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Standard Guide for Open-Path Fourier Transform Infrared (OP/FT-IR) Monitoring of Gases and Vapors in Air¹

This standard is issued under the fixed designation E1865; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide covers active open-path Fourier transform infrared (OP/FT-IR) monitors and provides guidelines for using active OP/FT-IR monitors to obtain concentrations of gases and vapors in air.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*²

E131 Terminology Relating to Molecular Spectroscopy

E168 Practices for General Techniques of Infrared Quantitative Analysis

E1421 Practice for Describing and Measuring Performance of Fourier Transform Mid-Infrared (FT-MIR) Spectrometers: Level Zero and Level One Tests

E1655 Practices for Infrared Multivariate Quantitative Analysis

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3. Terminology

3.1 For definitions of terms relating to general molecular spectroscopy used in this guide refer to Terminology **E131**. A complete glossary of terms relating to optical remote sensing is given in Ref (1).³

3.2 *Definitions:*

3.2.1 *background spectrum, n*—a single-beam spectrum that does not contain the spectral features of the analyte(s) of interest.

3.2.2 *bistatic system, n*—a system in which the IR source is some distance from the detector. For OP/FT-IR monitoring, this implies that the IR source and the detector are at opposite ends of the monitoring path.

3.2.3 *monitoring path, n*—the location in space over which concentrations of gases and vapors are measured and averaged.

3.2.4 *monitoring pathlength, n*—the distance the optical beam traverses through the monitoring path.

3.2.5 *monostatic or unistatic system, n*—a system with the IR source and the detector at the same end of the monitoring path. For OP/FT-IR systems, the beam is generally returned by a retroreflector.

3.2.6 *open-path monitoring, n*—monitoring over a path that is completely open to the atmosphere.

3.2.7 *parts per million meters, n*—the units associated with the quantity path-integrated concentration and a possible unit of choice for reporting data from OP/FT-IR monitors because it is independent of the monitoring pathlength.

3.2.8 *path-averaged concentration, n*—the result of dividing the path-integrated concentration by the pathlength.

3.2.8.1 *Discussion*—Path-averaged concentration gives the average value of the concentration along the path, and typically is expressed in units of parts per million (ppm), parts per billion (ppb), or micrograms per cubic meter ($\mu\text{g}\cdot\text{m}^{-3}$).

3.2.9 *path-integrated concentration, n*—the quantity measured by an OP/FT-IR monitor over the monitoring path. It has units of concentration times length, for example, ppm·m.

³ The boldface numbers in parentheses refer to a list of references at the end of this standard.

3.2.10 *plume, n*—the gaseous and aerosol effluents emitted from a stack or other pollutant source and the volume of space they occupy.

3.2.11 *retroreflector, n*—an optical device that returns radiation in directions close to the direction from which it came.

3.2.11.1 *Discussion*—Retroreflectors come in a variety of forms. The retroreflector commonly used in OP/FT-IR monitoring uses reflection from three mutually perpendicular surfaces. This kind of retroreflector is usually called a cube-corner retroreflector.

3.2.12 *single-beam spectrum, n*—the radiant power measured by the instrument detector as a function of frequency.

3.2.12.1 *Discussion*—In FT-IR absorption spectrometry the single-beam spectrum is obtained after a fast Fourier transform of the interferogram.

3.2.13 *synthetic background spectrum, n*—a background spectrum made by choosing points along the envelope of a single-beam spectrum and fitting a series of short, straight lines or a polynomial function to the chosen data points to simulate the instrument response in the absence of absorbing gases or vapors.

4. Significance and Use

4.1 This guide is intended for users of OP/FT-IR monitors. Applications of OP/FT-IR systems include monitoring for hazardous air pollutants in ambient air, along the perimeter of an industrial facility, at hazardous waste sites and landfills, in response to accidental chemical spills or releases, and in workplace environments.

