substances present in the sample and their concentrations.

This chapter briefly describes the interaction of infrared light with matter and how an FT-IR spectrometer is used to obtain the absorbance spectrum of a sample. Chapter 4 *Spectrometer Calibration* explains how a spectrometer is calibrated so that it can be used for quantitative analysis.

3.1 How light interacts with matter

Light can be considered as photons or as electromagnetic waves. Light interacts with matter at the atomic and molecular level by coupling to oscillating electric charge distributions. When the frequency of electromagnetic waves matches the resonance frequency of the oscillating charge, coupling is strong. Frequencies of electromagnetic waves in the infrared tend to couple effectively to oscillating charge distributions due to vibrations set up in the molecular structures. Frequencies of molecular vibrations are determined by the masses in motion and the binding force between them. Analogous to a weight suspended on a spring, frequencies of molecular vibration are directly related to molecular composition (the atoms making up the molecule) and the molecular structure (how the atoms are disposed in the molecule). The order of magnitude of a typical vibration of the structure of a molecule is 45 terra Hertz (45×10^{12} Hz). As an example, consider the water molecule shown in Figure 3-1.

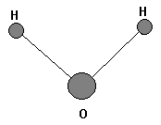


Figure 3-1. Water molecule

Two atoms of Hydrogen are bound together with an Oxygen atom. The binding force and the mass of the atoms behave as weights attached to a spring. Since there are three atoms, several different forms of vibration are possible each with its unique natural frequency of oscillation:

1. Both hydrogen atoms moving away and towards the oxygen atom (symmetric stretch vibration).

2. One hydrogen atom moving away while the other moves towards the oxygen atom (anti-symmetric stretch vibration).

3. Both hydrogen atoms moving away and towards each other only (bending vibration).

As a general approach each atom in a molecule can move in 3 directions in space. This means that there are 3 × N independent movements for a molecule with N atoms. All atoms together can move in 3 linear directions and rotate about 3 axes without inducing relative internal motion. Therefore there are 3 × N-6 internal motions of the atoms that deform the molecule. In this way there can be as many as 3 × N-6 distinct resonance frequencies some of which will interact with incident infrared radiation. When vibrations cause an oscillation of the electric charge (asymmetric vibrations), incident infrared radiation will be absorbed. For the example of the water molecule, of the 3 internal vibrations, two of these are observed as absorption bands in the infrared. The third vibration is totally symmetric and does not displace the electric charge distribution. Hence it does not interact with infrared radiation.

It is easily seen that molecules with 2 atoms have only one vibration. When the 2 atoms are the same, such as for N_2 and O_2, the vibration does not displace the electric charge and hence there is no interaction with infrared radiation. Homo-nuclear diatomic molecules such as N_2 and O_2 do not have an infrared spectrum due to their molecular vibration. Only molecules with non-symmetric vibrations absorb infrared radiation. For diatomic molecules, charge distribution vibration will occur only with unequal mass atoms such as carbon monoxide and hydrochloric acid.

3.2 Beer-Lambert's absorption law

When infrared radiation passes through a material, some intensity passes through without interacting with the molecules, while the remainder interacts with molecules and is absorbed. The proportion of absorbed intensity over the total intensity that enters the material is in direct relation to the concentration of absorbing molecules.

Figure 3-2 (a) shows infrared radiation coming from the left passing through a transparent reservoir. The reservoir contains a concentration of absorbing molecules shown as small circles. The molecules absorb some of the incident

intensity and the remainder passes through the reservoir. If the concentration is doubled in the reservoir, as shown in Figure 3-2 (b), the intensity absorbed doubles. Similarly, if the length of the reservoir (the path length) doubles while the same concentration is maintained, as shown in Figure 3-2 (c), the intensity absorbed also doubles.

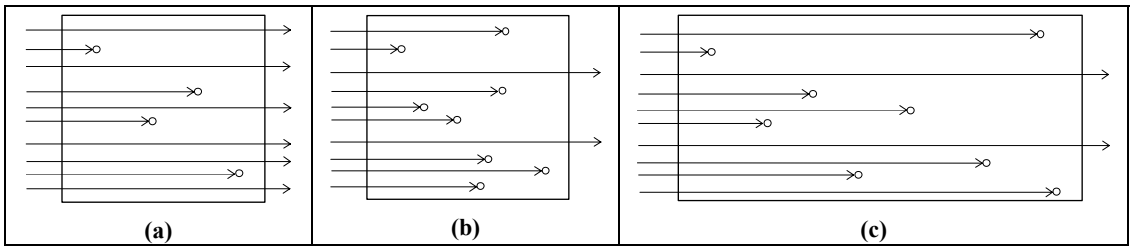


Figure 3-2. Light absorbed by molecules

This is the principle of Beer-Lambert's law.[1] It describes the absorption of infrared radiation by molecules by means of a simple equation:

$$A_\lambda = \varepsilon_\lambda \times b \times C \qquad \text{Equation 3-1}$$

For industrial applications, the concentration C is often given in percentage volume or weight.

The path length b can be only a few millimeters long for highly absorbent materials, or up to many meters long for gasses.

where A_λ is the measured absorbance at a specific wavelength (λ)

ε_λ is the absorption coefficient of the material at that wavelength

b is the path length through the sample

C is the concentration of the absorbing material

When the path length through the sample doesn't change in a particular application, and because the value of the absorption coefficient of a given material at a particular wavelength is a constant, the path length *b* and the absorption coefficient ε_λ can be combined into a single constant K_λ. Beer-Lambert's law can then be rewritten as:

$$A_\lambda = K_\lambda \times C \qquad \text{Equation 3-2}$$

[1] Fourier Transform Infrared Spectroscopy, by Peter R. Griffiths and James A. de Haseth, a Wiley-Interscience publication, John Wiley and Sons, 1986.

Figure 3-3 shows a graphic representation of Beer-Lambert's law.

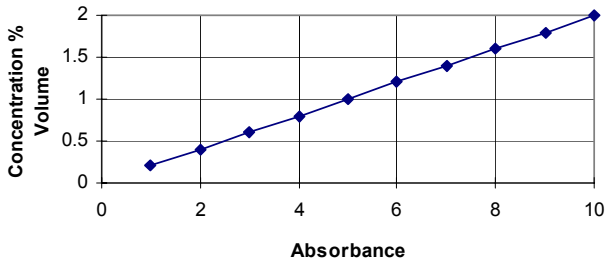


Figure 3-3. Beer-Lambert's law of absorption

By measuring the absorbance of an unknown sample at the appropriate wavelength, one can predict the concentration of the sample using Equation 3-3.

$$C = \frac{A_\lambda}{K_\lambda}$$ Equation 3-3

3.3 Absorbance spectra

In Section 3.2, the absorbance at a single wavelength is used in Beer-Lambert's law to predict the concentration of an unknown material. However, the absorbance at many different wavelengths is more commonly used. Since the absorption coefficient has a different value at each wavelength, the absorbance also varies with the wavelength.

An absorbance spectrum is a distribution of absorbance intensities for radiation passing through a sample over a range of wavelengths, arrayed in order of increasing or decreasing wavelength.

By the nature of the measurement of the infrared spectrum with an FT-IR, the minimum measurable interval of wavelength (the resolution) is not constant over the range of wavelengths. Instead the resolution is a constant interval when the x-axis scale is expressed in frequency of oscillation of the radiation. However, the frequency expressed in Hertz is a very large number for infrared radiation and is not practical to use. It is therefore common practice to express the x-axis scale in wavenumbers (sometimes the term Kaiser is also used). The units are wavenumbers or cm^{-1} (σ).[c] This corresponds to the frequency in Hertz divided by the speed of light *c*. It also corresponds to the number of wavelengths that fit in a 1 cm interval. The wavelength of infrared radiation is commonly in the range of a fraction of a micrometer up to 25 micrometers. This corresponds to a range of from over 10 000 cm^{-1} (waves/cm) to 400 cm^{-1}.

[c] *The wavenumber (σ) is the reciprocal of the wavelength (λ): $\sigma = \frac{1}{\lambda}$*

The unit of the wavenumber is $\frac{1}{cm}$ or cm-1.

The absorbance spectrum produced by the FT-IR spectrometer consists of a graph representing the absorbance at different wavenumbers. Figure 3-4 and Figure 3-5 show graphs of two different absorbance spectra.[c]

[d] *In absorbance spectra:*

the Y-axis (ordinate) is the absorbance (in absorbance units)

the X-axis (abscissa) is the wavenumber (in cm-1).

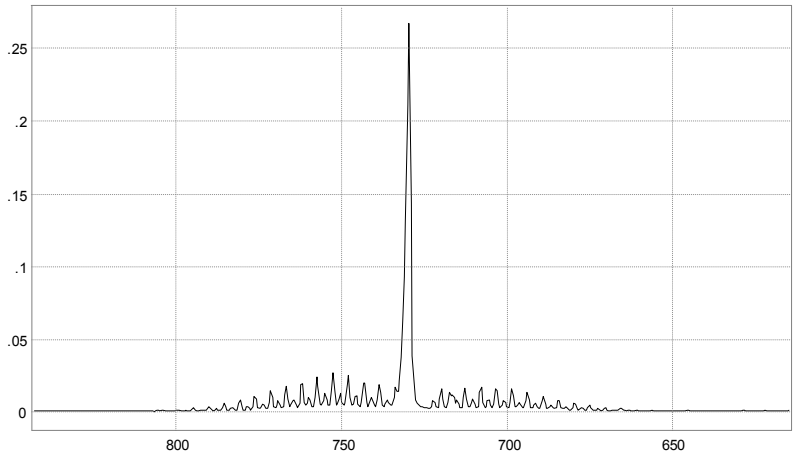


Figure 3-4. Acetylene absorbance spectrum (40 ppm in N_2 at 1 atm.)[e]

[e] *Acetylene has a vibration resonance at 730 cm-1. The small peaks shifted above and below 730 cm-1 are due to energy changes in the rotation of the molecule that are added or subtracted from the vibration.*

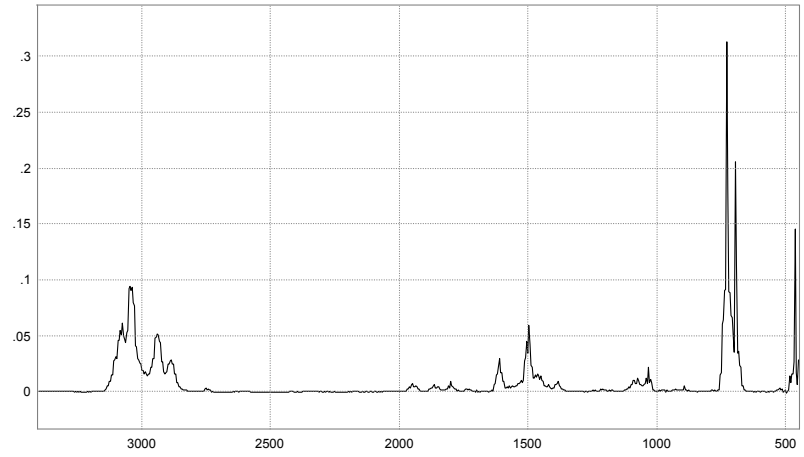


Figure 3-5. Toluene vapor MIR-absorbance spectrum (500 ppm in N_2 at 1 atm.)[f]

[f] *Many molecules have characteristic bands in the "fingerprint" region from 400 cm^{-1} to 2000 cm^{-1}. The stretch of a strong bond like C-H is observed near 2900 cm^{-1}.*

In some cases, the transmission spectrum, which represents the percentage of the infrared light transmitted through the sample, may be used.

The spectral positions of the sharp peaks and broad bands are determined by the type of change in molecular vibration produced by the incident infrared radiation when absorbed by the molecules. Changes in the rate of rotation of a molecule will also result in absorption of infrared radiation but this occurs in the far infrared below 200 cm^{-1}. It is most common to observe absorption at frequencies that combine a molecular vibration with rotations. This is called the rotation-vibration spectrum of the molecule. Often the rotational lines are so close together that they are merged into a continuous band.

Molecular vibrations are not purely harmonic. As a result infrared absorption can also occur at multiples of the fundamental frequency. Particularly multiples of the C-H stretch frequency found in all organic molecules (at multiples of 2900 cm^{-1}) are often used for infrared analysis. These frequencies which occur above 3000 cm^{-1} are in the Near infrared region of the spectrum. Near infrared spectra may also exhibit absorption due to combinations of overtones and other fundamental vibrations.

It is common practice to select certain regions of the spectrum to be used for analysis. The choice of spectral regions is normally determined by the limitation of sampling:

- In the fingerprint region, including the C-H stretch region (4000 $cm^{-1}$to 400 cm^{-1}), the pathlength through samples is generally in the range of a few micrometers to 0.1 mm.

- For the region where combination frequencies occur (6000 cm^{-1} to 3500 cm^{-1} in the near IR) the pathlength is less than 1 mm.

- In the 1st overtone region (7500 cm^{-1} to 5000 cm^{-1} in the near IR) the pathlength is typically 3 to 5 mm.

- In the 2nd overtone region (11000 cm^{-1} to 7000 cm^{-1} in the near IR) the pathlength is often as much as 10 mm.

- In the fundamental region (4000 cm^{-1} to 400 cm^{-1}), absorption bands due to different molecules are least overlapping.

  Here it is possible to detect small concentrations in mixtures of materials by increasing the pathlength such that the bands of the main components are highly absorbed while the weak features of the low concentration component occur between these.

3.3.1 Fingerprint region

Each molecule has its characteristic spectrum. The region between 400 cm^{-1} and 2000 cm^{-1} is often called the fingerprint region. This is a spectral region where it is relatively easy to find a unique spectral feature of a given material. It is also a strongly-absorbent region that can be used when the concentration is low, particularly for gas measurement.

3.3.2 Overtone and combination region

For liquids and solids, the near infrared (NIR) part of the overtone and combination region, from 4000 cm^{-1} to 10 000 cm^{-1}, is often used for quantitative analysis.[2]

Different molecules show less visible differences in their absorbance spectra in the near infrared making this region less useful for visual interpretation. Figure 3-6 shows a spectrum of liquid toluene in this region. The path length through the sample was a few millimeters.

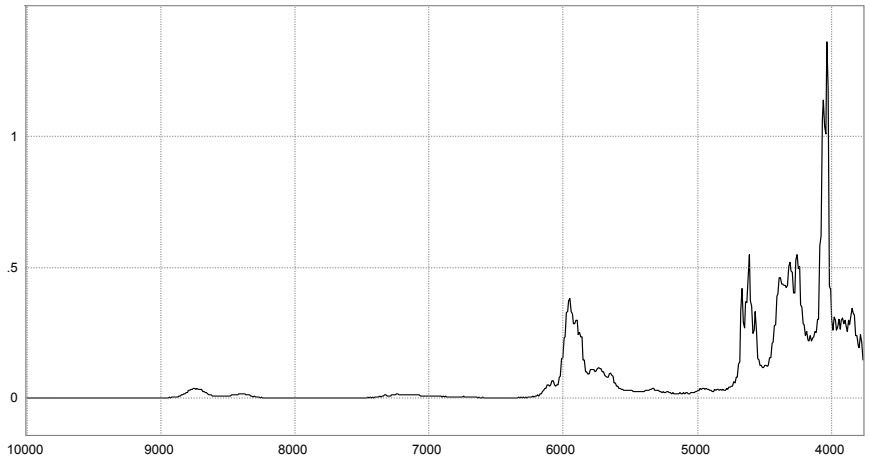


Figure 3-6. Liquid toluene NIR-absorbance spectrum

The spectral structure of this region is largely generic and it is not possible to obtain a specific spectral signature of a chemical compound without interference from other chemical signatures. However thanks to the great sensitivity and stability of FT-NIR, reliable quantitation of many species is possible based on the subtle differences in signature.

[2] Handbook of Near-Infrared Analysis, edited by Donald A. Burns and Emil W. Ciurczak, Practical Spectroscopy, Published by Marcel Dekker, Inc., 1992.

3.4 Operation of an FT-IR spectrometer

In order to obtain spectra of the samples, a spectrometer must be able to separate the optical frequencies of the infrared light after it passes through the sample. Dispersive spectrometers separate the optical frequencies spatially using a prism or a diffraction grating after the light has passed through the sample.

FT-IR spectrometers, however, modulate the infrared beam *before* passing through the sample. The interferometer causes each infrared frequency to be modulated with a unique frequency of modulation. After the infrared beam passes through the sample, the intensity is detected and the frequencies are demodulated via a Fourier Transform (see Section 3.4.3 on page 17). All ABB FT-IR spectrometers are single beam spectrometers. In order to obtain the absorbance or transmittance spectra further calculations are performed combining a pre-recorded instrument reference spectrum and the sample spectrum. Figure 3-7 illustrates the operating principle of an FT-IR spectrometer.

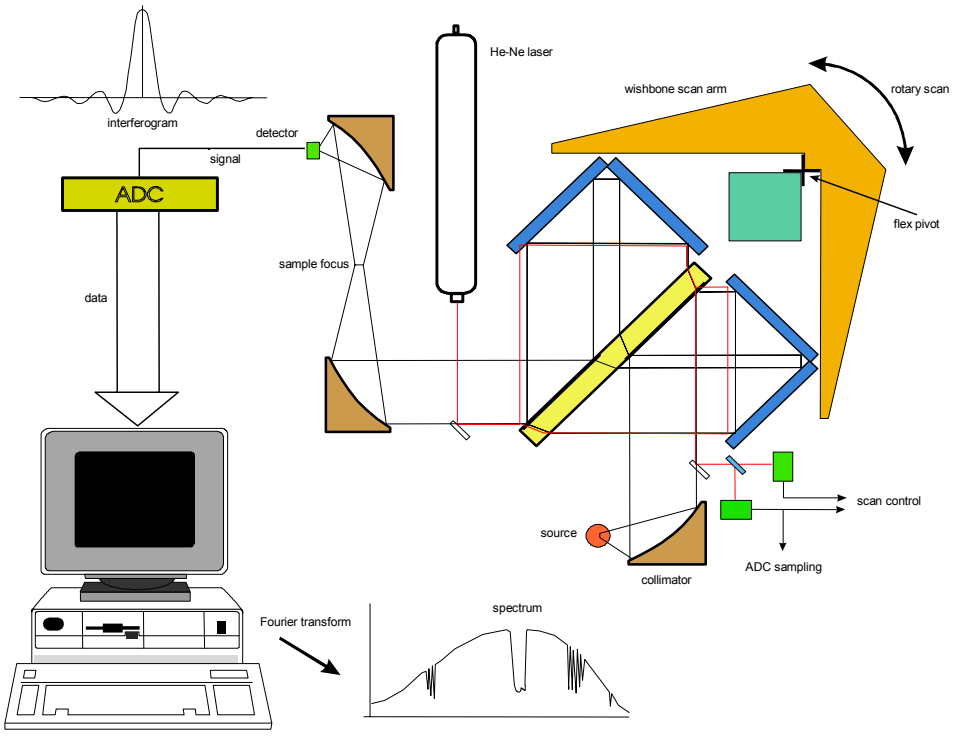


Figure 3-7. Operating principle

The spectrometer includes a source, a source collimator, an interferometer (see Section 3.4.1), a sample compartment with focusing optics, a detector, and a computer running analytical software. Some models have no sample compartment located on the spectrometer. Instead, samples are analyzed remotely using fiber-optic cables (see Chapter 8).

FT-MIR (mid infrared) and FT-NIR (near-infrared) spectrometers are two types of FT-IR spectrometers.[g] The difference between FT-MIR and FT-NIR spectrometers is mainly in their optical requirements.

- FT-MIR spectrometers require sources at about 1000K (727ºC) and optics transmitting from approximately 400 cm^{-1} to 4000 cm^{-1}.
- FT-NIR requires sources at about 2300K (2027ºC) and optics transmitting from approximately 4000 cm^{-1} to 12 000 cm^{-1}.

[g] ABB offers spectrometers that cover both optical regions (MIR and NIR) without any modification or adjustment other than selecting the spectral range for the acquisition.

The precision requirement on optical components is more stringent in NIR than in MIR, since the wavelength of the light is smaller.

3.4.1 Michelson interferometer

The heart of ABB's FT-MIR and FT-NIR spectrometers is the Michelson interferometer. An interferometer modulates light in such a way that the spectral information the light contains can be retrieved.[3]

The light from the infrared source enters the interferometer and is divided into two equal beams by a beamsplitter. One beam is reflected towards one cube corner mirror set , which reflects it back towards the beamsplitter. The other beam is transmitted towards the other cube corner mirror set, which also reflects it back towards the beamsplitter.

Both moving mirrors introduce a continuously changing optical path difference between the two beams (4× in Figure 3-7 on page 14). As the moving mirror is scanned, the two returned beams interfere with different phases. This creates intensity variations due to interference. At a given optical path difference, the interference is constructive for some frequencies and destructive for others. Because the optical path difference is constantly changing, the various frequencies present in the beam are modulated at different rates. The modulation rate of each frequency is proportional to the optical frequency.

[3] Fourier Transform Infrared Spectroscopy, by Peter R. Griffiths and James A. de Haseth, a Wiley-Interscience publication, John Wiley and Sons, 1986.

After leaving the interferometer, the modulated light passes through the sample (see Figure 3-7 on page 14). Some of the IR radiation is absorbed at specific frequencies. The remaining intensity then reaches the detector which converts it into an electrical signal.

Note: *In ABB spectrometers, high-precision cube-corner retroreflectors mounted on a swing arm are used instead of more traditional flat mirrors. The three mutual perpendicular flat mirrors of the cube corner insure that the light always reflects back parallel to the incident beam. This make permanent alignment of the interferometer possible.*

3.4.2 Interferogram

Figure 3-8 shows a representation of the electrical signal from the detector.