5. Principles of OP/FT-IR Monitoring

5.1 Long-path IR spectrometry has been used since the mid-1950s to characterize hazardous air pollutants (2). For the most part, this earlier work involved the use of multiple-pass, long-path IR cells to collect and analyze air samples. In the late 1970s a mobile FT-IR system capable of detecting pollutants along an open path was developed (3). The 1990 amendments to the Clean Air Act, which may require that as many as 189 compounds be monitored in the atmosphere, have led to a renewed interest in OP/FT-IR monitoring (4). The OP/FT-IR monitor is a spectrometric instrument that uses the mid-IR spectral region to identify and quantify atmospheric gases. These instruments can be either transportable or permanently installed. An open-path monitor contains many of the same components as those in a laboratory FT-IR system, for example the same types of interferometers and detectors are used, except that the sample volume consists of the open atmosphere. In contrast to more conventional point monitors, the OP/FT-IR monitor provides path-integrated concentration data. Unlike many other air monitoring methods, such as those that use canisters or sorbent cartridges, the OP/FT-IR monitor measures pollutants in situ. Therefore, no samples need be collected, extracted, or returned to the laboratory for analysis. Detection limits in OP/FT-IR depend on several factors, such as the monitoring pathlength, the absorptivity of the analyte, and the presence of interfering species. For most analytes of interest, detection limits typically range between path-integrated concentrations of 1.5 and 50 ppm-m.

NOTE 1—The OP/FT-IR monitor can be configured to operate in two modes: active or passive. In the active mode, a collimated beam of radiation from an IR source that is a component of the system is transmitted along the open-air path. In the passive mode, radiation emitted from objects in the field of view of the instrument is used as the source of IR energy. Passive FT-IR monitors have been used for environmental applications, such as characterizing the plumes of smoke stacks. More recently these systems have been developed to detect chemical warfare agents in military applications. However, to date, the active mode has been used for most environmental applications of OP/FT-IR monitoring. In addition to open-air measurements, extractive measurements can be made by interfacing a closed cell to an FT-IR system. This type of system can be used as a point monitor or to measure the effluent in stacks or pipelines.

6. Description of OP/FT-IR Systems

6.1 There are two primary geometrical configurations available for transmitting the IR beam along the path in active OP/FT-IR systems. One configuration is referred to as bistatic, while the other is referred to as monostatic, or unistatic.

6.1.1 *Bistatic Configuration*—In this configuration, the detector and the IR source are at opposite ends of the monitoring path. In this case, the optical pathlength is equal to the monitoring pathlength. Two configurations can be used for bistatic systems. One configuration places the IR source, interferometer, and transmitting optics at one end of the path and the receiving optics and detector at the other end (Fig. 1(A)). Typically a Cassegrain or Newtonian telescope is used to transmit and collect the IR beam. The advantage of the configuration depicted in Fig. 1(A) is that the IR beam is modulated along the path, which enables the unmodulated ambient radiation to be rejected by the system's electronics. The maximum distance that the interferometer and the detector can be separated in this configuration is limited because communication between these two components is required for timing purposes. For example, a bistatic system with this configuration developed for monitoring workplace environments had a maximum monitoring pathlength of 40 m (5). The other bistatic configuration places the IR source and transmitting optics at one end of the path and the receiving optics, interferometer, and detector at the other end of the path (Fig. 1(B)). This is the most common configuration of bistatic systems in current use. In this configuration the beam from the IR source is collimated by a mirror shaped as a paraboloid. The configuration shown in Fig. 1(B) allows the maximum monitoring path, in principle, to be doubled compared to that of the monostatic configuration. The main drawback to this bistatic configuration is that the IR radiation is not modulated before it is transmitted along the path. Therefore, radiation from the active IR source and the ambient background cannot be distinguished by electronic processing.