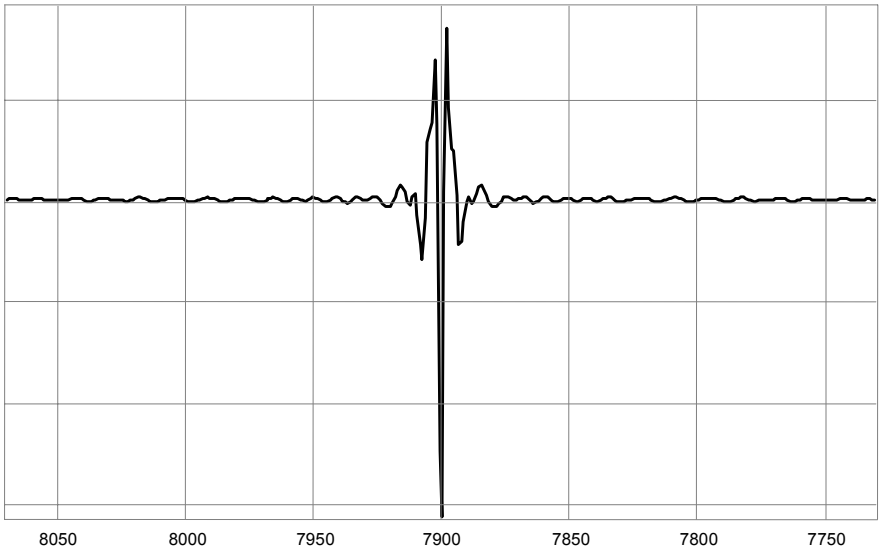


Figure 3-8. Interferogram

This representation is called an interferogram, since it is the result of the interference of all the wavelengths contained in the optical beam which reaches the detector. An interferogram is a graph of the electrical signal at the output of the detector as a function of the optical path difference. The Y-axis is a voltage and the X-axis is the number of He-Ne wavelengths of optical path from the beginning of the scan (or half wavelengths for near infrared).

3.4.3 Fourier Transform

The spectral information contained in the interferogram is retrieved using a Fourier transform. A Fourier transform is a mathematical function that can be used to relate the interferogram to the spectrum of the sample. Performing a Fourier transform on an interferogram yields a raw (or single beam) spectrum. The raw spectrum is a graph of the light intensity at the detector versus the optical frequency. This type of spectrum contains information not only about any sample present in the sample compartment or sampling accessory, but also about the whole instrument, including the source, all the optical components, the ambient air, as well as any contamination there may be in the optical path.

3.4.4 Reference and absorbance spectra

When analyzing a sample, only the information about the sample is of interest—all information not related to the sample has to be removed from the raw spectrum. To do this, before analyzing samples, a reference (or zero) spectrum[h] is acquired and stored for later use. The stored reference spectrum will be used to remove unwanted information from the raw spectra.

[h] *A reference spectrum is often simply called a "reference" or "zero". It is also called a "background spectrum".*

To acquire a reference spectrum, the sampling cell is filled with a blank sample — one which has no spectral signature in the region of interest. In some cases, ambient air is used; in other cases, dry air, dry nitrogen, or a liquid that has no spectral signature in the region of interest is used. Then a spectrum is acquired. Since the blank sample does not absorb light in the region of interest, this reference spectrum only contains information about the instrument. Figure 3-9 shows an example of a typical reference spectrum.

- *the Y-axis is the intensity of light measured by the detector (in arbitrary units*
- *the X-axis is the frequency in wavenumbers (cm^{-1})*

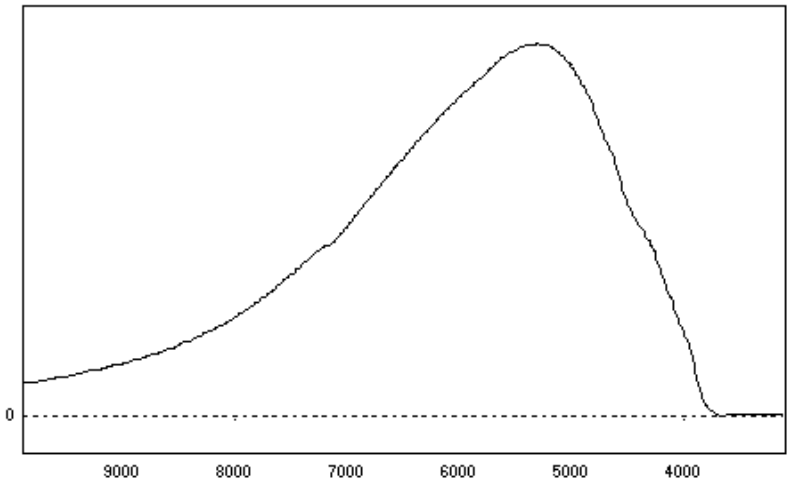


Figure 3-9. Reference spectrum

Although all reference spectra for FT-IR spectrometers have the same general shape, the exact shape depends on many different factors (source, type of transmission cell, type of optical fibers, type of detector, contamination, etc.). In this case, the cell as well as the spectrometer was purged with dry nitrogen. The detector was an extended InGaAs detector at room temperature. Once the reference spectrum is acquired and stored, analyzes of the sample can begin. The system acquires raw spectra of the sample, then processes each raw sample spectrum.

Figure 3-10 shows a reference spectrum and a raw sample spectrum. By comparing the two spectra, it can be seen that the sample absorbs light at different wavelengths.

- *the Y-axis is the intensity of light measured by the detector (in arbitrary units*
- *the X-axis is the frequency in wavenumbers (cm^{-1})*

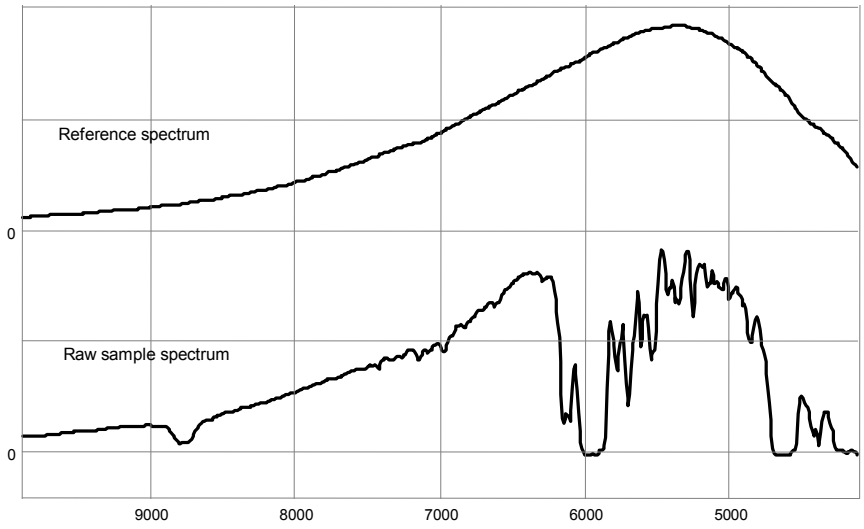


Figure 3-10. Reference and raw sample spectra

Equation 3-4 shows how the information in these two spectra is processed to produce an absorbance spectrum. The value at each wavelength in the sample spectrum is divided by the value at the corresponding wavelength in the reference spectrum, and the negative logarithm taken of the result. This give the absorbance value at that wavelength.

$$A = -\log_{10}\left(\frac{sample}{reference}\right)$$ Equation 3-4

Plotting the calculated absorbance values yields the absorbance spectrum shown in Figure 3-11. This spectrum shows the absorbance of the sample, as described by Beer-Lambert's law (Equation 3-2), for all wavelengths from 4000 cm^{-1} to 10 000 cm^{-1}.

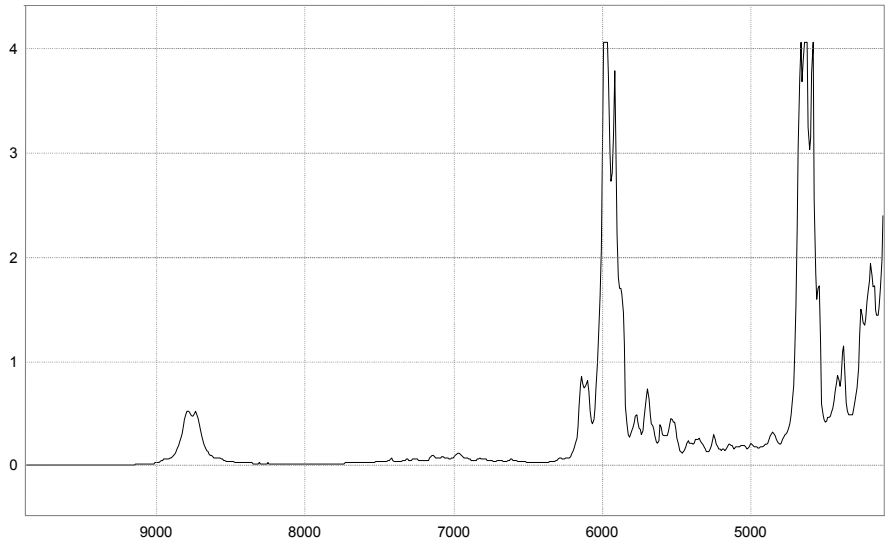


Figure 3-11. Absorbance spectra from a process sample

The advantage of using absorbance spectra is that the concentration of the sample is proportional to the absorbance (as shown in Equation 3-3). It is with such spectra that calibrations for spectrometers are developed.

SPECTROMETER CALIBRATION

In Chapter 3, we saw that the absorbance spectrum of a sample depends on the concentration[i] of the constituents in the sample. If we know the relationship between the absorbance spectrum and the concentrations, we should be able to use the absorbance spectrum to determine (predict) these concentrations. This allows the spectrometer to perform quantitative analysis.

[i] *Concentration is just one type of sample property that can be measured by infrared spectroscopy.*

The process of defining an equation, or a series of equations, which represents the relationship between the absorbance spectrum and the concentrations, is called calibration. The resulting equation, or series of equations, is called a calibration model.[j] Calibration can be very simple, as when measuring a single chemical having a simple spectral signature, or very elaborate, as when analyzing a complex mixture.

[j] *The terms "calibration" or "model" are often used instead of "calibration model".*

To help explain high-performance, multivariate calibration, such as PLS (partial least squares), we will start with basic calibration algorithms, such as peak height, and then progress towards more sophisticated concepts.

4.1 Peak height calibration

In peak-height calibration, the concentration (or other sample property) is related to the height of a peak in the spectrum by a simple linear equation. Peak-height calibration can be used when the constituent of interest has well-resolved bands and no interference with other constituents in the mixture.

The principle behind peak-height calibration will be illustrated using two examples for acetylene calibration. Peak-height calibration is an appropriate calibration algorithm for measuring the partial pressure of acetylene in nitrogen. Acetylene presents a well-resolved band between 700 cm^{-1} and 750 cm^{-1} and nitrogen does not absorb infrared radiation.

4.1.1 Example: Calibration based on a single spectrum

In this example, the calibration is based on the acquisition of a single spectrum of acetylene at a known[k] concentration (40 ppm).

[k] *The sample concentration is measured using a precise primary calibration method, such as gas chromatography (GC) or titration.*

Figure 4-1 shows the acetylene absorbance spectrum. Figure 4-2 shows a closer look at the highest peak. Since this peak is narrow, care must be taken in instrument and sampling system validation to insure that the frequency axis calibration is within specification. Otherwise a small frequency shift could introduce an error in analysis.

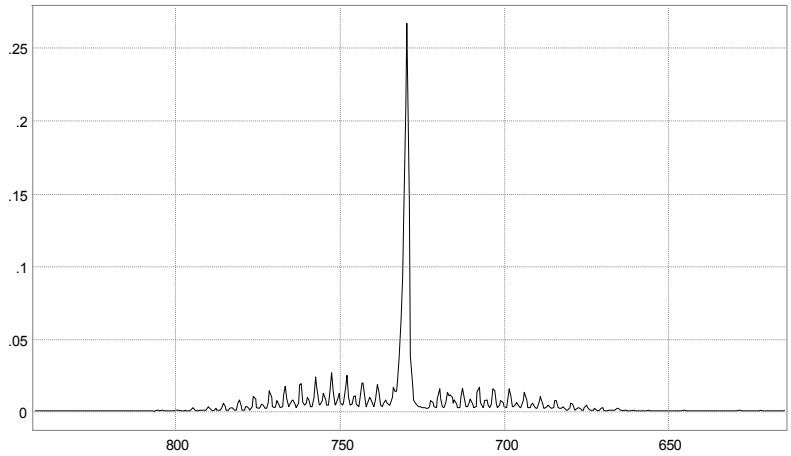


Figure 4-1. Acetylene absorbance spectrum (40 ppm in N_2 at 1 atm.)

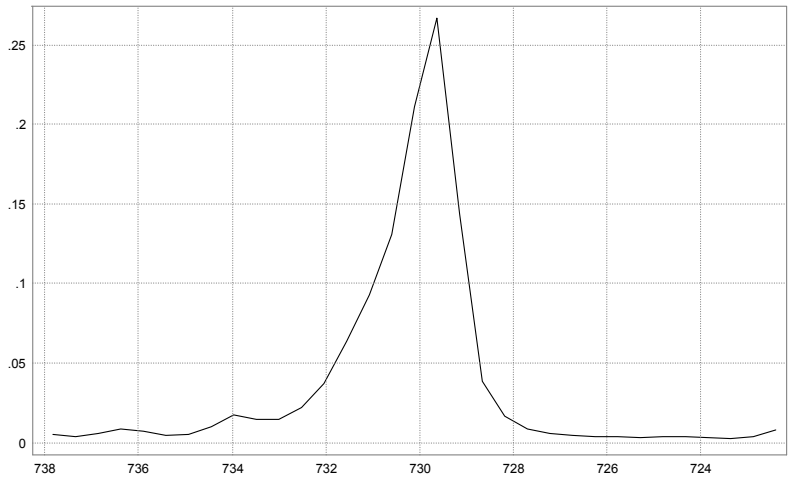


Figure 4-2. Peak absorbance for acetylene (40 ppm in N_2 at 1 atm.)

Table 4–1 shows the measured absorbance and wavenumbers of the main peaks of the spectrum. As shown in this table, at the wavenumber corresponding to the highest peak (729.75 cm^{-1}), the absorbance is 0.267 absorbance units for a concentration of 40 ppm. The calibration is developed using the absorbance at this wavenumber.

Peak center (X) (Wavenumber)	Peak height (Y) (Absorbance)
698.62915	.01576771
703.35478	.01598990
708.06820	.01724872
712.77409	.01674165
719.95797	.01568105
729.75008	**.26730788**
738.65265	.01873724
743.36883	.02066066
748.08314	.02531269
752.77861	.02665214
757.45214	.02433438
762.15293	.01956648
766.83768	.01839582
771.48785	.01488409

Table 4–1. Acetylene (40 ppm in N_2 at 1 atm.)

The calibration constant K_λ in Equation 3-2 on page 9 (Beer-Lambert's law) gives the relationship between the absorbance and the concentration at the selected wavenumber. The constant K_λ is calculated by rearranging Equation 3-2 to give Equation 4-1.

$$K_\lambda = \frac{A_\lambda}{C}$$ Equation 4-1

where C is the known concentration of acetylene

A_λ is the measured absorbance at wavelength λ

Once the constant K_λ has been determined, the concentration of unknown samples, measured under the same conditions, can be predicted by measuring the absorbance at the same wavelength and then using Equation 4-2.

$$C_x = \frac{A_{\lambda \cdot x}}{K_\lambda}$$ Equation 4-2

where C_x is the predicted concentration of acetylene in sample *x*

$A_{\lambda \cdot x}$ is the absorbance value at wavelength λ for sample *x*

For this example, the calibration constant at 729.75 cm^{-1} can be calculated using the absorbance from Table 4–1:

Equation 4-3

$$K_{729.75\ cm^{-1}} = \frac{A_{729.75\ cm^{-1}}}{C} = \frac{0.267\ absorbance\_units}{40\,ppm} \cong \frac{1}{150}\frac{absorbance\_units}{ppm}$$

Now that the calibration constant has been calculated, the concentration C_x for any unknown sample x can be determined from the absorbance at 729.75 cm^{-1}:

Equation 4-4

$$C_x = \frac{A_{729.75cm^{-1}\cdot x}}{K_{729.75cm^{-1}}} = A_{729.75cm^{-1}\cdot x} \times 150\ \frac{ppm}{absorbance\_units}$$

This is a simple linear relationship, as shown in Figure 4-3. The slope is $1/K_\lambda$ and the zero is at the origin.

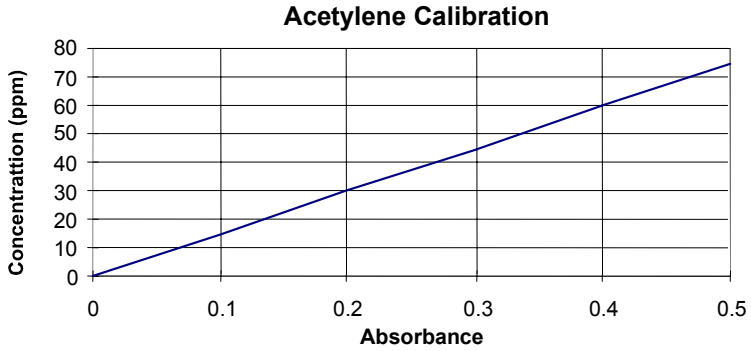


Figure 4-3. Peak-height calibration plot

The concentration of an unknown sample can now be predicted by acquiring a spectrum and using the calibration constant K_λ in Equation 4-4. For example, if the absorbance at 729.75 cm^{-1} for a particular sample is 0.2, the acetylene concentration is:

$$C_x = 0.2\ absorbance\_units \times 150\ \frac{ppm}{absorbance\_units}$$
$$= 30 ppm$$

Note that in this example, there is no indication of how accurate the predictions will be. Peak height determined by means of the height at a single frequency requires particularly good signal to noise ratio performance otherwise the predictions will fluctuate excessively.

4.2 Least-squares regression

When developing a calibration, it is possible to improve the accuracy of the calibration constant by acquiring several spectra of the same known sample, under the same conditions, to get an averaging effect. The calibration constant is then found using a statistical technique called least-squares regression.[1] This is a method of determining the relationship that best describes the observed data.

[1] *Most hand-held calculators as well as many types of software, such as Microsoft Excel™, support least-squares regression algorithms for linear regression.*

This algorithm is referred to as "least squares" because it minimizes the sum of the squares of the differences between the known concentrations and the concentrations predicted by the linear relationship. The differences are squared in order to prevent positive differences from canceling out negative ones when they are summed. This algorithm is illustrated in the following example.

4.2.1 Example: Calibration based on a number of spectra

Peak-height calibration using least-squares regression requires a number of sample spectra acquired on the same instrument under the same conditions.

Table 4–2 shows the absorbance values of the main peak (at 729.75 cm^{-1}) of the acquired spectra. Due to the many possible variations (such as noise, instrumental variations, sample handling errors, etc.) each result is slightly different. The fact that each measurement is slightly different shows that a calibration based on only one measurement would be less reliable.

Figure 4-4 shows a graphical representation of the information in Table 4–2.

Concentration (ppm)	Absorbance (Absorbance units)
40.5	0.261
39.8	0.292
40.4	0.258
39.8	0.289
38.7	0.255
40.5	0.254
40.8	0.290
40.6	0.305
40.6	0.298
39.9	0.299
40.0	0.263
40.5	0.267
40.7	0.291
40.5	0.300
40.6	0.291
39.6	0.297
39.9	0.249

Table 4–2. Acetylene data

There are two distinct groups of data values in this plot. This is due to the fact that the data was acquired by two different operators who had slightly different ways of carrying out the procedure, thus introducing a small systematic error in the data.

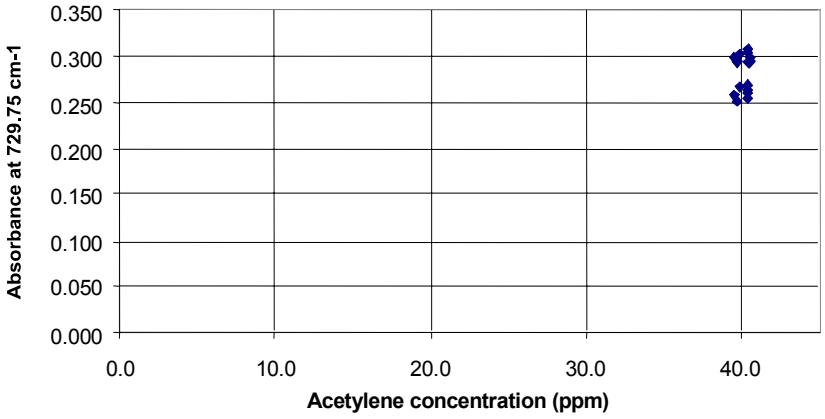


Figure 4-4. Plot of acetylene data

Instead of using the data from only one measurement, as in Example 1, the mean of all measurements, both for concentration and absorbance, are used for the calibration. This is the principle behind the least-square regression algorithm.[4]

The mean concentration is 40.3 ppm with a standard deviation of 0.4 ppm. The mean absorbance is 0.28 absorbance units with a standard deviation of 0.02. These values are used in Equation 4-1 to calculate the calibration constant:

$$K_\lambda = \frac{A_{729.75\text{cm}^{-1}}}{C}$$
$$= \frac{0.28 \pm 0.02\ absorbance\_units}{40.3 \pm 0.4\ ppm}$$
$$\cong \frac{1}{144 \pm 12}\ \frac{absorbance\_units}{ppm}$$

This calibration constant is used in Equation 4-4 to predict sample concentrations. Since this constant was calculated using several measurements, it should be more reliable than that calculated in Example 1. Another advantage of this method is that it gives an estimate of the precision of the prediction (±12 ppm), whereas in Example 1, the precision was unknown.

Note: *When errors are random, the precision of the calibration will increase as the square root of the number of measurements.*

It is important to mention that this mathematical approach (increasing the number of measurements) reduces statistical error but cannot counteract bias due to systematic error in calibration.

When there is more than one constituent in the samples, a separate band must be used for each constituent of interest, and it is necessary to calculate a calibration constant for each constituent.

Peak-height calibration will not produce accurate results if there are interfering constituents that have spectral bands that overlap those of the constituents of interest. In such cases, it is necessary to use more sophisticated mathematical techniques.