6.1.2 *Monostatic Configuration*—In monostatic configurations, the IR source and the detector are at the same end of the monitoring path. A retroreflector of some sort is required at the midpoint of the optical path to return the beam to the detector. Thus, the optical pathlength is twice the distance between the source and the retroreflector. Two techniques are currently in use for returning the beam along the optical path in the monostatic configuration. One technique uses an arrangement of mirrors, such as a single cube-corner retroreflector, at one end of the path that translates the beam slightly so that it does not fold back on itself (Fig. 2(A)). The

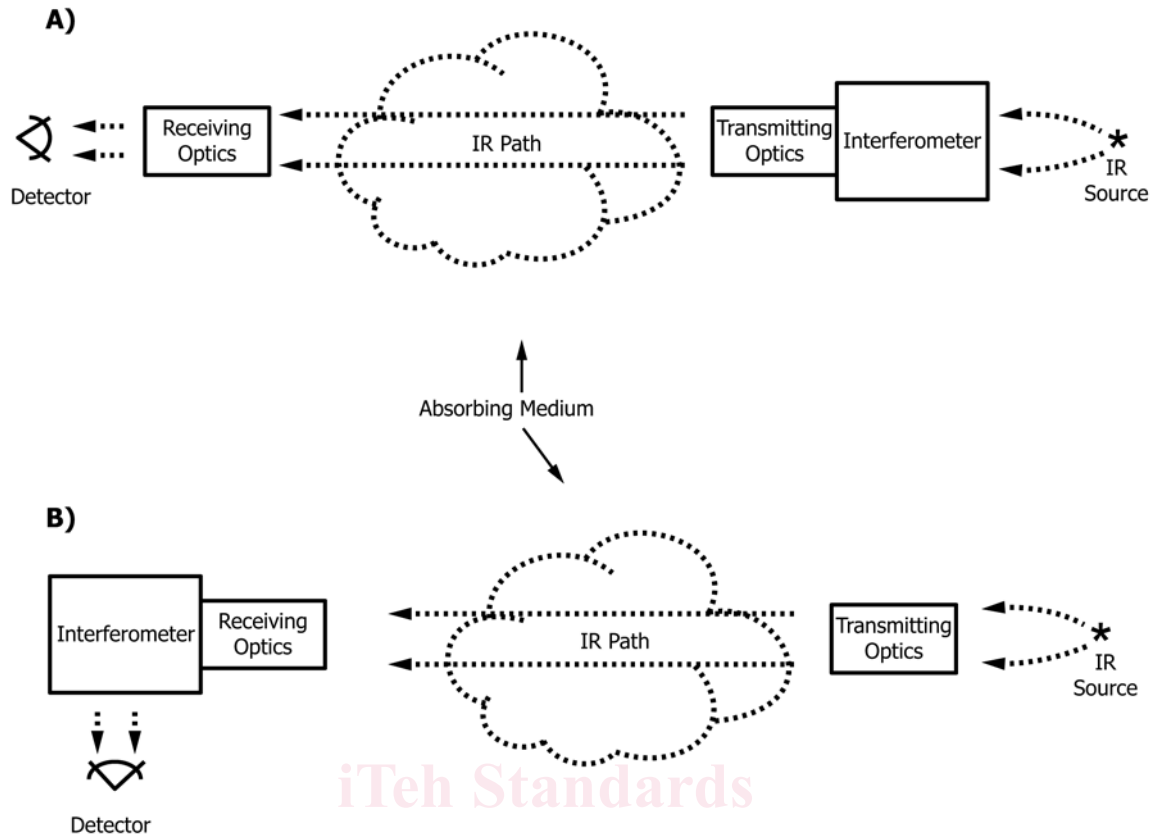


FIG. 1 Schematic Diagram of the Bistatic OP/FT-IR Configuration Showing (A) a System with the IR Source and Interferometer at One End of the Path and the Detector at the Opposite End, and (B) a System with the IR Source at One End of the Path and the Interferometer and Detector at the Opposite End

other end of the path then has a second telescope slightly removed from the transmitter to collect the returned beam. Initial alignment with this configuration can be difficult, and this type of monostatic system is normally used in permanent installations rather than as a transportable unit. Another configuration of the monostatic monitoring mode uses the same telescope to transmit and receive the IR beam. A cube-corner retroreflector array is placed at the end of the monitoring path to return the beam (Fig. 2(B)). To transmit and receive with the same optics, a beamsplitter must be placed in the optical path to divert part of the returned beam to the detector. A disadvantage to this configuration is that the IR energy must traverse this beamsplitter twice. The most efficient beamsplitter transmits 50 % of the light and rejects the other 50 %. Thus, in two passes, the transmission is only 25 % of the original beam. Because this loss of energy decreases the signal-to-noise ratio (S/N), it can potentially be a significant drawback of this configuration.

7. Selection of Instrumental Parameters

7.1 Introduction and Overview—One important issue regarding the operation of OP/FT-IR systems is the appropriate instrumental parameters, such as measurement time, resolution, apodization, and degree of zero filling, to be used during data acquisition and processing. The choice of some of these parameters is governed by the trading rules in FT-IR spectrometry and by specific data quality objectives of the study.

7.2 Trading Rules in FT-IR Spectrometry—The quantitative relationships between the S/N , resolution, and measurement time in FT-IR spectrometry are called “trading rules.” The factors that affect the S/N and dictate the trading rules are expressed in Eq 1, which gives the S/N of a spectrum measured with a rapid-scanning Michelson interferometer (6):

$$\frac{S}{N} = \frac{U_{\nu}(T) \cdot \theta \cdot \Delta \nu \cdot t^{1/2} \cdot \xi \cdot D^*}{(A_D)^{1/2}} \quad (1)$$

where:

- $U_{\nu}(T)$ = spectral energy density at wavenumber ν from a blackbody source at a temperature T ,
- θ = optical throughput of the spectrometric system,
- $\Delta \nu$ = resolution of the interferometer,
- t = measurement time in seconds,
- ξ = efficiency of the interferometer,
- D^* = specific detectivity, a measure of the sensitivity of the detector, and
- A_D = area of the detector element.

NOTE 2—This equation is correct but assumes that the system is detector noise limited, which is not always true. For example, source fluctuations, the analog-to-digital converter, or mechanical vibrations can contribute to the system noise.

7.3 Measurement Time—As shown in Eq 1, the S/N is proportional to the square root of the measurement time ($t^{1/2}$). For measurements made with a rapid scanning interferometer operating at a constant mirror velocity and a given resolution, the S/N increases with the square root of the number of