[4] Mathematics of Physics and Modern Engineering, by I.S. Sokolnikoff and R. M. Redheffer, Edited by McGraw Hill Book Company, 1966.

4.3 Matrices

Matrix mathematics allows calibration of complex mixtures, or calibration of simple mixtures of very similar materials. It makes it possible to develop calibrations even in the presence of interfering constituents.

In matrix mathematics, instead of using scalar values, vectors and matrices are used. It is not necessary to understand the mathematics behind this, since most calibration software used in quantitative analysis performs this type of calibration. In this document, bold-face type is used in equations to represent vectors and matrices.[m]

[m] Experts in vector and matrix mathematics may see a lack of rigor in these equations, however, the principle as presented here is more illustrative.

4.3.1 K-matrix

To predict the concentrations of constituents that have overlapping bands, it is necessary to perform calculations using many wavelengths. It is also necessary to take advantage of part of Beer-Lambert's law which states that the absorbance values of multiple constituents at the same wavelength are additive. The total absorbance at a particular wavelength can be calculated from the sum of all the constituent concentrations multiplied by their calibration constants at that wavelength.

It is necessary to have at least as many equations as there are unknowns. If more than two constituents are present or more than two wavelengths are used, matrix mathematics (linear algebra) can be used to solve simultaneous equations. The algorithm is known as K-matrix, or classical least squares (CLS). It is based on the following matrix equation, similar to Equation 3-2:

$$\mathbf{A} = \mathbf{KC} \qquad \text{Equation 4-5}^{5}$$

where **K** is a matrix of calibration constants

C is a matrix of the known concentrations of the constituents

A is a matrix of absorbance values at the selected wavelengths

The K-matrix calibration can only be applied in the case where the concentration of every constituent in the sample is known. K-matrix calibration has the advantage of being able to use a large number of spectral intervals for calibration, or even the entire spectrum, to gain an averaging effect for the prediction accuracy of the final model.

[5] It is important to note that the mathematical representation of vectors and matrix equations used in this document does not follow normal conventions. This is done in order to explain the principles of calibration rather than to develop a computer program that will perform the computation.

Equation 4-6 is used to calculate the calibration constants from samples with known concentrations. In K-matrix calibration, many points from each spectrum are used, each point having its own constant, and many measurements are taken. Equation 4-6 is similar to Equation 4-1. The matrix of calibration spectra is used for the numerator, and the concentration matrix for the denominator. The concentration of unknown samples, measured under the same conditions, can be predicted using Equation 4-7.

$$\mathbf{K} = \frac{\mathbf{A}}{\mathbf{C}} \qquad \text{Equation 4-6}$$

$$\mathbf{C_x} = \frac{\mathbf{A}}{\mathbf{K}} \text{ or } \mathbf{C_x} = \mathbf{A}\mathbf{K}^{-1} \qquad \text{Equation 4-7}$$

where $\mathbf{C_x}$ is a matrix of the predicted concentrations of the constituents in sample **x**

K-matrix equations

In the case where two constituents are present at two different wavelengths, two equations are needed:

$$A_{\lambda 1} = K_{\lambda 1 \cdot a} \times C_a + K_{\lambda 1 \cdot b} \times C_b$$
$$A_{\lambda 2} = K_{\lambda 2 \cdot a} \times C_a + K_{\lambda 2 \cdot b} \times C_b$$

In matrix terms, these equations are formulated as:

$$\begin{vmatrix} \mathrm{A}_{\lambda 1} \\ \mathrm{A}_{\lambda 2} \end{vmatrix} = \begin{vmatrix} \mathrm{K}_{\lambda 1 \cdot a} & \mathrm{K}_{\lambda 1 \cdot b} \\ \mathrm{K}_{\lambda 2 \cdot a} & \mathrm{K}_{\lambda 2 \cdot b} \end{vmatrix} \begin{vmatrix} \mathrm{C}_\mathrm{a} \\ \mathrm{C}_\mathrm{b} \end{vmatrix}$$

Note: *This is a simple example using the spectrum of one sample. When many samples are included in the training set, the matrices are larger.*

This matrix equation can be reformulated as: $\mathbf{A} = \mathbf{KC}$

The K-matrix calibration applies the principles described in Section 4.2 “Least-squares regression” to each spectral point involved in the calibration, and uses the average of all the predictions as the output. For approximately equal absorption intensities over many spectral intervals, the gain in sensitivity improves as the square root of the number of intervals.

Because it uses spectral information from different regions, the K-matrix algorithm can be used to develop a calibration even when there is band overlap, provided the concentrations of all the constituents having a spectral signature in the regions selected are known. This is an important improvement over peak-height calibration.

4.3.2 P-matrix

Knowing the complete composition (the concentration of every constituent) of the calibration mixture is not always possible. Moreover, sometimes only the concentrations of a few constituents in a complex mixtures are of interest. In this case, P-matrix calibration, also known as multiple-linear-regression or inverse least squares (ILS), can be used.

With P-matrix calibration, Beer-Lambert's law is rearranged so that the concentration of each constituent is expressed as a function of the absorbance at a series of given wavelengths:

$$C_a = \frac{A_{\lambda 1}}{\varepsilon_{\lambda 1 \cdot a}} + \frac{A_{\lambda 2}}{\varepsilon_{\lambda 2 \cdot a}} + \cdots$$

By combining each absorption coefficient ε_λ and the path length b into a single constant P_λ, this equation can be expressed as:

$$C_a = A_{\lambda 1} P_{\lambda 1 \cdot a} + A_{\lambda 2} P_{\lambda 2 \cdot a} + \cdots$$

This can be expressed as the matrix equation:

$$\mathbf{C} = \mathbf{PA} \qquad \text{Equation 4-8}$$

where **P** is a matrix of calibration constants

C is a matrix of the concentrations of the constituents

A is a matrix of absorbance values at the selected wavelengths

The P-matrix calibration can be applied to systems where only the concentration of the constituents of interest is known, no knowledge of the complete sample composition is needed. The calibration matrix **P** is calculated using Equation 4-9. Once **P** has been calculated, the concentration of unknown samples, measured under the same conditions, can be predicted using Equation 4-8.

$$\mathbf{P} = \frac{\mathbf{C}}{\mathbf{A}}$$

Equation 4-9

P-matrix equations

To predict the concentration of two specific constituents in a complex mixture, two equations are needed:

$$C_a = A_{\lambda 1} P_{\lambda 1 \cdot a} + A_{\lambda 2} P_{\lambda 2 \cdot a}$$
$$C_b = A_{\lambda 1} P_{\lambda 1 \cdot b} + A_{\lambda 2} P_{\lambda 2 \cdot b}$$

In matrix terms, these equations are formulated as:

$$\begin{vmatrix} \mathbf{C_a} \\ \mathbf{C_b} \end{vmatrix} = \begin{vmatrix} \mathbf{P}_{\lambda 1 \cdot \mathbf{a}} & \mathbf{P}_{\lambda 1 \cdot \mathbf{b}} \\ \mathbf{P}_{\lambda 2 \cdot \mathbf{a}} & \mathbf{P}_{\lambda 2 \cdot \mathbf{b}} \end{vmatrix} \begin{vmatrix} \mathbf{A}_{\lambda 1} \\ \mathbf{A}_{\lambda 2} \end{vmatrix}$$

Note: *This is a simple example using the spectrum of one sample. When many samples are included in the training set, the matrices are larger.*

This matrix equation can be reformulated as: $\mathbf{C} = \mathbf{PA}$

The calibration matrix **P** can be seen as a weighted average of all spectra included in the training set used for the calibration, the weighting being given by the concentration matrix. It is this weighting that makes the calibration suitable for cases where unknown products are in the sample. However, these unknown constituents must be correctly represented in the training set, otherwise, the calibration will not be precise. The selected wavelengths must be in a region where there is a contribution of the constituents of interest. A measurement of the absorbance at a different wavelength is needed for each constituent of interest. Due to the dimensions of the matrix equations, the number of selected wavelengths cannot exceed the number of training samples. Otherwise, the calibration will be sensitive to colinearities, and therefore less reliable.

The gain in precision with P-matrix calibration comes at the cost of more work—more calibrated spectra are required, and several trials have to be performed before deciding what spectral regions will be selected and what concentration mixture will be used.

4.4 PLS (partial least squares)

There are many different variations in a system that influence the shape of the sample spectra, such as the constituent concentrations in the sample mixture, inter-constituent interactions, instrument variations, changing environmental

conditions, and differences in sample handling. When developing a calibration, however, the largest variations in the training set spectra would normally be due to varying concentrations of the constituents of the mixture.

Each of these variations has a specific effect on the spectra. For example, a change in the concentration of one constituent will affect the height of all bands where that constituent has a spectral signature. A change in environmental conditions may affect the baseline of all spectra.

The PLS algorithm decomposes the training set spectra into a relatively small number of variation spectra which are called factors. These factors represent the most common variations in the spectra. The number of factors used depends on the number of varying parameters in the training set. PLS weights the factors according to the known sample properties (such as sample concentrations), taking advantage of the correlation that exists between the spectral data and the property values, to produce factors which are directly related to the properties of interest.

Once the factors have been computed, the spectrum of a sample can be reconstructed by multiplying each factor by a different scaling constant and adding the results together. The scaling constants are called scores. (The reconstructed spectrum only approximates the sample spectrum. The difference between the two is called the spectral residual. The spectral residual gives an indication of how closely the reconstructed spectrum matches the sample spectrum.)

Different algorithms have been developed to compute a PLS calibration. Each results in a series of calibration vectors that completely model the relationship between the absorbance spectra and the properties to be measured.

4.4.1 Example: Calibration using PLS

If three spectroscopically active chemical constituents are present in a mixture, it should be possible to describe all of them with two calibration vectors. In this case, because the total concentration is 100%, only two chemical constituents can vary independently, the third one will always depends on the two others.

Figure 4-5 shows the spectral signatures of the three chemical constituents included in the mixture. They are mixed in different concentrations in nitrogen, a gas without a spectral signature in the region of interest. Only

the concentration of ethylene is known and two values are used in the mixture: 106 ppm and 53 ppm.

In this example, no data preprocessing is used.

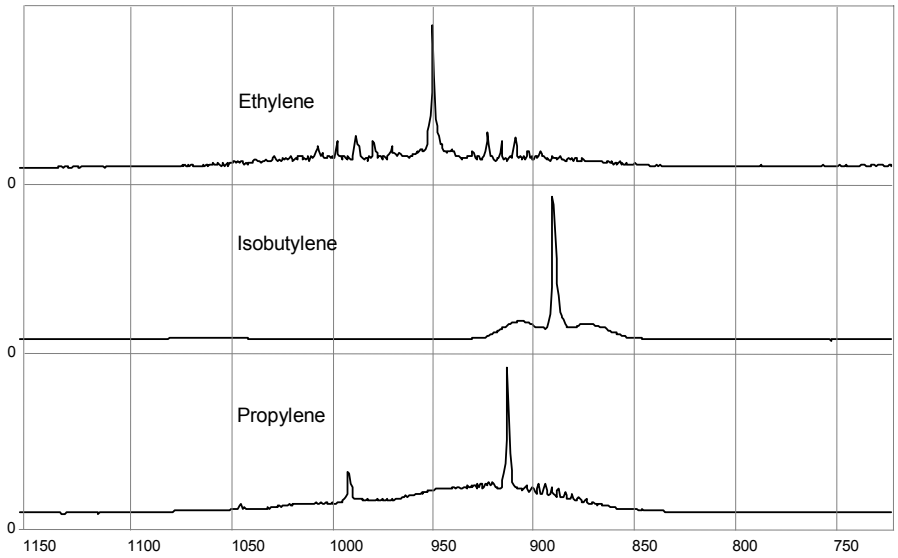


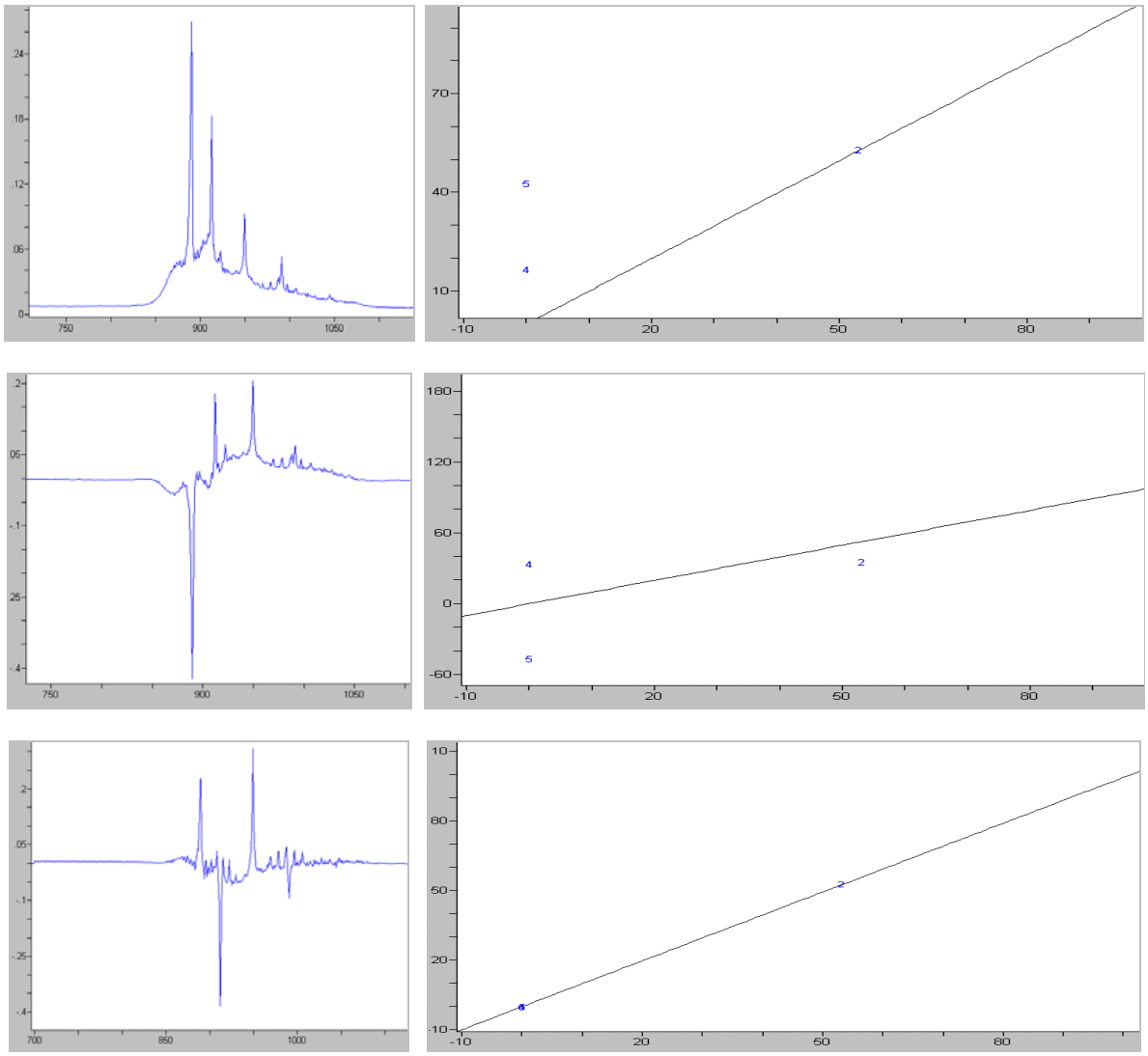
Figure 4-5. Chemical and spectral signature

The calibration is developed using PLS-IQ from Galactic Industries Corp. PLS-IQ suggests using three factors. Figure 4-6 on page 34 shows the three factors computed by PLS-IQ, as well as the correlations between the measured concentration values and the PLS-predicted values.

When an unknown sample is analyzed, a spectrum of the sample is acquired, then the analysis software attempts to reconstruct the sample spectrum from the factors. The three factors are each multiplied by a specific score and then added together to rebuild the sample spectrum. The software determines the three scores which best reconstruct the spectrum. These scores are then used by the software to compute the concentration using the correlation table constructed during the calibration process.

In this example, although there are spectral colinearities and although the concentrations of two chemical constituents are not known, PLS-IQ is able

to give a precise calibration. This is possible, because the generated factors are directly related to the constituent of interest.



PLS factors **Actual vs. predicted correlations for each factor**

Figure 4-6. PLS factors and predicted correlations for each factors

4.5 Validation and good practice

Analysis of chemical composition or physical properties via infrared analysis is based on correlating absorbance spectra with these concentrations or properties as determined by other (primary) techniques. In this sense infrared analysis is a secondary method of analysis which is calibrated against primary techniques.

Given this, it is essential to regularly and independently validate the analysis obtained by infrared against the primary methods. In particular the multivariate techniques of correlation can attain a certain self consistency that may not reflect the true agreement with the primary methods. It is essential to test a calibration against the primary technique using separate samples that have not been used for the calibration development. Also to insure that the calibration is constant in time, a program of statistical quality control is recommended.

For further reading on the subject of calibration development and verification, the following documents are recommended:

"*Standard Practice for Infrared, Multivariate, Quantitative Analysis*", ASTM document E 1655-97.

"*Standard Practices for Applying Statistical Quality Assurance Techniques to Evaluate Analysis Measurement System Performance*", ASTM document D 6299-98.

Note: *ABB follows the above guidelines when developing multivariate calibrations.*

4.6 Selecting the appropriate calibration algorithm

When developing a calibration, it is important to select the appropriate calibration algorithm. Using the most elaborate one may result in wasting time acquiring too many spectra.

Among the parameters to be considered is the real need for precision. High-precision calibration algorithms require many spectra and the use of complex statistical algorithms.

Table 4–1 gives an overview of parameters that should be considered in the choice of the appropriate calibration algorithm.

Calibration algorithm	Number of spectra required	Supports interference from unknown elements in calibration	Able to model non-linearity	Requires specialized software
Peak Height	One	No	Never	No (can be done manually)
Least Square	A few (2 to 30)	No	Never	No (can be done manually)
K-matrix	At least one per spectroscopically active chemical in the compound.	No	Never	Yes (such as CAAP, Array Basic, Microsoft Excel)
P-matrix	At least one per spectro-scopically active chemical in the compound.	Yes	Sometimes	Yes (such as CAAP, Array Basic, Microsoft Excel)
PLS	As many as there are variables in the spectra: spectroscopically active chemicals, instrument spectral variations, etc. (We suggest at least 10 per factor for high precision calibration)	Yes	Often	Yes (Many commercial packages are available: PLS-plus, PLS-IQ, CAAP, Unscrambler, Pirouette)

Table 4–1. Selecting the appropriate calibration algorithm

CALIBRATION TRANSFER

5.1 Introduction

Infrared spectroscopy, both in the mid IR and near IR, is increasingly used for the quantitative determination of chemical and even physical properties for a wide variety of petrochemical, pharmaceutical and processed food products.

Quantitative analysis is based on the linear relationship between concentration and absorbance as expressed by the Beer-Lambert law. For an isolated band, a simple peak-height calibration model will perform well provided there is no interaction effect between the analyte and the product matrix. When bands are overlapped, the peak height model can be replaced by a classical least squares multivariate model which takes account of the overlapping bands. In case of deviations from the Beer-Lambert relationship it is often still possible to develop a model using the Partial Least Squares (PLS) multivariate approach.

ABB has many years of experience in applying FT-IR and FT-NIR spectroscopy to quantitative analysis applications. Many of our FT-IR and FT-NIR spectrometers have been integrated into analyzer systems for specific analysis applications. Usually the same calibration model can be used interchangeably on any analyzer.

ABB FT-IR instruments have 3 unique features that make it possible to obtain highly repeatable spectra on one spectrometer, and to obtain identical absorbance spectra for a given stable sample from spectrometer to spectrometer. These are:

- The instrumental line shape function depends on the scan length of the moving mirror and the uniformity of modulation. It is not dependent on the tolerance of a mechanical slit. It is therefore highly reproducible.

- The position of the moving mirror is constantly monitored with a highly stable internal reference laser which follows the same optical path as the IR beam. Its position is known to 1 part in 10^7 at all times.

- There is virtually no (effective) stray light.

ABB has developed manufacturing methods that insure that every FT-IR and FT-NIR spectrometer produced is highly stable over time, has a highly linear photometric response, and provides identical absorbance spectra from spectrometer to spectrometer.

Note: *The reference spectrum of each spectrometer is not the same. For this reason the absorbance spectrum of a sample is obtained as the Log of the ratio of the sample spectrum divided by the reference spectrum. In this way the effect of differences in reference spectra for different spectrometers is removed.*

The reference spectrum may also change slightly over time (with temperature). As long as the reference spectrum is renewed regularly, this causes no degradation in reproducibility.

The degree of repeatability and reproducibility achieved with the ABB FT-IR and FT-NIR spectrometers sets a new standard of performance that is significantly better than that achievable with any classical dispersive spectrometer.

5.2 Using calibrations on different spectrometers and over time

Calibration transfer is a frequently used term to indicate that a spectrometer is sufficiently reproducible from spectrometer to spectrometer to permit observing the same quantitative results with different spectrometers applying the same calibration model. Sometimes calibration transfer is achieved by reprocessing spectral data to reflect differences between individual spectrometers. In other cases there are spectrometer calibration procedures which when followed permit calibration transfer.

With FT-IR spectrometers it has become possible to insure, during manufacture, that each spectrometer provides the same absorbance or transmittance spectrum to within a small tolerance of error when presented with the same sample. Therefore, with proper attention given during manufacture, FT-IRs can provide calibration transfer without any additional calibration effort or data manipulation. There are also well-defined verification and maintenance protocols that, when followed, will insure that calibrations will not change or drift.

5.3 Repeatability and reproducibility

Prior to developing a calibration model, we can evaluate the performance of the spectrometer in terms of its precision (repeatability) and accuracy of measurement.

5.3.1 Spectrometer repeatability

Repeatability is conceptually simple—it is the precision of repeated measurement of a spectrum. However there are a number of circumstances to be considered. A common way to demonstrate repeatability of the spectrometer is to repeat the recording of (reference) spectra without any sample in the IR beam.

By computing the ratio of two repeat spectra we can evaluate the deviation in repeatability. This is commonly called the "open beam 100% line". Open beam 100% lines evaluated for two successive spectra taken one after the other provide a measure of short-term repeatability. Also we can record open beam reference spectra some time apart to get information on long-term repeatability. This is a measure of stability.

Interpreting open beam 100% line data provides several important features of spectrometer performance:

- It provides an estimate of the sensitivity of the spectrometer:

  In the ideal case, the 100% line will be a straight line at 100% over a wide frequency range. With scale expansion eventually the (random) noise of the spectrometer will become evident. Noise levels as small as 0.003% T rms (0.000015 Absorbance rms) for a scanning time of 1 minute are not uncommon. Please consult the spectrometer specifications for the expected signal-to-noise ratio of your spectrometer, your spectral region of interest and your measurement setup.

- It provides an overview of variations that exceed the noise level:

  In FT spectroscopy, the physical measurement is not performed on the spectrum but rather on its interferogram. The information regarding the overall intensity of the spectrum is represented by only a few measurements near the centerburst (ZPD) position. Both this statistical under-representation and the fact that the interferogram signal varies greatly at the centerburst dictate that the overall intensity of the spectrum is less well measured than the finer details. It is therefore common to see a 100% line that is repeatable to within a straight line with random noise but with a position that deviates from 100% by more than the random noise. This is the 100% line offset and tilt.

  In quantitative analysis we are interested in the determination of band heights. An offset and a tilt of an otherwise straight 100% line will not influence band heights when measured with respect to their adjacent baselines. With FT-IR it is common practice to develop calibration models where the band heights are referenced to a local baseline. This significantly improves the repeatability of analysis. This is called baseline correction. Taking the first derivative of a spectrum removes the offset and creates a new offset proportional to the tilt of the original spectrum.

Some FT-IR spectrometers may display curved or wavy 100% lines where the curvature or waviness exceeds the random noise. This is generally due to an optical component that contributes to the spectral shape and which is not stable over time. Curved or wavy baselines occur more readily when comparing open beam spectra taken some time apart, depending on the long-term repeatability. Spectrometers that manifest curved or wavy 100% lines may show drift or reduced repeatability (with respect to expected repeatability based on signal-to-noise ratio) in analysis methods. Frequent renewal of the open beam reference is a way to reduce such drift from influencing analysis results.

Examples of optical elements subject to unstable spectral response are: interference filters, beamsplitters with complex coatings, antireflection coated optics, fiber optic cables and any device with two flat parallel faces close together such as capillary liquid cells. The spectral response of these elements tends to undergo shifts in frequency with small variations in temperature.

5.3.2 Analysis repeatability

Analysis repeatability is tested by repeat analyzing the same sample a number of times. Short-term repeatability such as is obtained by analyzing a sample 10 or 20 times in a row shows the precision of analysis of the analyzer. If repeat determinations are done over an extended period of time we also obtain an evaluation of the drift of the analyzer.

Repeatability can be evaluated in several ways. If analysis is repeated with the same sample stationary in the sampling accessory, we obtain an evaluation of the repeatability of the spectrometer. This is useful to assess the influence of random noise in the spectrum on analysis repeatability. The relationship between random noise in the spectrum and the errors in repeatability is not straightforward. It depends on the response in the spectrum for a change in concentration, and on interference in the spectrum due to other analytes, etc. In general, the static repeatability will be proportional to the random noise in the spectra. This in turn can be improved with longer signal averaging. As a general rule the random noise in the spectrum decreases inversely as the square root of observation time.

Random noise also varies linearly with resolution. Over-resolving spectra simply increases the noise without increasing band intensities. The optimum resolution is where bands are slightly under-resolved.

A comparison of the static sample repeatability and the repeatability obtained by taking a new sample repeatedly from the same sample lot will show

the influence of sample preparation, presentation, and the sample accessory on the repeatability. If this repeatability is worse than the static repeatability, the signal-to-noise ratio of the spectrometer is not the limiting element in the analysis performance. There can be many factors degrading the analysis repeatability with respect to the static repeatability. Some of these are sample homogeneity, variations in sample presentation such as variability in the placement of the sample in the IR beam, variability in absorption path length etc.

5.3.3 Spectrometer reproducibility

Even though there are several certified standards for the verification of spectrometer accuracy, the accepted tolerance of these standards is not compatible with the high degree of repeatability that can be achieved with FT-IR and FT-NIR. Many analysis applications have become feasible only because of the high degree of repeatability that FT-IR and FT-NIR can offer. These standards may be used to verify some conformance to accepted norms of spectrometer accuracy but will not provide adequate spectrometer control for many analysis methods.

At ABB, we have developed several spectrometer tests, some with standards, that permit verification of the spectrometer reproducibility to a level that closely matches the repeatability.

The reproducibility of an FT-IR spectrometer depends on three relatively independent factors:

- the frequency scale calibration
- the instrumental line shape function and its resolving power
- the effective “Fourier stray light”

“Fourier stray light” is the presence of spectral intensities at frequencies where the light does not have these frequencies. An example is harmonic distortion creating (false) intensities at twice the true frequency of the light. Photometric linearity is an important element for absorbance reproducibility. It is not verified directly but it related to Fourier stray light. When the Fourier stray light is controlled to below an acceptable limit, the photometric linearity will be likewise controlled to a similar tolerance. In the ABB FT-IRs and FT-NIRs spectrometers, the three factors mentioned above are controlled so that the absorbance spectrum of a stable sample recorded with each spectrometer is exactly the same to within a small error.

The validation of spectral reproducibility is performed by measuring a stable sample and comparing its absorbance with that from other spectrometers produced. At ABB, all FT-NIR spectrometers are validated by measuring an absorbance spectrum of high purity Toluene in a liquid cell with 0.5-mm path length and maintained at 28°C ±1°C. Each spectrum is compared against a composite standard Toluene spectrum that consists of the average of a group of spectra obtained from different spectrometers produced. The difference after baseline correction and scaling to account for small path length errors is maintained within 0.002 A for all spectrometers produced.

5.4 Importance of the primary method

A calibration model represents the relationship between some property or several properties of a sample and its IR spectrum. There are very few cases in which an a priori band strength in a spectrum is known precise enough to use directly for analysis. The band strength of an analyte can be affected by the matrix of the product and can vary with temperature. For this reason it is common to calibrate the IR spectrometer by means of the IR measurement of reference samples and correlating the reference values of a property with the spectra. For this, the reference values of the property must be measured by a (primary) technique, or method, other than IR analysis. The precision of analysis by the primary method dictates the quality of IR analysis derived from it.

When a method has been developed, we can estimate the error in agreement of the IR analysis with the primary method by evaluating the RMS deviation of the values derived by IR from the primary values. This deviation includes errors in the repeatability of the primary method as well as the IR spectrometer.

To distinguish the spectrometer repeatability from the repeatability of the primary method, we can separately estimate the repeatability of the spectrometer by repeat analyzing the same sample many times. It is often seen that the spectrometer repeatability is better than the repeatability of the primary method. This suggests that as the precision of the primary method improves, the analysis by IR will improve.

If the precision of the primary method is not well known, it can be determined by several statistical methods. The most reliable method is a round robin test that includes all the variations that can occur in analysis; e.g. different operators, different test setups, etc. A simple method is the Standard Deviation of Duplicate Determinations (SDD). A work sheet for the determination of SDD is available from ABB.

5.5 Definition of calibration transfer

When validating the performance of an analyzer with a pre-established calibration method, we determine the error of the IR analysis compared with analysis of the same samples by the primary method. This is called the Standard Error of Prediction (SEP). The validation sample set may be several samples or an extensive set prepared to determine any trends in the deviation between analyzer and primary method.

A calibration is considered transferred successfully from one analyzer to another if the SEP for a validation sample set is the same to within the statistical error for the set.

5.6 Insuring long term stability and calibration transfer

To insure constant analysis with an ABB FT-IR or FT-NIR spectrometer, it is essential to insure that it continuously meets its specifications. Performing spectral quality control tests using a program such as AIRS or SpecTest insures this. These tests are described in the manual for each program. It is also prudent to establish a program of statistical quality control (SQC) for the analysis performance. This is done by regularly analyzing one or several test samples for which the reference values are well known.

The frequency of testing is not readily specified because the FT-IR or FT-NIR spectrometer can operate for long periods with no drift in analysis. It is essential however to run all the tests if any changes have occurred. For example if the source has been changed or the sampling accessory has been removed and replaced, all tests should be performed. Also, if the analyzer has been moved around or has not been used for a long time it is advisable to run the tests.

Before transferring a calibration from one analyzer to another, all spectral quality control tests should be performed for both the analyzer where the calibration originates from, and the one on which the calibration is to be installed. If there are differences in the results beyond the accepted norms, these should be reconciled before validating the calibration on the target analyzer.

5.7 Influences on absorbance and transmittance spectra

It is not totally surprising that the absorbance or transmittance spectrum of the same sample measured on different spectrometers should give the same result. The transmittance is derived from the ratio of the sample plus instrument spectrum divided by the instrument spectrum. Here the instrument effect should cancel. The absorbance is the log of 1/T and should have the same cancellation of instrument response. The instrument spectrum is frequently also referred to as the reference or background spectrum.

There are some instrument conditions that influence the absorbance and transmittance spectra. For example, if the absorbance spectrum of a sample was recorded at two different resolutions, there may be differences between them where there are narrow bands in the spectrum. So resolution can cause a difference in the representation of the spectrum due to instrument effects even though the instrument response was "removed" by the ratio with the reference spectrum.

Infrared spectroscopy is based on the precise reproducibility of the positions of bands. Most quantitative analysis techniques do not allow for a matching of spectra by means of a shift in the frequency scale. So errors in the calibration of the frequency scale from spectrometer to spectrometer is another way in which spectra will not be reproducible.

Finally, spectrometers may have spurious intensities that are due to photons that do not have frequencies where these intensities occur. This is referred to as a "stray light" signal. Because the absorption due to a sample at a given wavelength does not act on the stray light at this wavelength, the stray light is an additive component in the reference and is not accounted for by the ratio of sample plus instrument spectrum divided by the instrument spectrum.

In summary, reproducibility of spectra from spectrometer to spectrometer is affected by the instrumental line shape function, including the resolution width, the frequency calibration and the control of stray light.

5.7.1 Stray light

The presence or absence of stray light is determined by observing the spectrum of a sample that has regions of total absorption. In these regions, the intensity in the spectra should go to zero. Traditional grating spectrometers suffered greatly from stray light. This arose from scattering at the grating surface, grating ghosts, and poor shielding of light through the spectrometer.

As long as no light from the output of the spectrometer can pass around the sample, FT-IR spectrometers exhibit extremely low levels of stray light. However, an appearance of stray light can be observed when the detector and or signal processing electronics exhibit nonlinearity. As in audio systems, signal nonlinearity results in harmonic distortion. Harmonic distortion means that spurious signals can occur at multiples of the frequency of a given signal. This causes effectively stray light.

In the manufacture of ABB spectrometers, great care is taken to insure that harmonic distortion is virtually absent in the signal processing electronics. This

aspect is tested with all spectrometers produced and must meet rigorous standards. Typically, when using a highly linear detector, the amount of stray light is well below 0.1% of the intensity at high throughput.

5.7.2 Frequency scale calibration

Thanks to the use of an internal He-Ne laser, the frequency scale of ABB FT-IRs is highly reproducible. The frequency of the laser is stable to better than 1 part in 10^7. Nevertheless, small errors in frequency can be introduced by the residual skew angle between the axis of the He-Ne laser and the axis of the IR beam. The He-Ne laser is employed to measure the optical retardation of the IR beam through the interferometer. With an angle θ between the two beams, the IR beam retardation is measured as the He-Ne laser wavelength multiplied by the cosine (θ). An alignment error of $\theta = 0.0033$ radians (3.3 milliradian) results in a frequency error of 0.0005 %. This corresponds to an error of 0.04 cm^{-1} at 7300 cm^{-1} and is the maximum allowable error for any ABB spectrometer.

5.7.3 Line shape function and resolution

5.7.3.1 Scan length and apodization

The resolution of an FT-IR is firstly set by the length of the scan and the apodization function selected. In the ABB spectrometers, the length of scan is selected according to the desired resolution and is based on a precise, reproducible count of the number of laser wavelengths the mirror travels. It is highly repeatable and reproducible from spectrometer to spectrometer.

The apodization function is a mathematical function applied on the numeric data and is also repeatable and reproducible. However, software programs frequently permit selection of different apodization functions. In order to achieve calibration transfer, a consistent choice of apodization function must be applied. The default selection in all of the ABB software packages is “Cosine” apodization. This provides a well behaved line shape function and is recommended.

The selected resolution can vary when the modulation of the spectrometer is not consistent over the scan distance. ABB spectrometers have excellent consistency of modulation along their scan. Therefore the resolution based on the scan length is consistently achieved to within a few percent of the line width.

5.7.3.2 Distribution of angles of IR beam

Resolution is also affected by the distribution of angles with which the IR beam traverses the spectrometer. (See Kauppinen et al *(J. Kauppinen and P. Saarinen, Applied Optics. 31, 69 (1992)) for a detailed account of line shape functions) As the divergence increases away from the optical axis, the resolution width

increases as the square of the divergence angle. The increase in resolution width is proportional to the frequency where it is determined; i.e. the increase in width is greater at high frequencies than at low frequencies. The increase in resolution width occurs only on the low frequency side of the line shape function. This means that the effect of the distribution of angles is measurable by a shift in frequency in the spectra: The increase in resolution line width is twice the frequency shift.

Example:

Operating in the near IR in the region of 7000 cm^{-1}, a near IR source element (tungsten halogen lamp) has a filament length of 2 mm and width of 0.9 mm. It is placed at the focus of the collimator with focal length of 40 mm. As a result, the distribution of the light falls between a minimum angle of 0 and a maximum angle of ±0.025 radians (±1 mm/40 mm) with respect to the optical axis. The addition to the resolution width of this angle distribution is given by Equation 5-1. The amount of shift in frequency introduced by the angle distribution is 1.1 cm^{-1} at 7000 cm^{-1}.

$$(1 - \cos(\text{half angle})) \times \text{frequency} = (1 - \cos(0.025\ \text{rad})) \times 7000\ \text{cm}^{-1} = 2.2\ \text{cm}^{-1}$$ Equation 5-1

5.7.3.3 Jacquinot stop

The distribution of angles is usually determined by the size of the source in the focal plane of its collimator. It can be further controlled by a Jacquinot stop either at the focal plane of the collimator or the output focusing mirror. The latter is the sample beam focus.

The basic ABB spectrometers have no Jacquinot stop. However a Jacquinot stop can be defined by either an aperture placed at a focus conjugate to the source or by a sampling accessory that restricts the angular divergence at the sample beam focal plane.

In case that the Jacquinot stop is defined by the source element it is essential to insure that the same type of element is always employed when replacing the source element and that it is aligned correctly. The correct alignment as well as the correct distribution of angles of the IR beam can be verified using the appropriate software (see Section 5.8).

When the sampling accessory restricts the full light output of the source element, the Jacquinot stop is effectively defined by the sampling accessory.

Examples of accessories that restrict the full light output are:

- Any fiber optic interface:
  - In the sample compartment of an MB Series Spectrometer
  - At the output of a Network*ir*
- The disposable vial accessory:
  - This has a slit to insure that light passes through the diameter of the vials.

During the manufacture of the ABB FT-IRs and FT-NIRs spectrometers, particular attention is paid to alignment of the internal laser and IR beam with respect to the optical axis of the spectrometer. As well, the scanning quality is verified to determine that there is no loss of modulation as a function of moving mirror position. Finally the data acquisition electronics are carefully tested to insure that there is minimal distortion. These measures insure that the 3 factors influencing reproducibility are controlled. As can be seen above, both the frequency calibration and the line shape function are also dependent on the way the IR beam passes through the spectrometer and the sampling accessory (IR beam divergence distribution). It is necessary to control this in operation.

5.8 Verification of IR beam divergence effect

The IR beam divergence is the aspect most likely to vary when using the spectrometer. This is because it is not only determined by the spectrometer optics but also by the sampling accessory and possibly the sample itself. Any change in IR beam divergence will manifest itself by changing the frequency calibration and the resolution width.

These parameters are verified by measuring the position (frequency) and width of a narrow spectral line of the residual water vapor in the air path of the spectrometer using the appropriate software.[n] The test is performed at 2 cm^{-1} apodized resolution. At this resolution, the line position can be reliably determined to within 0.01 cm^{-1}. Also, at this resolution, the effect of changing divergence is manifested in slight changes in line width. Note that the spectrometer must not be thoroughly purged when performing this test.

[n] The Frequency Validation test in AIRS or SpecTest can be used to measure the frequency of the water vapor line but not its width or line, shape. In most cases, this is sufficient because frequency and line width are closely related.

If the sampling accessory and the sample are sufficiently large to not obscure any part of the IR beam, their alignment is less important than when they

obscure the beam. In this case the IR beam divergence effect comes mostly from the source and its alignment. It is essential to follow the appropriate alignment and verification procedures when changing the source. It is also essential to return to the same frequency validation result as prior to the source change. The tolerance of ±0.04 cm^{-1} is usually easy to maintain.

If the sample accessory and/or the sample obscure part of the IR beam, they will be the defining elements of the divergence. In this case, to achieve consistent results, the accessory and sample must always obscure the beam the same way, including for the case of taking a new reference. Unless the sampling accessory has been supplied by ABB and comes with a test report, the result of the frequency validation test with a user supplied accessory will not correspond to any results specified by ABB. In this case the user must maintain a record of the frequency validation test results for the analysis setup used.

Normally no adjustment is made to the frequency axis as a result of shifts due to changing divergence. A consistent divergence will give a consistent frequency calibration. If it is necessary to match up spectra recorded with different divergence conditions, a software utility is available in AIRS and as a separate module to shift the frequency axis.

Note: *All spectral analysis is based on a precise assignment of spectral intensities to the evenly spaced discrete spectral data points. Changes in divergence introduce slight shifts in the position of spectral features with respect to the data points.*

Never change the frequency assignment of the He-Ne reference laser in order to adjust the frequency scale. This would have the effect of changing the assigned frequencies for the discrete spectral data points but it will not re-align the data points with respect to spectral features.

TEMPERATURE EFFECTS ON THE DETECTOR AND FIBER-OPTIC CABLES

Variations in ambient temperature modify the response of the detector used in a spectrometer-based analyzer. They also alter the spectral behavior of fiber-optic cables used to connect the analyzer to the remote sampling accessories. Both of these phenomena affect the acquired spectra, and therefore, the results of the analyzes. The effect of temperature variations is different in different spectral regions. There are two ways to deal with temperature effects:

- select only those spectral regions where it is relatively easy to compensate for the effect, and build a method which includes compensation. (This is the more economical solution.)
- control the temperature of the detector and/or of the fiber-optic cables. (This is a more costly solution.)

When planning an analyzer system, it is important to understand these considerations in order to make the most judicious design decisions.

6.1 Detector

Figure 6-1 shows how the response of an InGaAs detector varies with temperature during a long-term stability test.

The test was performed by slowly varying the detector temperature from 25°C to 35°C and acquiring spectra at regular intervals.

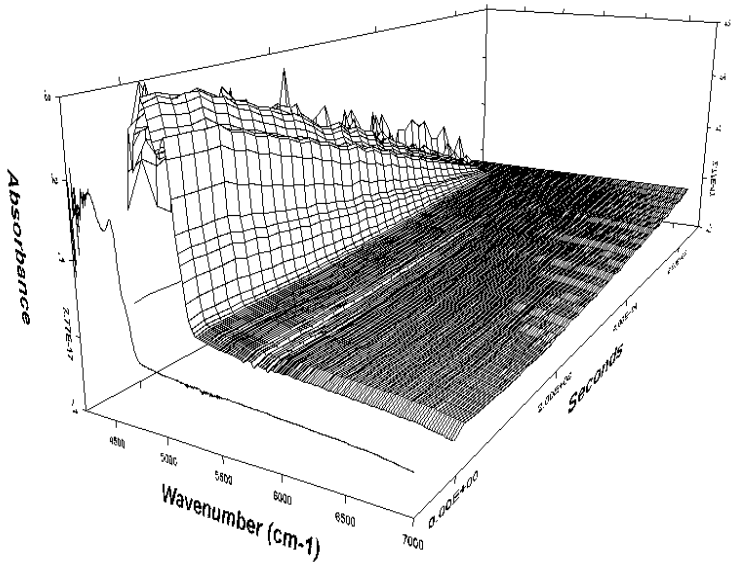


Figure 6-1. Spectra of a long-term InGaAs detector stability test

[o] PCA (Principal Component Analysis) is a data reduction technique which, like PLS (Partial Least Squares), decomposes a set of spectra into mathematical spectra called factors which represent the most common variations to all the data.

At frequencies where the energy of the incident radiation is sufficient to fully turn on the detector (the region above 5000 cm^{-1} in Figure 6-1), the variation of detector response with temperature is a monotone function that is easily modeled by a small number of PCA[o] factors.

Figure 6-2 below shows that 3 factors are sufficient to model the variation of detector response with temperature in region above 5000 cm^{-1}, since the fourth factor contains only noise. If baseline correction is used, 2 factors usually suffice to model the variation. If possible, only this region should be selected for analysis when building the method.

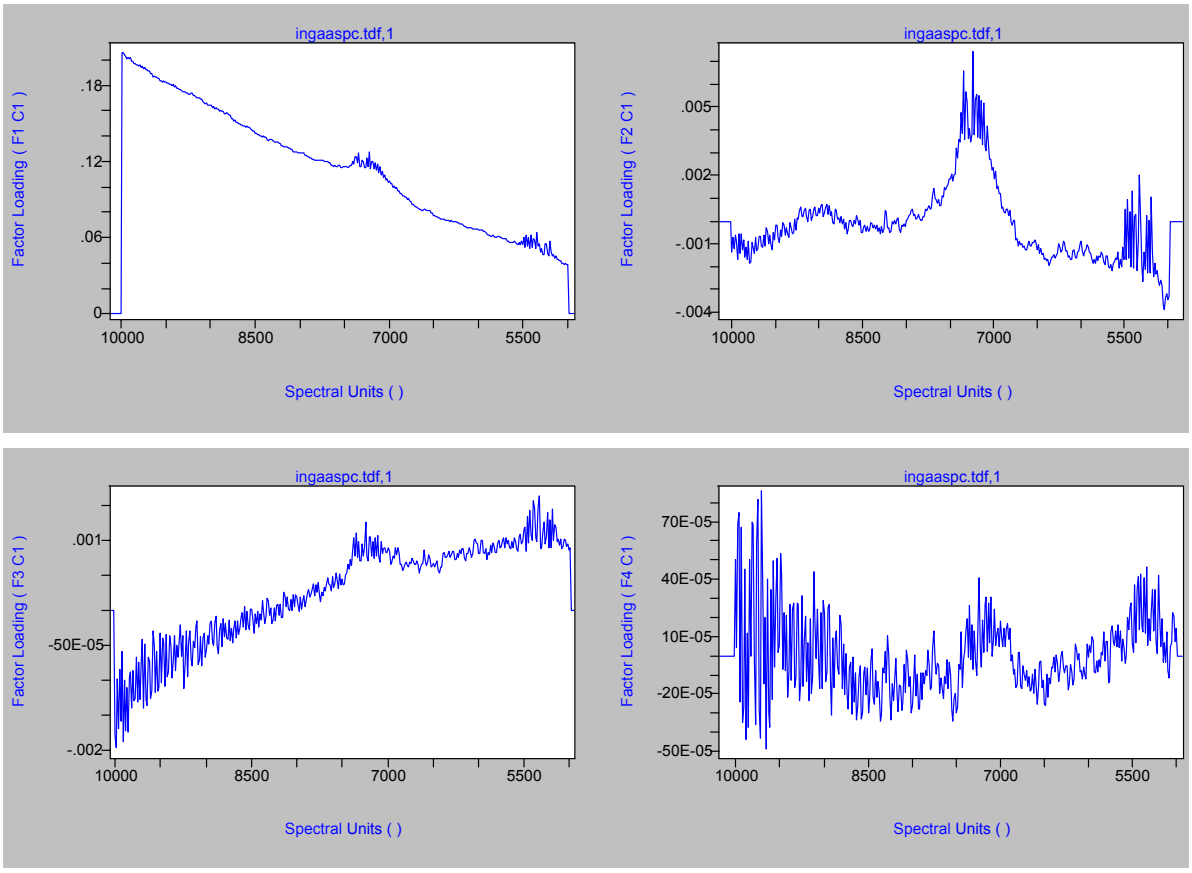


Figure 6-2. PCA factors for modeling detector behaviour above 5000 cm^{-1}

At lower frequencies, down to the cutoff frequency of the detector, modeling of the variation of detector response is not satisfactory, even with as many as 20 factors. Figure 6-3 shows that there is no convergence to noise after the first 9 PCA factors.

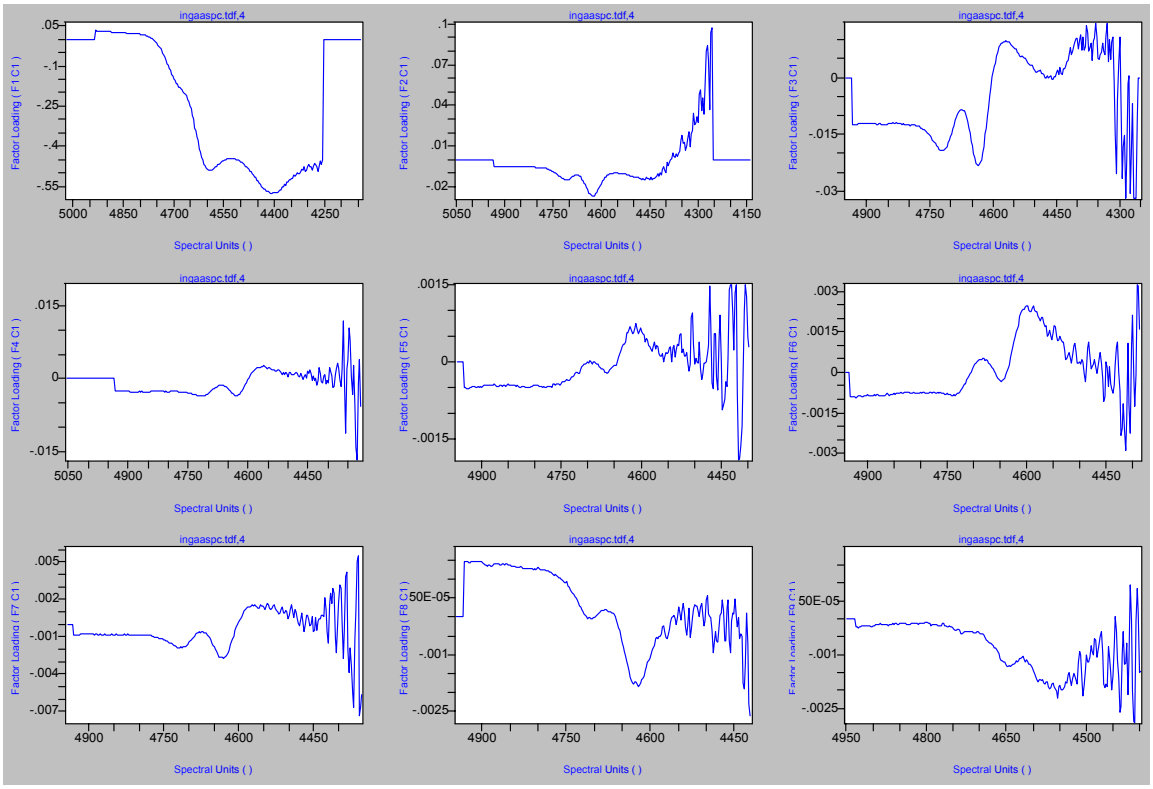


Figure 6-3. PCA factors in an attempt to model detector behaviour below 4200 cm^{-1}

If high precision analysis is required in this region, the detectors should be thermo-electrically cooled. The cooling unit, while lowering the temperature of the detector element also stabilizes its temperature.

Some limited precision calibrations may work using this lower spectral region without detector temperature stabilization. This is because of the relatively strong second overtone and combination band of C-H stretch. However, the second overtone and combination band is usually used for high precision applications with ambient temperature detectors.

6.2 Fiber-optic cables

Fiber-optic cables have an absorbance peak in the NIR region of their spectral response which corresponds to the OH-band (at 7230 cm^{-1}), as shown in Figure 6-4.

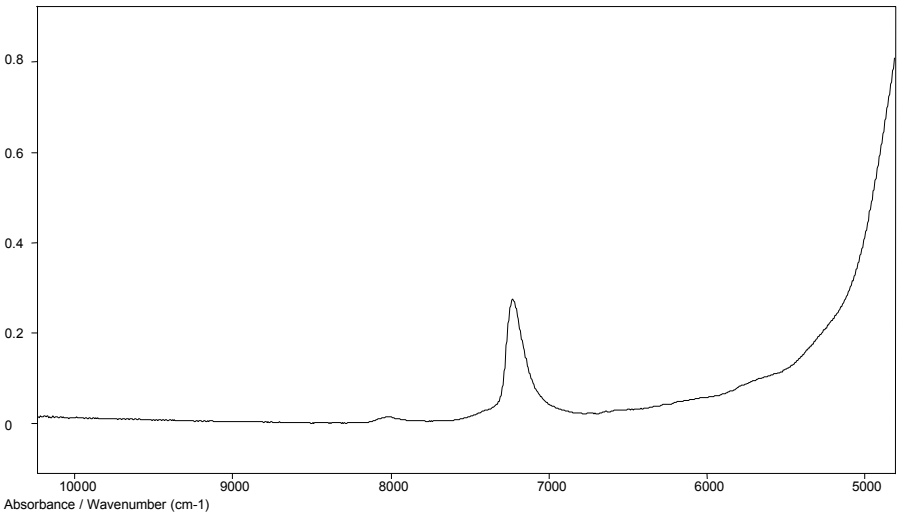


Figure 6-4. Spectral response of a 100-m fiber-optic cable

Since the absorbance is high in this band, the signal attenuation is high (roughly 30 dB/km for ultra-low OH fibers). With long fibers, this significantly reduces the transmittance in this band. Absorption in this band varies with temperature. For these reasons, it is recommended to excluded this band from the spectral regions selected for analysis and to use ultra-low OH fibers. Outside of the OH band, the fibers should display no CH or NH spectral signature, and the effect of temperature variations should be taken into consideration.

Figure 6-5 shows the behavior of a fiber as the temperature is varied over a 5°C range. The OH band is clearly seen to evolve during the test. The absorbance spectrum corresponding to the last measurement appears in the foreground. Above the OH band, the variation is essentially a monotone function which can be easily modeled by 2 or 3 PCA factors, as shown in Figure 6-6. Below the OH band, the variation is usually more pronounced. This region is affected by the presence of water. The behaviour of this region can be modeled, but at the cost of increased complexity. Including this region is roughly

equivalent to adding 2 constituents to the method (i.e. the number of spectra required in the training set by is increased by a factor of 4).

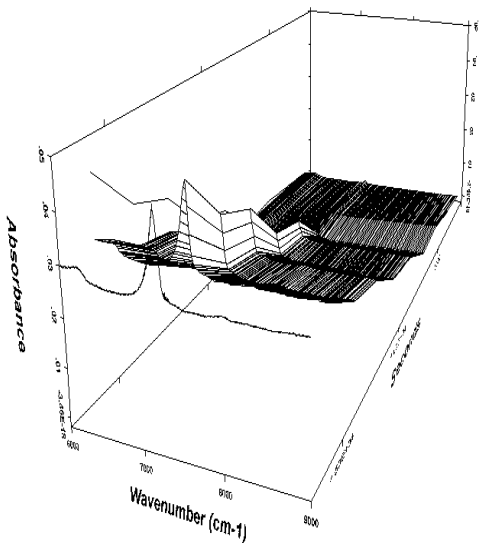


Figure 6-5. Spectral response of an optical fiber as temperature is varied

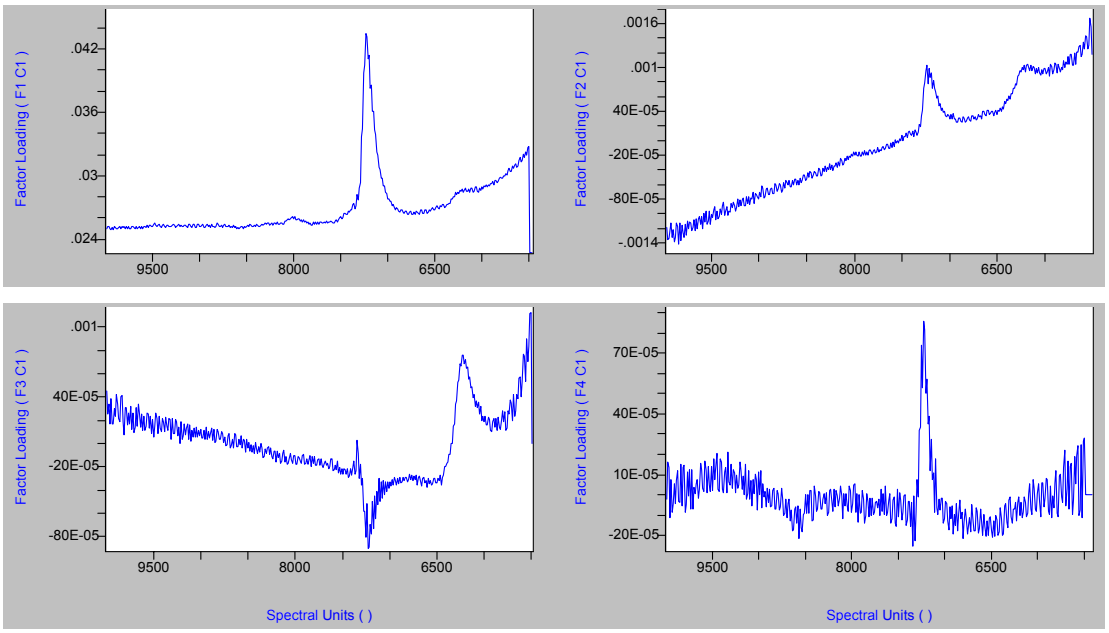


Figure 6-6. PCA factors for modeling fiber-optic behaviour above the OH band

6.3 Recommendations

The detector(s) should be selected to provide the sensitivity and spectral range required for the application. If high precision analysis is required near the detector cutoff, the detectors should be thermo-electrically cooled.

To avoid problems due the fiber-optic cable behaviour:

- Use ultra-low OH fibers
- Avoid including the OH band in the selected spectral regions
- If possible, use only the region above the OH band. Using the region below the OH band increases the complexity of the method.

CHAPTER 7

PURGING

7.1 Principles and objectives

The ABB spectrometers can be equipped with purge inlets. Purging is recommended for spectrometers which have hygroscopic optical components or if ambient water vapor may interfere with measurements.

The recommended purge flow rate into the spectrometer is 5 L/min. Once the spectrometer is purged, a continuous flow rate of 1 L/min is normally sufficient to maintain the purged condition.

An automatic relief valve is installed to prevent accidental over-pressurization of the spectrometer. This relief valve opens if the internal pressure exceeds 1/3 psi.

For purge gas requirements and connections, refer to the documentation provided with your spectrometer.

7.2 Using Nitrogen

Purging should be done using dry nitrogen when an application is sensitive to changes in air humidity, or when the sensitivity of the analyzer is compromised by the absorption of CO_2 and H_2O found in normal concentrations in the ambient air. When water vapor alone is to be eliminated, dry, oil-free instrumentation air can be used for purging (see Section 7.3 below).

7.3 Using Dry Air Generators

If a supply of dry nitrogen is not available, the spectrometer can be purged with dry, oil-free instrumentation air. For this, **ABB** recommends the use of a dry air generator.

Whatman Inc. manufactures excellent dry air generators that either work from plant compressed air (model 75-45 is recommended) or from its own compressor (model 74-5021 is recommended). Both units can deliver up to 14 liters per minute of water free (-73^{o}C dew point) and CO_2 free (<1 ppm) purging gas. These dryers have proven to be a good, cost-effective alternative to the use of nitrogen.

Note: *The information given below is applicable to the Whatman Air Dryer model 75-45.*

If you are using any other model, use the following information only as a general guide.

7.3.1 Installation

The Whatman Air Dryer model 75-45 may be table mounted or wall mounted. The handle on top makes it well suited for portable or temporary setups.

- Pipe the supply air (60-125 psig) to the 1/4" NPT inlet port. To facilitate routine maintenance, we recommended the use of a ball type shut-off valve before the dryer.

[p] *The Whatman type 72-400 Flow Control Unit offers these components in a ready-to-use accessory.*

- It is important to control output pressure and flow to the process or spectrometer, so as not to exceed the rated capacity of the dryer. We recommend the use of a pressure regulator and flow control valve.[p]

- The transformer, supplied with the Whatman Air Dryer model 75-45, must be plugged into a suitable 115/230 VAC supply. The line cord is then plugged into the power socket on the dryer.

The transformer is not a universal power supply; make sure your unit is ordered to work with your utilities.

- The Whatman Air Dryer model 75-45 is supplied with a coalescing pre-filter, with integral automatic float drain. The 1/8" NPT drain port may be piped away to a suitable containment device or drain line.

7.3.2 Maintenance

The Whatman Air Dryer model 75-45 is essentially maintenance free. The only required maintenance is to change the filter element in the coalescing pre-filter (Whatman part No. 100-12-BX). For most installations, this filter element should be changed yearly.

Refer to the Whatman manuals for additional maintenance and troubleshooting information.

CHAPTER 8

SAMPLING ACCESSORIES

ABB spectrometers are compatible with industry-standard sampling accessories from ABB and from other manufacturers. The purpose of a sampling accessory is to present the sample in such a way that the spectrometer can analyze it correctly. Analysis may be done continuously or on individual samples.

The type of sampling accessory used depends on factors such as:

- the type of analysis (continuous or on individual samples)
- the state of the sample (solid, liquid, or gas)
- the temperature of the sample
- the reactivity of the sample

If the analysis is done continuously, the type of sampling accessory used will also depend on factors such as:

- the viscosity of the sample
- the frequency at which the sampling accessory must be referenced, and the use of automatic referencing and flow control
- the complexity of installing a process by-pass loop, and the type of piping or vessel used in the process

The following table describes the principal accessories available and their uses.

Accessory	Typical use
Flow-through sampling cell	Continuous analysis in a process or by-pass.
Immersion probe	Batch analysis in a reactor or continuous analysis in a process or by-pass. (Allows retracting the probe out of the sample without having to stop the flow in the process line.)
Attenuated total reflectance (ATR) accessory	Analysis on individual samples. In mid IR, for solid or liquid samples that require a very short path length to produce satisfactory strong absorption bands.
Diffuse reflectance (DRIFT) accessory	Analysis on individual samples. In mid IR, for diluted samples or for low-level components with unique absorption bands. In near IR, for powdered sample or solid samples with textured surfaces.

8.1 Flow-through cells

One technique used to sample a process is to install a sampling system in a process bypass loop, as shown in Figure 8-1. The sampling system includes a flow-through sampling cell connected to the spectrometer by fiber-optic cables. The process bypass loop provides a parallel flow for sampling that can be completely isolated from the process for maintenance or repair. Details of the sampling system are shown in Figure 8-4.

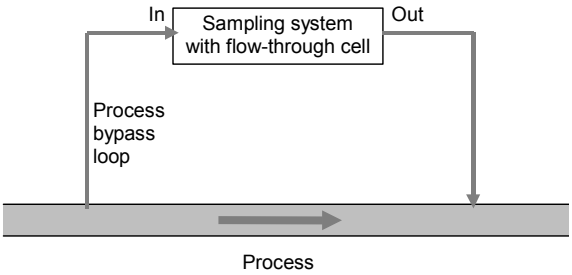


Figure 8-1. Process bypass loop

Figure 8-2 shows a typical flow-through cell. The sample (the liquid extracted from the process for analysis) flows through the cell from the bottom to the top. This prevents the formation of bubbles in the cell. The optical beam modulated by the interferometer enters the cell through the input optical fiber, passes through the sample, and is returned to the detector through the output fiber.

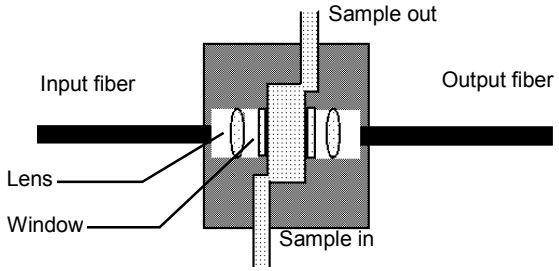


Figure 8-2. Flow-through cell

Figure 8-3 shows an installation of flow-through cells, which can be used when the sample has relatively low viscosity. With this type of cell, it is important to install valves to allow purging the sampling cell periodically in order to reference. The reference spectrum can be obtained using dry instrumentation air, nitrogen, or a liquid that has no absorbance in the fingerprint region of the sample.

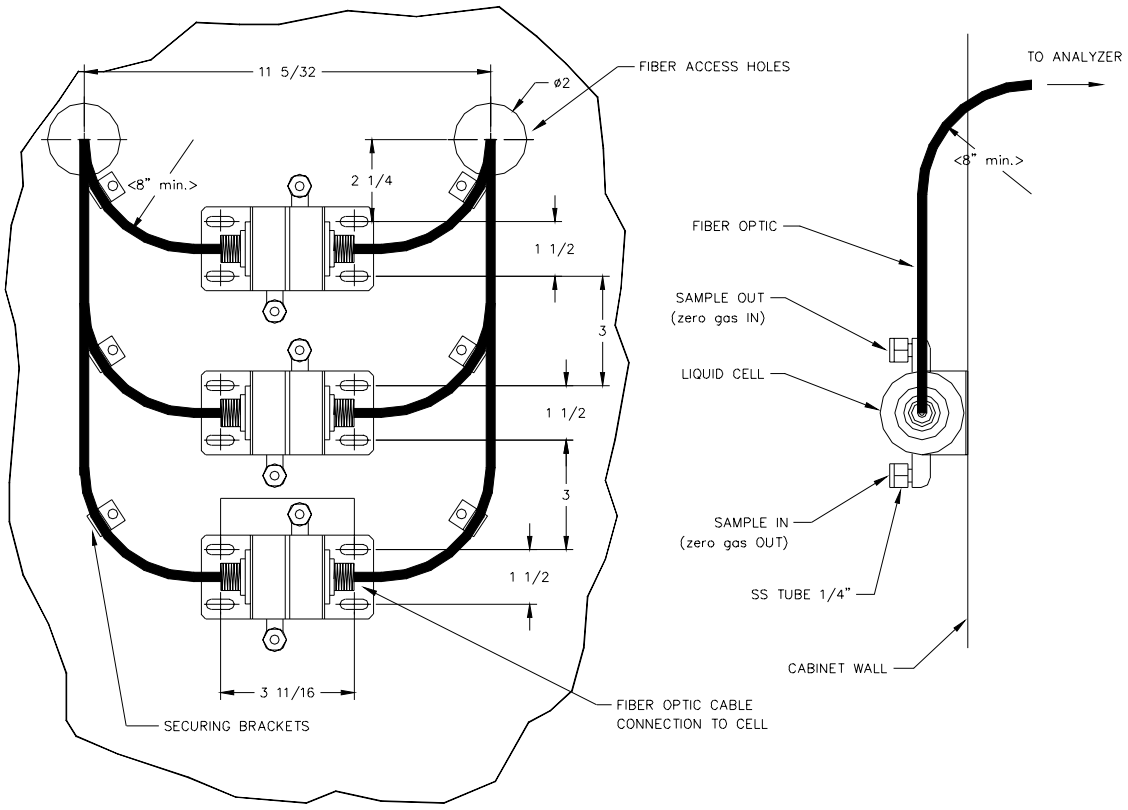


Figure 8-3. Installation of flow-through cells

8.1.1 The sampling system

Figure 8-4 shows a typical sampling system using a flow-through sampling cell, for analyzing a clean liquid sample. In this example, nitrogen gas is used to purge the cell to obtain a reference spectrum.

Note: *Before performing analyzes, it is necessary to obtain a reference spectrum (also called background spectrum or zero spectrum). Refer to Section 3.4.4 on page 17 for more information.*

For applications where the sample contaminates the cell windows, it may be necessary to inject a cleaning fluid into the cell before it is purged with dry nitrogen. The layout will then be different. Some applications may require purging with a fluid instead of dry nitrogen for the reference spectrum.

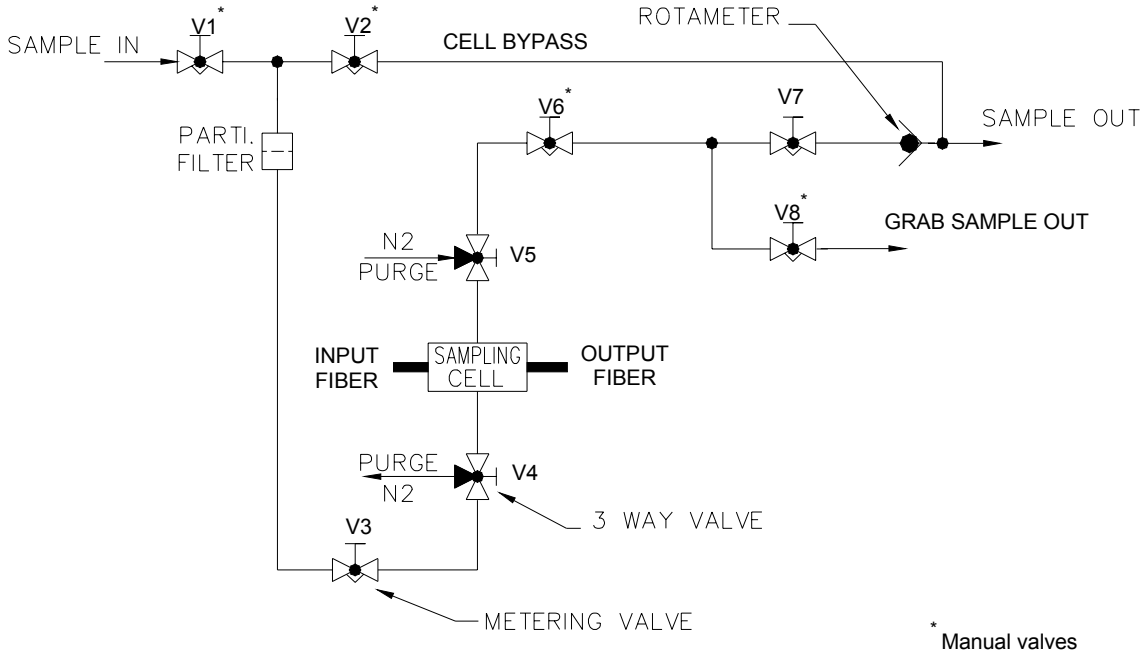


Figure 8-4. Sampling system for a flow-through cell

The sample enters the sampling system through V1. When a reference spectrum is required, V3 and V7 are closed and the sample bypasses the cell through V2 and the cell bypass. Before and during the acquisition of the reference spectrum, V4 and V5 are set to let nitrogen flow through the cell. V4 and V5 are three-way valves. After the reference spectrum is acquired, V4 and V5 are set to let the sample flow through the cell. Then, V3 and V7 are opened.

In the case where automatic referencing and flow control is used, V3, V4, V5, and V7 in Figure 8-4 are computer controlled.

V1, V2, V6, and V8 are manual valves. V1 is used to adjust the flow through the entire sampling system, and can be closed for maintenance purposes. V2 is adjusted so that enough pressure is generated through the cell. V6 is adjusted for a sampling flow of about 3 L/min, as indicated by the rotameter. V8 remains closed during normal operation; it is only used to manually grab samples for on-line calibration development and maintenance.

Important:

If the following conditions are not met, the accuracy of the calibration, and of the analyzes, may be reduced.

- *The flow rate through the sampling cell should be approximately 3 L/min in order to have laminar flow inside the cell.*
- *There should be adequate flow in the cell bypass at all times. This ensures that the sample in the sampling system is analyzed in a timely manner useful for real time process optimization.*
- *Experience has shown that cell flow should be between 25% and 100% of the cell bypass flow. This means that the flow rate in the cell bypass should be between approximately 3 and 12 L/min.*
- *The grab sample output should be as close as possible to the sampling cell. For calibration purposes, a spectrum is acquired of the sample in the sampling cell and a sample is grabbed manually. It is essential that the grab sample accurately represent the sample in the cell at the time of spectral acquisition.*

8.1.2 Problems to avoid

8.1.2.1 Air bubbles in the cell

It is important to prevent the formation of air bubbles in the cell, because these diffuse light and produce measurement errors. Figure 8-5 on page 62 shows an example of signal loss due to such light-diffusing phenomena. Here, phenol and acetone are being measured in a mixture containing a small quantity of water as an emulsion.

In this example, the emulsion has raised the base line to 1 absorbance unit. This means that only 10% of the light is getting through the cell. Since all frequencies are equally attenuated, we can conclude that the non-homogeneities are much larger than the wavelength of the near-infrared beam.

Note that:

- the loss of light raises the baseline of the spectrum.
- a higher absorbance means that less light is transmitted through the cell.

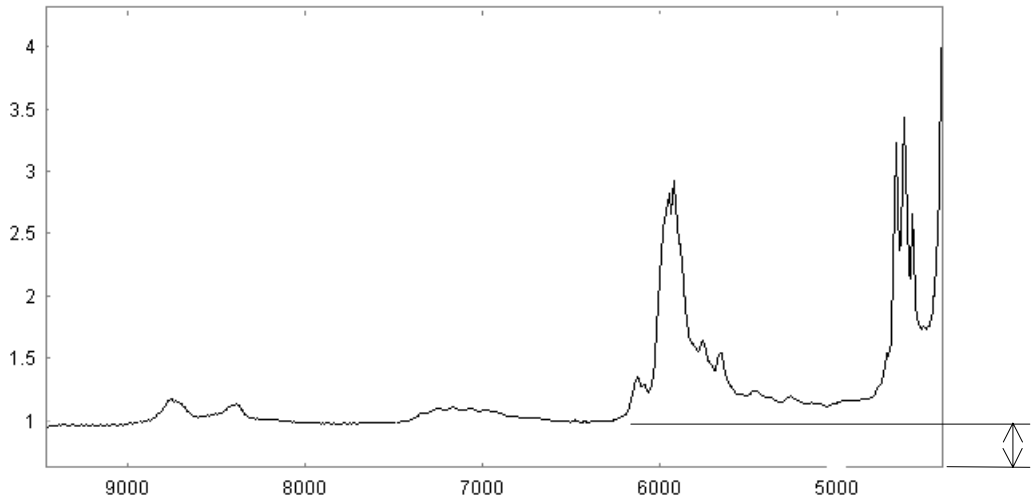


Figure 8-5. Signal loss due to air bubbles

8.1.2.2 Deposits on the cell windows

Some samples may leave a deposit on the surface of the two windows that are in contact with the liquid. In this case, the cell must be cleaned and a new reference spectrum obtained fairly frequently. When frequent referencing is required, it can be automated and controlled by software.

In some cases, the cell must be cleaned with a cleaning fluid before it is purged with the reference liquid or gas. In other cases, the reference liquid used will also clean the cell windows.

8.1.2.3 Particles in the sample

Any particles or particle-like material in the sample will diffuse or absorb light when present in the optical path of the cell. This causes conditions where the signal-to-noise ratio may be poor, which in turn reduces the precision of the calibration, and may even prevent the calibration from working. Filters should be used in a sampling system that samples a flow containing particles or particle-like emulsions such as air bubbles, water emulsion, etc. We recommend stainless steel filters with a particulate retention of 0.1µ to 1µ as the final filtering step before the sampling cell.

8.1.2.4 Ambient gas

An ambient gas signature may be included in the PLS calibration. If a high precision calibration is required, or if the training set does not contain an ambient gas signature, the sample and reference spectra must be free from contamination from the ambient air. This can be accomplished by purging the spectrometer, as well as the fiber-optic connections to the sampling cell, with dry nitrogen.

Figure 8-6 shows the configuration of a flow-through sampling cell with purge caps. The caps are mounted where the input and output optical fibers are connected. These caps are purged through the purge inputs. Vent holes located at the top of the caps prevent pressure buildup inside the cap. Purging the caps reduces the time required to carry out the calibration since it removed all water vapor around the fiber connectors. Purging the caps is also useful when the cell environment may be contaminated with a gas (e.g. volatile hydrocarbon gas) that could be detected by the spectrometer.

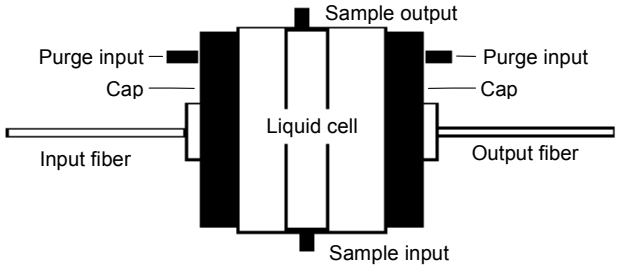


Figure 8-6. Flow-through cell with purge caps

Note: *If the calibration is developed with spectra which are free from water vapor, then all analyzes must be performed under the same conditions. Therefore, if a purge is used for calibration, it must be also used for sample analysis.*

If water vapor was not present in the reference spectrum, and it is later found that the spectra acquired during analysis contain water lines, it is possible to add a water signature to the calibration spectra to correct the method. This must be done with great care since some spectra may be used many times in the calibration training set, and this may end up modeling part of the noise. The same approach can be used to add information about sample temperature, fiber temperature, and base line variations. This works best when the required precision is relatively low.

8.1.2.5 Moving particles or bubbles

Earlier it was indicated that bubbles and particles in the sample stream will cause attenuation of the infrared beam due to scattering. Depending on the uniformity of the density of particles and bubbles and the flow rate of the sample past the infrared beam, a perturbation effect may be observed on the spectra.

Moving particles or bubbles will cause scattering of the IR beam in a time varying manner. The way of obtaining IR spectra with an FT-IR also consists of modulating the IR beam in a time varying manner. When the frequency components of the perturbations of passing particles or bubbles overlaps with the frequency components of the FT-IR modulation, there will be an interference effect on the spectra.

The passage of a particle or bubble through the IR beam represents an impulse with a rise and fall time and pulse width. These time intervals depend on the particle or bubble size, rate of movement and size of IR beam. It can be shown that the beam intensity perturbation due to the particle or bubble will manifest itself at low frequencies with a characteristic cutoff frequency determined by the parameters stated above. Typically the FT-IR modulation is in the range of several kHz. As a rule, for beam transit times of greater than 20 ms (for a 5 mm diameter beam this corresponds to flow speed of up to 25 cm/s) the transient behavior of the intensity of the beam caused by the particle or bubble will not perturb the spectrum.

Perturbation of the spectrum due to transient particles or bubbles is rarely of concern with an FT-IR analyzer because the modulation frequency of the interferometer is high compared with scanning grating spectrometers or even fast scanning AOTF analyzers. Also the density of particles or bubbles needs to be in a narrow range in order to create a perturbation: Too high a density will make the particle or bubble density homogeneous and too low a density will make the perturbation too infrequent to influence the final averaged result.

8.2 Immersion probes

For some applications, it is not possible to use a process bypass loop and a flow-through cell for sampling. It may not be possible, for example, to withdraw a sample from the process, or the sample may be too viscous to use a flow-through cell. In cases like these, it is possible to immerse a probe directly into a process line or a tank. This simplifies the measurement, but may make it difficult to implement an automatic periodic reference spectrum acquisition.

The probe is connected to the spectrometer by two fiber-optic cables. The modulated light from the interferometer is sent to the probe through the input fiber. Inside the probe, the light is guided across the sample gap. The output fiber returns this light to the spectrometer.

8.3 Attenuated total reflection (ATR) accessories

Infrared radiation incident on the internal interface to air from a transparent medium such as germanium, silicon, or diamond will be totally internally reflected when the angle of incidence of the radiation is sufficiently large. However, if a less dense and partially transmitting substance is placed in contact with the transparent medium, then the radiation will be partially absorbed.

In the ATR (Attenuated total reflection) technique, a polished crystal of IR-transmitting material is placed in the sample beam of the instrument so that the radiation is internally reflected along its length. The sample is smeared or pressed against the polished side of the crystal to modify its reflectance. In this case, the reference spectrum is that of the crystal without the sample applied.

ATR sampling accessories are used in the mid IR region for solid or liquid samples that require a very short path length to produce satisfactory strong absorption bands.

With ATR, calibration transfer is feasible using peak height calibrations but is difficult to impossible using multivariate calibrations such as PLS because of the band shape variability (see Chapters 4 and 5).

8.4 Diffuse reflectance (DRIFT) accessories

Diffuse reflectance occurs when light strikes a material and is partially reflected and partially transmitted. Light that passes into the material may be absorbed or reflected out again. The radiation that reflects from an absorbing material is composed of both surface-reflected and re-emitted components, which summed are the diffuse reflectance of the sample.

In the DRIFT (Diffuse Reflectance Infra-red Fourier Transform) technique, the sampling accessory sends radiation to the sample and collects the energy reflected back over a large solid angle. Thus, the accessory must account for the sample particle size, and the light beam must cover a large part of the sample.

DRIFT accessories are used:

- in the mid-IR region for diluted samples or for low-level components with unique absorption bands

- in near-IR region for powdered sample or solid samples with textured surfaces

With DRIFT accessories, the reference spectrum is that of a transparent powder such as KBr.

8.5 Avoiding detector saturation

Some sensitive near-IR detectors are provided with selectable preamplifier gain. After installing a sampling accessory, the preamplifier gain must be set so that sufficient signal amplitude is obtained and detector saturation is avoided.

For instructions on setting the preamplifier gain, refer to the *User's Guide* of your spectrometer or analyzer. For instructions on checking for detector saturation, refer to the manual of your acquisition software.

Note: *When performing quantitative analysis without normalization, a new reference spectrum must be taken when the preamplifier gain is changed. Make sure the same preamplifier gain setting is selected for both the reference spectrum and the sample spectrum.*

For qualitative analysis, or quantitative analysis with normalization, it is possible to use different gain settings for reference and sample spectra.

CHAPTER 9

HANDLING AND CARE OF HYGROSCOPIC MATERIALS

Hygroscopic materials are substances that can take up water directly from the atmosphere. Optical components made of hygroscopic material can be damaged if exposed to humidity.

Important: *Refer to the* User's Guide *of your spectrometer or analyzer to determine if it is sensitive to humidity.*

The purpose of this chapter is to introduce the user to practices by which hygroscopic components may be handled and used routinely while attempting to prevent hygroscopic optical material deterioration. Adhering to these practices will serve to prolong the life of integral components used in the spectrometer as well as uphold the experimental integrity associated with measurement concerns.

Note: *Hygroscopic components installed on a spectrometer are protected when the spectrometer has fresh desiccant or is purged, is left on at all times, and is not exposed to excessive humidity.*

The hygroscopic components in humidity-sensitive ABB spectrometers include:

- Beamsplitters made of CsI, KBr, or KCl. (Beamsplitters made of ZnSe or BK7 are not sensitive to humidity.)
- Windows made of CsI, KBr, KCl, or NaCl. This may include:
  - The window between the sample compartment and the interferometer cavity.
  - The side port window.
  - The window in front of the detector element. This is the case for many IR detectors, such as the common DTGS detector. (Some detector windows are made of ZnSe and are not sensitive to humidity.)

These hygroscopic components can be damaged by exposure to moisture in the surrounding environment of the instrument or in the storage location.

9.1 Hygroscopic materials

The most hygroscopic materials are the alkali halide components. While these components provide relatively high transmittance of infrared radiation, they are also susceptible to be damaged by interaction with atmospheric moisture. This damage may introduce absorption features (water bands) in the spectra and/or may degrade the quality of polished surfaces that may cause scattering of radiation. In both cases, the resulting effect is to reduce the amount of infrared radiation that passes through the optical material. The level to which any halide material will be affected by atmospheric moisture can be approximately related to known water solubility data for the specific material (see Figure 9-1 and Figure 9-2).

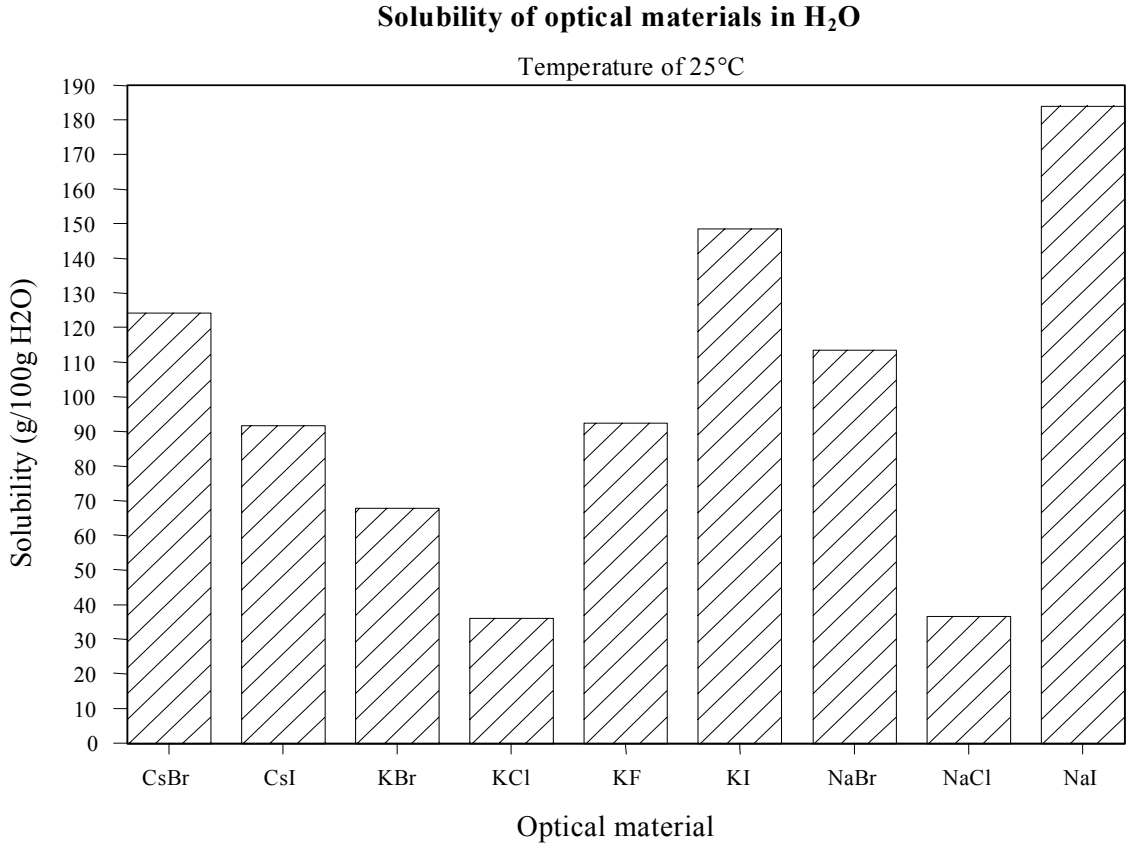


Figure 9-1. Highly hygroscopic material

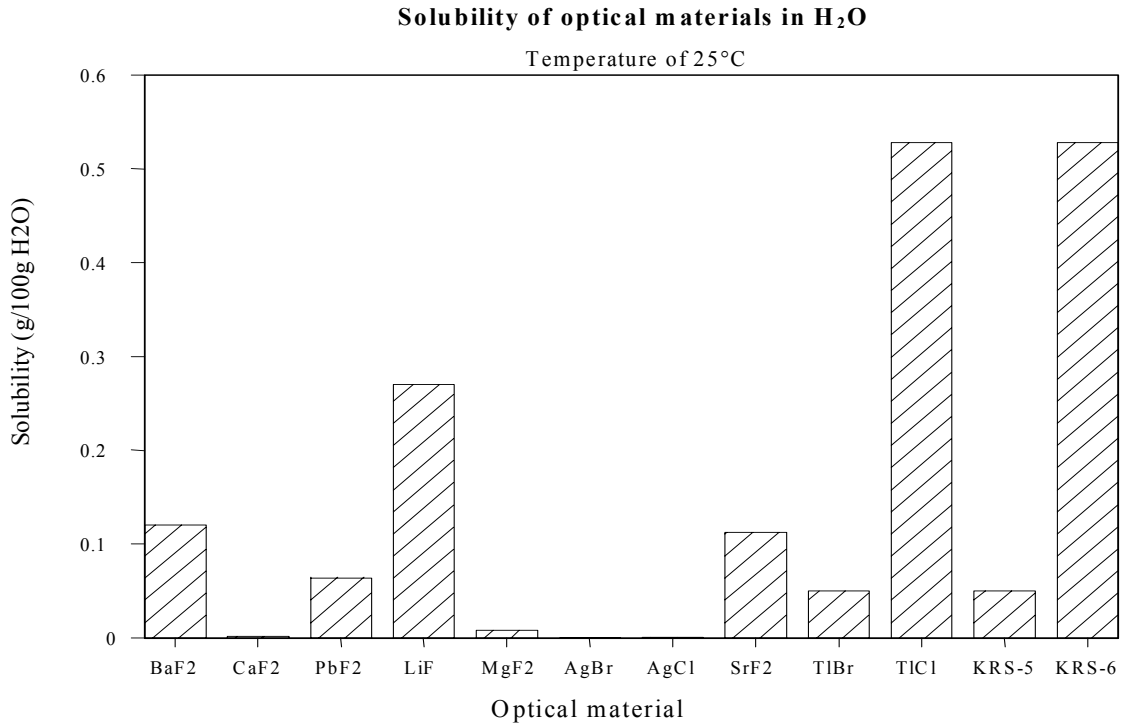


Figure 9-2. Non- or weakly hygroscopic material

[q] *Water damage is commonly called "fogging".*

Many of the highly hygroscopic alkali-halide materials are typical optical materials used in spectrometers. These hygroscopic optical materials tend to be less expensive than other optical materials and provide excellent transmittance of infrared radiation. However, because of their high solubility in water, they will be more susceptible to water damage.[q] These hygroscopic optical materials should be handled and used with care.

9.2 Handling and care guidelines

The handling and care of hygroscopic materials is not very difficult. These guidelines, if followed scrupulously, will help you to preserve yours hygroscopic optical materials for years without moisture damage.

Note: *Most cases of hygroscopic optical materials failure are caused by fogging of the component due to exposure to moisture.*

9.2.1 Environment

Installation, use, and storage of alkali halide components should be done in a temperature and humidity controlled environment, by qualified personnel familiar with the handling of these components.

- The relative humidity (see Section 9.3) should remain below 35% at all times to preserve the quality of the alkali halide components.
- Do not expose alkali halide components to any environmental conditions or changes to environmental conditions that can cause condensation to form on these components.
- Do not unpack or expose cold alkali halide components. Allow at least 24 hours for these components to warm up to room temperature before unpacking or exposing to air.

9.2.2 Handling

When handling alkali halide components:

- Any person in contact with these components should wear a face mask and full surgical gloves.

  This is necessary to avoid damaging the components by moisture from breath or from skin.
- Never breathe directly on or near hygroscopic optical materials.
- Only the outer edge of hygroscopic optical components should be handled.

  If absolutely necessary, the component can be carefully wiped using a clean tissue and isopropyl alcohol to remove any talcum powder, lint, finger oil, or moisture that may collect during handling.

Note: *Unused solvents should be discarded as they have a high affinity to absorb water vapor from the air. Moreover, materials that are likely to absorb moisture (tissues, tape, clothing, etc.) should be removed from close proximity of hygroscopic optical materials.*

9.2.3 Storage

When hygroscopic optical materials are not in use, it is recommended that they be stored in a warm dry place. The relative humidity should always be maintained below 35%. To ensure that hygroscopic optical materials are preserved, a combination of slight heating above ambient temperature along and the use of desiccant material is recommended.

The preferred storage location is a heated desiccator cabinet or else an enclosure that is purged with a dry, oil-free instrumentation air or nitrogen (N_2). Avoid placing any materials that may retain moisture near hygroscopic optical materials or inside the cabinet or the enclosure. Hygroscopic optical materials may also be sealed (airtight) in a plastic storage envelope with a suitable desiccant material.

In practice, such cabinets or enclosures are not always readily available and the ability to seal hygroscopic optical materials is not always possible. In this case, hygroscopic optical materials can be stored in their original shipping containers with suitable desiccant material, and can be heated slightly (approximately 5ºC) above ambient temperature level.

9.2.3.1 Desiccant materials

A desiccant material absorbs moisture from the air and can, therefore, minimize the atmospheric level of moisture within a confined volume. Desiccant materials come in a variety of forms. In environments where the storage location is not well controlled, a desiccant material that changes colour with increasing absorption of water is a very good indicator of humidity levels encountered by the hygroscopic optical material. An appropriate amount of desiccant material, usually in a pouch or capsule, should be stored near the hygroscopic optical material. The amount of desiccant material will depend on the volume of the instrument and the level of dryness required, which may vary from application to application.

A maintenance schedule should be made by the user to check that the condition of the desiccant material is satisfactory. Typically, the desiccant material should be checked on a monthly basis. If the desiccant material is not checked periodically, it can become a source of moisture that may damage the hygroscopic optical material.

Most ABB spectrometers are equipped with a humidity indicator, which indicates the relative humidity inside the spectrometer.

Note: *Desiccant materials that change colour can usually be regenerated by heating them in an oven at 100°C until their colour comes back to the colour of the dry state.*

An alternate method can be to place desiccant materials in a microwave oven. A power level of 80% for approximately 10 minutes should

regenerate desiccant materials to their dry state. Make sure that the evaporated moisture can escape from the desiccant enclosure. Refer to your desiccant materials supplier for more information.

9.2.3.2 Heating

Heating the hygroscopic optical material above ambient temperature levels ensures that the optical material remains above the temperature at which condensation may occur onto its surface. The temperature can be raise locally by using a heating element. A 25W light bulb placed under and near the hygroscopic optical material may be used as a heat source. The temperature should be maintained at least 5°C over the ambient temperature to avoid condensation. Note that this will not account for relative humidity levels reaching levels that may harm the hygroscopic optical material. Despite a 5°C temperature difference, the relative humidity may approach levels much greater than the specified 35% level (see Section 9.3).

9.2.4 Transport

The best and safest way to transport hygroscopic optic materials is to place them in a well packed and sealed container using desiccant material. Do not unpack or expose hygroscopic optic materials in a receiving area. Move the containers to a designated storage area at constant temperature where the relative humidity is below 35%. Allow at least 24 hours for the containers to warm up to room temperature before unpacking or exposing hygroscopic optic materials.

9.3 Relative humidity

The relative humidity is the ratio, expressed as a percentage, of the amount of water in a volume of air to the amount of water that this volume of air would contain if it were saturated at the same temperature and pressure.

$$\mathrm{RH}(\%) = \frac{\mathrm{Wa}}{\mathrm{Ws}} \times 100\% \qquad \text{Equation 9-1}$$

where Wa is the actual mixing ratio water-air

Ws is the saturation mixing ratio water-air

As air is heated, its ability to hold water increases, the saturation level increases. While, as air is cooled, its ability to hold water decreases, the saturation level decreases. When the temperature drops to the point where the actual mixing ratio and saturation mixing ratio become equal, the dew point is reached and condensation may occur. The dew point is the temperature at which the water vapor in the air begins to condense as droplets of water.

When the relative humidity is required to be below a certain level, it is important to consider this temperature dependency. This is especially important when moving hygroscopic optic materials between environments of different temperatures. Moving from a warm environment to a cooler one will not cause condensation onto the hygroscopic optic material, as the dew point will be higher than the temperature of the cooler environment.

However, moving from a cooler environment to a warmer will cause condensation onto the hygroscopic optic material, as the temperature of the hygroscopic optical material may already be below the dew point. For example, taking hygroscopic optic material from outside at 15^{o}C to an inside location at 25^{o}C, when the relative humidity for each environment is 35%, will expose the hygroscopic optic material to an effective relative humidity of 65%, if it is immediately unpacked.

USING FIBER-OPTIC CABLES

When the sampling accessories are located away from the spectrometer, a fiber-optic cable links each sampling accessory to the spectrometer.

The two most common sampling accessories used with fiber-optic cables for the process sampling of liquid components are:

- the flow-through sampling cell. This can be used when the sample has relatively low viscosity.
- the immersion probe. This can be used when the sample is relatively viscous or where it is difficult to bring the sample out of the process for analysis.

Fiber-optic cables are fragile and expensive optical components. They require more precautions when handling than do electrical cables.

You should read this chapter carefully before handling fiber-optic cables. Poor handling of fiber-optic cables can result in damage and/or breakage.

A fiber-optic cable consists of a thin optical fiber covered by a protective cable jacket. Figure 10-1 shows the different parts of a fiber-optic cable assembly.

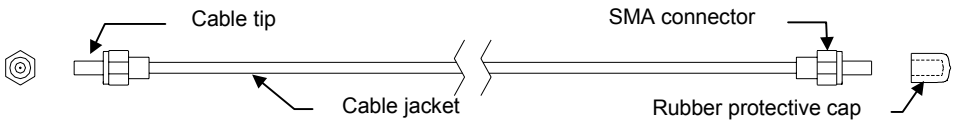


Figure 10-1. Fiber-optic cable with connectors on both ends

10.1 Handling and care guidelines

The handling and care of fiber-optic cables is not very difficult. These guidelines, if followed scrupulously, will help you to preserve your fiber-optic cables.

10.1.1 Precautions

- Never leave the cable tips exposed. When the fiber-optic cables are not being used, the cable tips must always be protected with rubber protective caps.
- Never touch the cable tips with your fingers or with tools. If you do touch a cable tip, you will have to clean it (refer to Section 10.1.3).
- Never step on fiber-optic cables, and do not leave them lying on the floor.
- The minimum bending radius for fiber-optic cables, to avoid breaking the optical fiber, is 600 times the diameter of the fiber (see Figure 10-2.

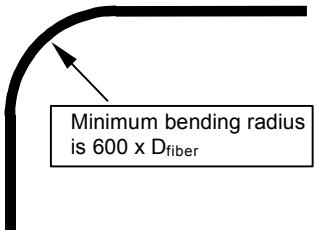


Figure 10-2. Minimum bending radius for fiber-optic cables

10.1.2 Cable protection

- Optical fibers must be protected from contact with liquids, dust, and other contaminants. In many cases, the cable jacket offers sufficient protection. For greatest protection, the fiber-optic cables should be installed in wiring conduits (see Section 10.2).
- When the fiber-optic cables are to be installed inside conduits, they do not need industrial-grade jacketing. A standard PVC flame-retarding jacket is sufficient.
- Note, however, that the heavier the jacket, the more difficult it will be to pull the cable through the conduit and the more chances to damage the cable due to its pulling weight and conduit bends. Make sure that the bends have a minimum radius of 8 inches, refer to Section 10.1.1 for more details about the bending radius.
- If the fiber-optic cable comes in contact with liquids or vapors, make sure the cable jacket provides adequate protection. Industrial jacketing should be used for locations where the fiber-optic cables will not be passed through conduits.

10.1.3 Cleaning and maintenance

Note: *Once installed, the cable jacket and SMA connectors usually require no cleaning or maintenance.*

- To clean a cable tip, use a soft optical cloth moistened with methanol. Gently wipe the tip with the cloth. With a magnifying glass (30X), make sure the tip is clean. Cover the tip with a rubber protective cap.

- If dust or contaminants are present on the thread of an SMA connector, soak the cable end in methanol for few minutes. Dry the cable tip with a soft optical cloth. Remove the excess methanol using dry instrumentation air.

10.2 Pulling a fiber-optic cable

This section provides instructions for pulling a fiber-optic cable through a wiring duct or conduit.

Important:

The most fragile part of a fiber-optic cable is at the connector. This part is stiff and excessive pulling onto the cable jacket will force the optic fiber to break at the connector, where it is glued.

To prevent breaking the optic-cable cables at the connectors during the pulling, it is recommended that the connectors be supplied separately and installed after the fiber-optic cables have been pulled through the conduits. This is particularly important when the length of fiber-optic cable is over 100 feet (30 m).

The cord serving to pull the fiber-optic cable must not be attached to the SMA connector but to the cable jacket.

To correctly attach the cord to the fiber-optic cable, use the following procedure:

1. Put the rubber protective cap on the cable tip (see Figure 10-3).

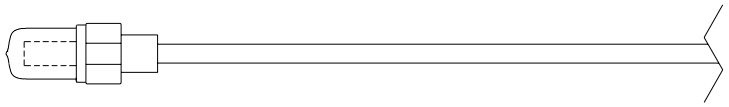


Figure 10-3. Rubber protective cap on the cable tip

2. Slip a 1- to 3-meter piece of shrinkable tubing on the cable jacket (see Figure 10-4).

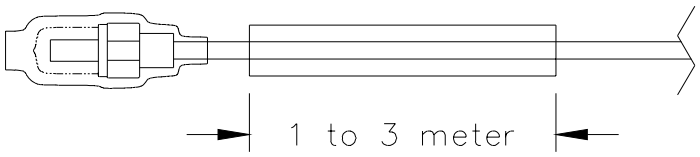


Figure 10-4. Shrinkable tubing on the cable jacket

3. Slip a 1¼ in. (3 cm) piece of shrinkable tubing over the SMA connector and the rubber protective cap to prevent them from slipping out of the cable tip (see Figure 10-4).

4. Shrink the 1¼ in. shrinkable tubing with a heat gun.

When shrinking the shrinkable tubing, shrink small sections at a time and use minimal heat. Keep the heat-gun as far as possible from the fiber-optic cable. Shrink a small section of tubing, and then let it cool down. Repeat until the tubing is completely shrunk.

If these precautions are not taken, serious damage could be done to the optical fiber.

5. Pass a solid single cable (fisher) through the shrinkable tubing. (see Figure 10-5).

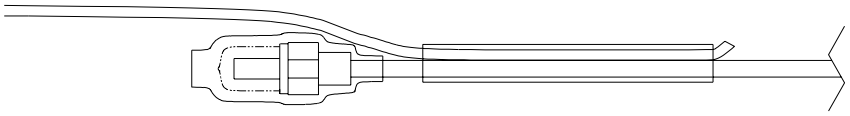


Figure 10-5. Solid single cable (fisher) through the shrinkable tubing

6. Shrink the 1 to 3 meter shrinkable tubing with a heat gun, make sure the single fisher cable is well secured, if any doubts, secure the end of the fisher with electrical tape.

7. Loosely secure the 1¼ in. piece of shrinkable tubing, covering the SMA connector and the rubber protective cap, to the cord with electrical tape (see Figure 10-6). This will prevent the fiber-optic cable from bending while it is pulled.

   It is important not to attach the electrical tape too tightly to prevent pulling directly on the SMA connector.

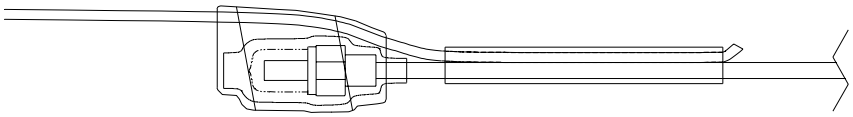


Figure 10-6. Electrical tape securing the piece of shrinkable tubing

8. Carefully pull the cable through the conduit.

10.2.1 Fiber-optic cables longer than 100 feet (30 m)

Important: *When the total length of the fiber-optic cable is more than 100 feet, due to the amount of pulling force needed, there must be a cable pulling station[r] every 100 feet.*

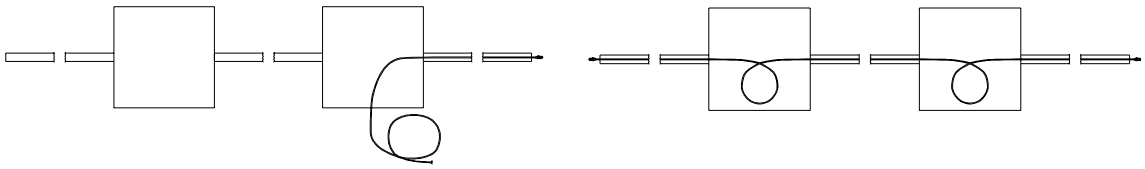
You should leave a loop of fiber-optic cable in each pulling station to allow some flexibility in the fiber-optic cable after installation.

[r] A cable pulling station is simply a box with a door that joins two sections of wiring conduit.

To correctly pull long cables, use the following procedure:

1. Open the first cable pulling station and pull the entire length of cable through the first conduit (Figure 10-7 (a)).

2. Repeat this operation for each subsequent cable pulling station, leaving a loop in each station (Figure Figure 10-7 (b)).



(a) **(b)**

Figure 10-7. Pulling fiber-optic cable through conduit

10.3 Storing fiber-optic cables

When storing a fiber-optic cable, make sure that the rubber protective caps are in place and put the cable coiled up on a shelf or in a box.

Never hang a fiber-optic cable by a hook on a wall; the cable could bend too sharply because of its weight, causing the optical fiber to break.

It is strongly recommended to keep unused fiber-optic cables in a sealed plastic bag along with desiccant. This will prevent the cables from being damaged by absorption of moisture.

10.4 Connecting fiber-optic cables

Before mating a fiber-optic cable to a sampling accessory, make sure that the cable tip and the connector on the accessory are clean and dry. The presence of contaminants may damage the cable tip and the sampling accessory.

10.4.1 Optical matching gel

Optical matching gel is used when the gap between two optical surfaces produces Fabry-Perot interference, also called channel spectrum. For more details on spectral artifacts such channel spectrum, refer to the document *Introduction to On-Line PLS Calibration*. Not all applications require optical gel. The use of optical gel is normally determined by a spectroscopist.

Do not use optical matching gel at the connection to the spectrometer.

Optical matching gel must be applied very carefully. The gel is viscous and easily traps dirt.

Improper use of optical gel may do more harm than good!

To make a connection using optical matching gel:

1. Clean the cable tip. Using a soft optical cloth moistened with methanol, gently wipe the tip. With a magnifying glass (30X), make sure the tip is clean.

2. Clean the matching connector. If necessary, soak this connector in methanol for few minutes. Dry it with a soft optical cloth. Remove the excess methanol using dry instrumentation air.

3. Apply a small quantity of optical matching gel (part no. OC-431A) on the cable tip and the matching connector, as shown in Figure 10-8.

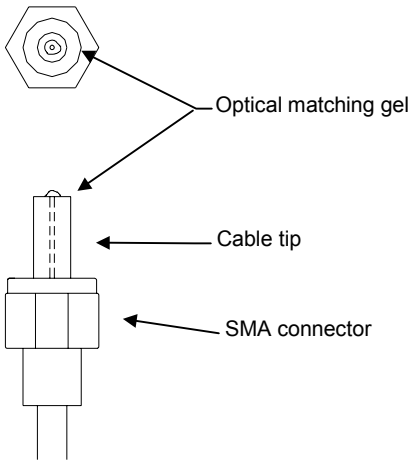


Figure 10-8. Optical matching gel on cable tip and matching connector

4. Make the connection and tighten as explained in Section 10.4.2.

10.4.2 Tightening SMA connectors

When connecting an SMA connector, first tighten it by hand. Then, with a torque wrench, further tighten the connector. A torque of 50 ozf-in. is recommended.

If a torque wrench is not available, carefully tighten the connector using a small wrench after it has been tightened by hand.

Over-tightening an SMA connector may damage the cable tip and may put the sampling accessory out of alignment.

10.4.3 Securing fiber-optic cables

Once a permanent installation is made, it is important to secure the fiber-optic cables to a fixed surface to prevent the SMA connectors from loosening with time due to mechanical vibrations. Loose SMA connectors may cause inaccurate analytical results.

SPECTRAL CHARACTERISTICS

The following figures illustrate the spectral characteristics of different detectors, MB Series Spectrometer models, and IR sources.

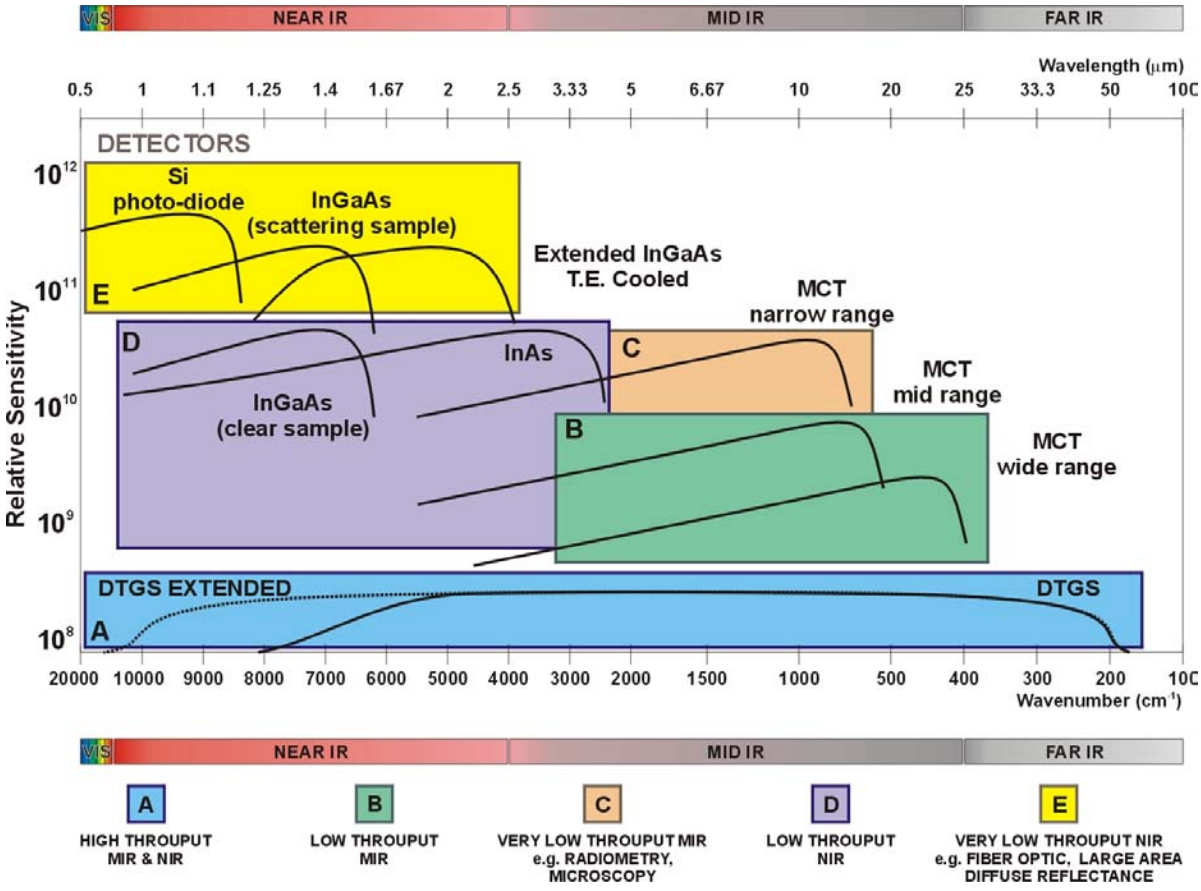


Figure A-1. Spectral characteristics of different detectors

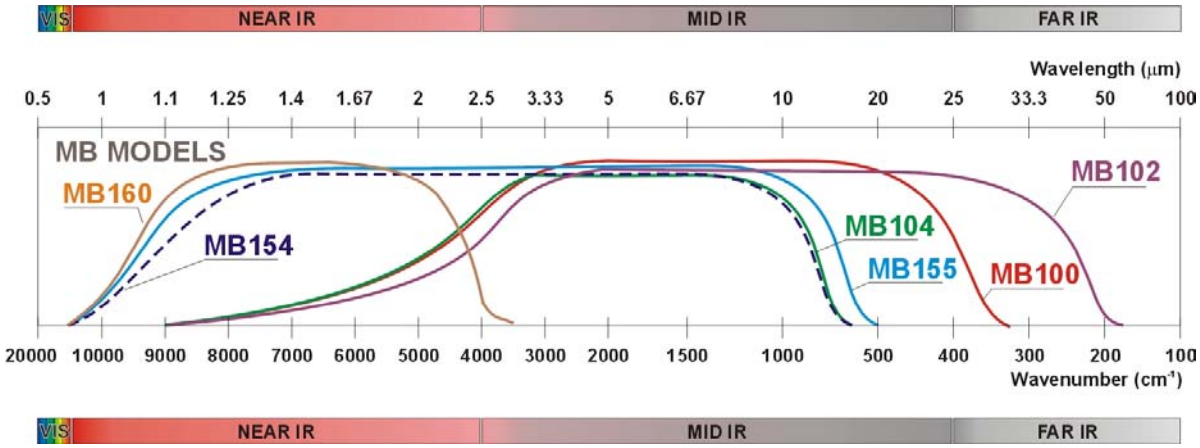


Figure A-2. Spectral characteristics of different MB Series Spectrometer models

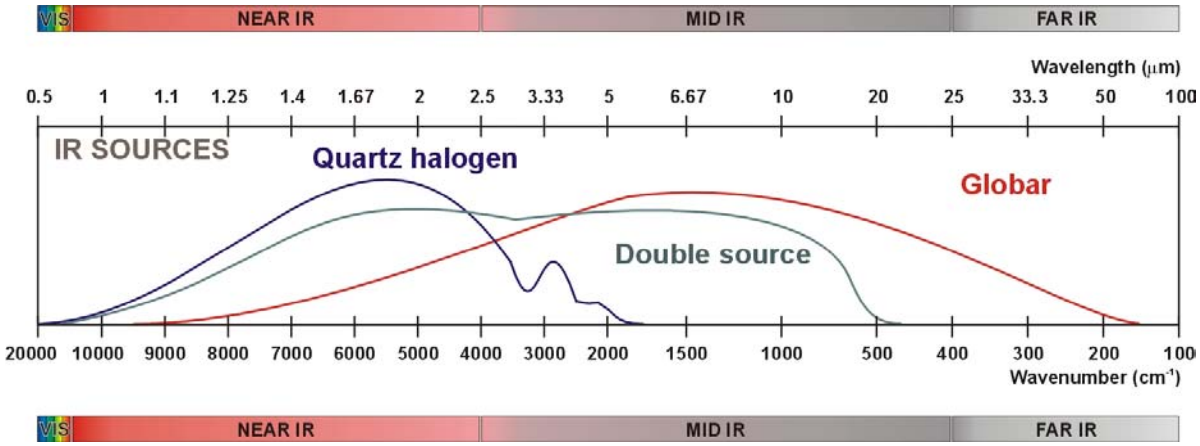


Figure A-3. Spectral characteristics of different IR sources

REFERENCE DOCUMENTS

The following documents are recommended as sources of further information. The book *Fourier Transform Infrared Spectroscopy* by Griffiths, Peter R. and James A. de Haseth is particularly recommended for the principles of FT-IR spectroscopy.

Author	Title	Publication
Banwell, C. N.	Fundamentals of Molecular Spectroscopy	McGraw-Hill Book Company (UK) Limited, Second edition (1972).
Buback, Michael and Hans Peter Vögels	FT-NIR Atlas	VCH
Burns, Donald A. and Emil W. Ciurczak	Handbook of Near-Infrared Analysis	Marcel Dekker, Inc.
Ferraro, John R. and Louis J. Basels	Fourier Transform Infrared Spectroscopy, Application to Chemical Systems	Academic Press
Geladi, Paul and Bruce R. Kowalski	Partial Least-Squares Regression: A Tutorial	Analytical Chimica Acta, 185 1-17, Elsevier Science Publishers B.V. Amsterdam (1986)
George, Bill and Peter McIntyre,.	Infrared Spectroscopy, Analytical Chemistry by Open Learning	John Wiley & Son (1987)
Griffiths, Peter R. and James A. de Haseth	Fourier Transform Infrared Spectroscopy, a Wiley-Interscience publication	John Wiley & Son (1986)
Haaland, David M. and Edward V. Thomas	Partial Least-Squares Methods for Spectral Analyzes. 1. Relation to Other Quantitative Calibration Methods and the Extraction of Quantitative Information	Anal. Chem. 60, 1193-1202 Sandia National Laboratories, Albuquerque, New Mexico 87185 (1988)
Hifghield, J. et al Paul Scherrer Institute Switzerland	Steam-Reforming of Ethanol for Efficient and Clean Energy Applications Beyond 2000 AD	10^{th} Int'l Symposium on Alcohol Fuels CO, USA (1993)
Hildrum, K.I. et al	Near Infrared Spectroscopy	Ellis Horwood
Leblanc, M. et al ABB. Canada	Improved FT-IR Measurement of Oil in Water with a Permanent Transferable Calibration	ABB (formerly Bomem) Application Bulletin (1993)
Leblanc, M. et al ABB. Canada	Quantitative Measurement of D_2O in Water	ABB (formerly Bomem) Application Bulletin (1993)
Manne, Rolf	Analysis of Two-Partial-Least-Squares Algorithms for Multivariate Calibration	Chemometric and Intelligent Laboratory Systems, 2 187-197, Elsevier Science Publishers B.V. Amsterdam (1987)

Author	Title	Publication
Marten, Herald	The philosophy of partial least squares regression	Consensus Analysis AS Ski Business Park, PO Box 1391 N-1401 Ski, Norway Spectroscopy Word 3é4 (1991).
Michiels, Erick	Industrial hygiene analyzer	ABB (formerly Bomem) Application Bulletin (1996)
Michiels, Erick	Quantitative analysis of mineral oil	ABB (formerly Bomem) Application Bulletin (1996)
Roberge, R. et al, Bomem Inc. Canada	The Evolution of Spectrometric Performance of FT-IR Relation to Quantitative Chemical Composition and Physical Parameter Determination	9th Int'l FT-IR Conference Proceedings Calgary, Canada SPIE Vol 2089, p. 534-535 (1993)
Sokolnikoff, I.S. and R. M. Redheffer	Mathematics of Physics and Modern Engineering	McGraw Hill Book Company (1966)
Stark, E. (KES Analysis, NY, USA)	Near-Infrared Spectroscopy: The New FT Frontier–Spectroscopic and chemometrics Considerations	SPIE Vol 1575, p. 70-86 (1991)
Stark, E. KES Analysis NY, USA	NIR Analysis of Combined Aromatic-Aliphatic Hydrocarbon Mixtures	(1992)
Swarin, S.J. et al General Motors Research Lab. Warren, MI, USA	Prediction of Gasolin Properties with Near-Infrared Spectroscopy and Chemometrics	SAE Technical Paper Series Int'l Fuels and Lubricants Meeting and Exposition Toronto (1991)
Trishnan, K.	Practical Fourier Transform Infrared Spectroscopy, Industrial and Laboratory Chemical Analysis	Academic Press, Inc
Trowell, W. et al Cape Industries, NC, USA)	A Protocol for Statistical Quality Control of FT-NIR PLS Predictions	The Pittsburgh Conference Atlanta, GA, USA (1993)
Trygstad, M. et al (Bomem Inc. Canada	Aspects of Calibration Transfer for Quantitative Mid- and Near FT-IR Analyzer: Keep It Spectrometrically Sound; KISS	The Pittsburgh Conference Atlanta, GA, USA (1993)
Trygstad, M. et al ABB. Canada	The Union of Mid- and Near-IR Spectroscopy Disciplines (Illustrated Through Determination of Hydroxyl Values with FT-Technology	The Pittsburgh Conference Atlanta, GA, USA (1993)
	Standard Practice for Describing and Measuring Performance of Fourier Transform infrared (FT-IR) Spectrometer: Level Zero and Level One Tests	American Society for Testing and Materials 1916 Race St Philadelphia, PA 19103 (1991)
	HOval Analyzer: With Disposable Vials Sampling	ABB Product Announcement

Author	Title	Publication
		(1994)
	Bomem Introduces the Diffus*ir,* a Large Area Reflectance Sampling Accessory	ABB (formerly Bomem) New Product Announcement (1997)
	Standard Practices for Infrared, Multivariate, Quantitative Analysis	American Society for Testing and Materials 100 Bart Harbor Dr West Conshohocken, PA 19428 (1997)
	Measurement of Moisture, Fat, and Protein by Bomem's FT-NIR On-line Meat Analyze	ABB (formerly Bomem) Application Note (1998)

APPENDIX C

GLOSSARY

Note: *The following terms are defined as they are used in ABB manuals.*

absorbance (also called optical density or extinction)

A measure of the amount of light absorbed as it passes through a sample.

The absorbance A is the logarithm of the ratio of the intensity I0 of the light striking the sample to the intensity I of the light which passes through the sample.

$$A = \log_{10} \frac{I_0}{I} = \log_{10} \frac{1}{T}$$

The absorbance is equal to the logarithm of the reciprocal of the transmittance T.

absorbance spectrum

The absorbance of a sample as a function of the frequency or wavelength over a given spectral range.

The absorbance spectrum is calculated point-by-point from the sample and reference spectra as follows:

$$Absorbance = -\log_{10}\left(\frac{sample}{reference}\right)$$

ADC

Analog-to-digital converter

agreement

The error between the analyzer result and the result obtained with a laboratory primary method. This is often expressed as accuracy.

analyzer

A complete system for FT-IR or FT-NIR analysis (see Figure C-1).

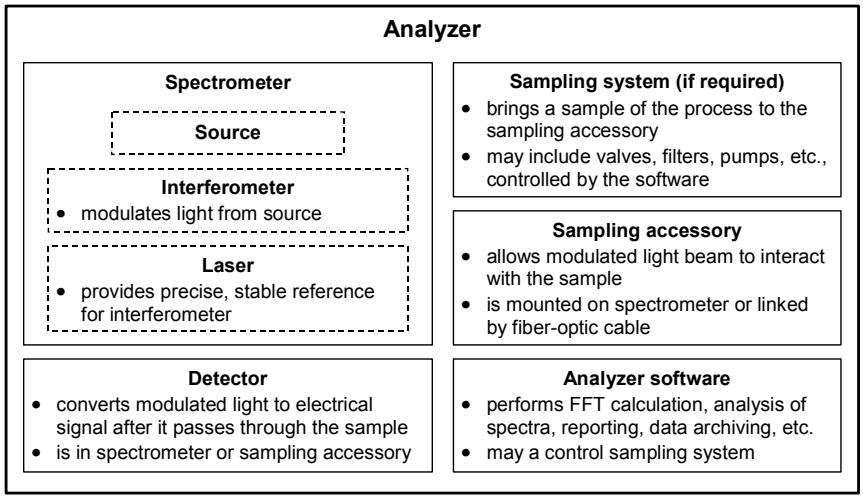


Figure C-1. Analyzer

background spectrum (see reference spectrum)

beamsplitter

A semi-reflecting mirror in the interferometer used to divide the radiation from the infrared source into two beams, and to recombine the two beams into a single beam.

Beer-Lambert's law

An equation relating the absorption of light by a sample to the absorption coefficient of the sample, the path length, and the concentration.

$$A_\lambda = \varepsilon_\lambda \times b \times C$$

where $A\lambda$ is the sample's absorbance value at a specific wavelength (λ)
$\varepsilon\lambda$ is the absorption coefficient of the material at that wavelength ($\ell \cdot mol^{-1} \cdot cm^{-1}$).
b is the path length through the sample (cm)
C is the concentration of the analyte ($mol \cdot \ell^{-1}$)

BK7

A high quality optical grass.

BK7 is not hygroscopic. Its refractive index is 1.50 at 8000 cm^{-1}. Its spectral range is from 25000 cm^{-1} to 3700 cm^{-1}.

blank sample

A sample that does not absorb infrared radiation within the spectral range where the measurement is performed.

calibration

The process of aligning analyzer measurements to agree with reference measurements obtained using a primary method.

calibration (or model or calibration model)

The set of equations that represents the relationship between the absorbance spectra of a set of samples and the properties of the samples.

Some common types of models are peak height, peak ratio, PLS and autosubtract models.

calibration set (or training set)

In spectrometer calibration, a set of standard samples used in calibration model development. The calibration set covers the expected ranges of property values, as well as any other variations that may affect the spectra, such as temperature. When there is more than one property, the calibration set must include independent variations of each property.

channel

An optical channel on the spectrometer. Each channel is associated with one sampling accessory and one detector.

The Network*ir* spectrometer,for example, has multiple channels. Each channel can be connected to a sampling cell by a fiber-optic cable. This allows one Network*ir* to do the same job as several single-channel spectrometers.

It is possible to have more than one sampling point on a channel. This is accomplished using valves to direct the sample from different sampling points into the sampling cell. In most cases, however, there is only one sampling point per channel and the two terms can be used interchangeably.

coadded spectrum

The spectrum resulting from averaging, on a point-by-point basis, a number of spectra or interferograms. Coaddition is used to increase the signal-to-noise ratio of a spectrum.

DCS

Distributed control system.

desiccant

A substance used as a drying agent.

detector

A device in a spectrometer that produces an electrical signal that is proportional to the intensity of the light striking it.

detector cut-off

The frequency or wavelength at lower end of the spectral range.

detector saturation

A condition of the detector whereby an increase in the light intensity striking it no longer produces a linearly proportional change in the output signal. This is a nonlinear condition and can cause Fourier stray light.

D-star (D*)

A value used to designate the specific detectivity. This is a performance measure independent of detector size. The higher is the D* value, the better is the detector.

$$D^* = (A \times \Delta f)^{1/2} D$$

where A is the sensitive area

Δf is the bandwidth frequencies

D is the reciprocal of noise equivalent power (NEP)

factor

In analysis using the PLS algorithm, one of a series of synthetic spectra which represent the most common variations in a given set of spectra (also known as latent vectors, characteristic vectors, spectral loadings, loading vectors, principal components, or variation spectra.).

Fast Fourier transform (FFT)

A mathematical algorithm for efficient calculation of the Fourier transform.

Fourier transform

A mathematical function that transforms the time-dependent information contained in the interferogram into the corresponding optical spectrum.

F-ratio

An indicator of spectral residual after modeling that can help detect whether an abnormal condition has occurred during analysis. The F-ratio should normally be low (typically less than 10, depending on the application). An F-ratio higher than average may indicate that the wrong material is being analyzed or that there is a problem with the system.

FT-IR (or FTIR)

Fourier transform infrared.

FT-MIR

Fourier transform mid-infrared.

FT-NIR

Fourier transform near-infrared.

grab sample

A sample taken from the process at the precise time that a spectrum is recorded. Laboratory analysis of the grab sample using a primary method is used to validate or improve the analyzer calibration.

hygroscopic

Able to absorb moisture from the atmosphere.

hygroscopic optical component

An optical component made of hygroscopic material. Such optical components can be damaged if exposed to humidity because they can absorb moisture from the atmosphere.

infrared

A region of the electromagnetic spectrum between visible light and radio waves where the wavelengths are longer than those of red light.

initial (or first) reference (or zero)

The first reference spectrum collected when the system was commissioned. This is used as a base to monitor changes in the analyzer response over time.

Installation Qualification (IQ)

A procedure used to ensure that an instrument has been correctly installed.

interferogram

A representation of the electrical signal from the detector of a FT-IR spectrometer. The interferogram is a graph of the voltage at the output of the detector as a function of the position of interferometer scan mechanism. The spectrum is calculated from the interferogram using a Fourier transform.

interferometer

The device in an FT-IR spectrometer that modulates the infrared beam coming from the source.

The interferometer splits the infrared beam into two beams, introduces a continuously-varying optical path difference (OPD) between the two beams, and recombines the beams. When the beams are recombined, interference caused by the OPD modulates the beam.

least-squares regression

A regression procedure used to establish a parameter value derived from multiple absorbance values such that the sum of the squares of the differences between the model absorbances and the actual absorbances is minimized.

model (see calibration model)

NEMA

National Electrical Manufacturers Association

nonlinearity

A deviation from the normally linear relation between the output and the input of a device. Nonlinearity occurs when the output of a device does not vary in direct proportion to the input, for example, when saturation occurs.

open beam

A condition in which there is no sample in the sample accessory.

open-beam spectrum

A spectrum acquired in the open-beam condition.

Operation Qualification (OQ)

A test procedure used to ensure that an instrument is operating within specifications.

optical density (see absorbance)

outlier (or outlier sample)

A sample in a set of samples for which a predicted property value or spectral structure lies significantly outside the main cluster of the corresponding property values or structures for that set.

Outliers can be caused by several different factors including unexpected variations in the property value, inconsistent sample handling, or changes in the performance of the instrument.

path length

The distance that light travels through the sample during analysis.

PLC

Programmable logic controller.

predict

In spectroscopy, to obtain the value for a specific property of a sample from its spectrum by using one or more calibration models.

prediction

In spectroscopy, the value obtained from predicting a property.

preprocessing

Mathematical treatment applied to a spectrum before the calibration model is applied to it. There are a number of standard preprocessing algorithms commonly used in spectroscopy.

primary method

The accepted standard laboratory technique for measuring the properties of samples. When developing a calibration model, the "known" property values of the training set samples are determined by measurement using the primary method.

property

A single, measurable characteristic of a sample, whether it be a physical property such as temperature or a chemical property such as concentration.

raw spectrum

1. A spectrum that has not undergone any mathematical alterations.
2. A single-beam spectrum.

reference spectrum (also called background spectrum or zero spectrum)

A single-beam spectrum that only contains information about the analyzer, including the sampling accessory and the air present in any part of the modulated beam optical path. This is required in order to obtain a transmittance or absorbance spectrum of the sample.

A reference spectrum is obtained by removing the sample from the sample accessory or by filling the sample accessory with a blank sample and acquiring a spectrum.

repeatability

The precision of repeated measurements on the same instrument.

reproducibility

The precision of repeated measurements on different instruments.

resolution

The smallest frequency interval that can be distinguished over a spectral range. The lower the resolution setting on the spectrometer, the more data points there are in the spectrum.

Lowering the resolution setting on the spectrometer yields spectra with a "higher" resolution, since there are more data points covering the same spectral range.

sampling accessory

A device that permits interaction of the modulated light beam from the spectrometer with the sample, for the purpose of obtaining a transmittance, absorbance, or reflectance spectrum of the sample.

Flow-through cells and immersion probes are commonly used sampling accessories.

sampling point

A sampling point is a point in a process where the material in the process (the sample) is analyzed (see Channel).

saturation (see detector saturation)

scan

With the ABB FT-IR spectrometers, a forward and a reverse sweep of the interferometer scan mechanism.

A single scan results in two interferograms, one for the forward sweep and one for the reverse sweep (see Coadded spectrum).

single-beam spectrum

The spectrum which results from performing a Fourier transform on the interferogram obtained from a spectrometer.

The single-beam spectrum contains information not only about any sample present in the sample compartment or sampling accessory, but also about the instrument (the source, all the optical components, the ambient air, as well as any contamination there may be in the optical path).

spectral range

The range of frequencies (or wavelengths) over which the amplitude of a spectrum is above the acceptable noise level. It is application dependent.

spectrometer

An instrument for producing a spectrum and measuring the wavelengths, energies, etc. involved.

An FT-IR spectrometer has a photoelectric detector and produces a spectrum that shows how the transmittance, absorbance, or reflectance of

the sample varies with wavelength. Such instruments are also called spectrophotometers.

spectrum

1. A range of electromagnetic energies arrayed in order of increasing or decreasing wavelength.
2. A distribution of transmission or absorbance levels over a range of wavelengths, arrayed in order of increasing or decreasing wavelength.

stray light

1. Apparent optical energy, caused by nonlinearity, in a spectral region where no energy is expected (Fourier stray light).
2. Modulated light reaching the detector without having passed through the sample.

stream

A current or flow of material in a process. A process may have one or more streams. A stream may be analyzed at one or more sampling points.

training set (see calibration set)

transmittance

A measure of the amount of light that passes through the sample, often expressed as a percentage.

The transmittance T is the ratio of the intensity I of the light which passes through the sample to the intensity I_0 of the light striking the sample.

$$T = \frac{I}{I_0} \qquad \%T = 100T$$

transmittance spectrum

The percent transmittance of a sample as a function of the frequency or wavelength over a given spectral range.

The transmittance spectrum is calculated point-by-point from the sample and reference spectra as follows:

$$\%Transmittance = \frac{sample}{reference} \times 100$$

validation

Tests used to establish that an analyzer is providing results within the expected degree of agreement. This can include predictions with known samples and diagnostics on the reference and sample spectra.

validation set

In spectrometer calibration, a set of standard samples similar to a training set but used to validate a calibration model.

wavelength

The distance (λ) between successive points of equal phase in a wave.

In FT-IR spectrometry, wavelength is usually expressed in micrometers (μm) or nanometers (nm).

wavenumber

The number (σ) of cycles of a wave in unit length. The wavenumber is the reciprocal of the wavelength:

$$\sigma = \frac{1}{\lambda}$$

The unit of the wavenumber is $\frac{1}{\text{cm}}$ or cm^{-1}.

zero spectrum (see reference spectrum)

ZPD (Zero Path Difference)

The point where the scan mechanism of a Michelson interferometer is positioned so that the two beams from the beamsplitter travel exactly the same distance before being recombined.

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W

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