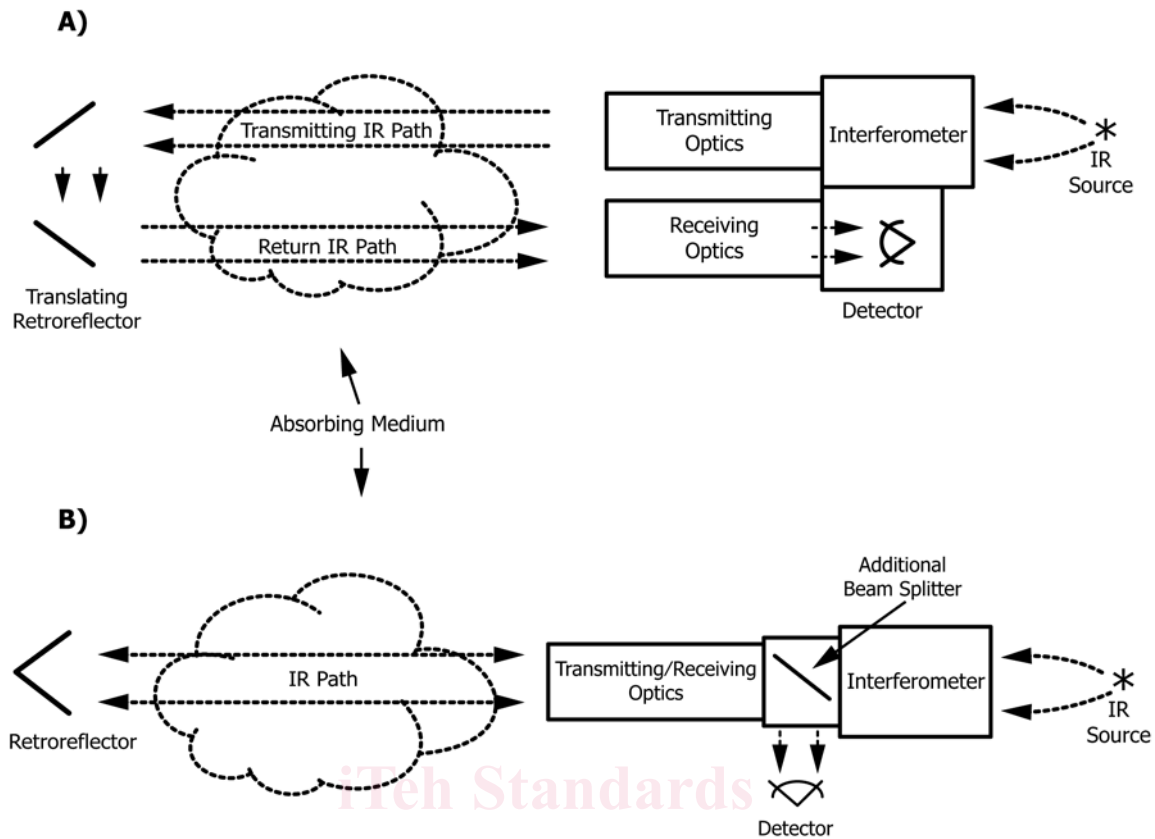


FIG. 2 Schematic Diagram of the Monostatic OP/FT-IR Configuration Showing (A) a System with a Retroreflector that Translates the Return IR Beam to Separate Receiving Optics, and (B) a System that Uses the Same Optics to Transmit and Receive the IR Beam

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co-added scans. The choice of measurement time for signal averaging in OP/FT-IR monitoring must take into account several factors. First, a measurement time must be chosen to achieve an adequate S/N for the required detection limits. However, because monitoring for gases and vapors in the air is a dynamic process, consideration must be given to the temporal nature of the target gas concentration. For example, if the concentration of the target gas decreases dramatically during the measurement time, then there would be a dilution effect. In addition, varying signals cannot be added linearly in the interferogram domain. Nonlinearities and bandshape distortions will be observed if the concentrations of gases in the path vary appreciably during the measurement time.

7.4 Resolution—Several factors must be considered when determining the optimum resolution for measuring the IR spectra of gases and vapors along a long, open path. These factors include (1) the ability to distinguish between the spectral features of target analytes and those of ambient interfering species in the atmosphere, such as water vapor; (2) the tradeoffs between resolution, IR peak absorbance, and S/N ; (3) practical considerations, such as measurement time, computational time to process the interferogram, and the size of the interferogram file for data storage; (4) procedural considerations, such as the choice of background spectrum and the development of an adequate water vapor reference spectrum; and (5) logistical considerations, such as the size and the cost of the instrument.

7.4.1 Effect of Resolution on S/N Ratio—The S/N is directly related to the resolution, $\Delta\nu$, although this relationship is not as straightforward as implied in Eq 1. If the physical parameters of the spectrometer, such as the measurement time, optical throughput, and the interferometer efficiency, are assumed to be constant for measurements made at both high and low resolution, the S/N will be halved upon decreasing the quantity $\Delta\nu$ by a factor of 2 (for example, changing the resolution from 1 cm^{-1} to 0.5 cm^{-1}). Because the S/N is proportional to the square root of the measurement time, the measurement time required to maintain the original baseline noise level must be increased by a factor of 4 each time $\Delta\nu$ is decreased by a factor of 2 for measurements made at a constant optical throughput. However, the optical throughput does not necessarily remain constant when the resolution is changed. In low-resolution measurements, a large optical throughput is allowed for the interferometer, and the throughput is limited by the area of the detector element or the detector foreoptics. The throughput of OP/FT-IR systems is generally limited by the size of the telescope and the pathlength, not the FT-IR spectrometer. Most commercial low-resolution FT-IR spectrometers operate with a constant throughput for all resolution settings. Instruments capable of high-resolution measurements are equipped with adjustable or interchangeable aperture (Jacquinot) stops installed in the source optics that reduce the solid angle of the beam passing through the interferometer. Spectra collected at high resolutions are generally measured with a variable

throughput, which decreases as the spectral resolution improves. In high-resolution measurements made under variable throughput conditions, the throughput is halved as $\Delta\nu$ is decreased by a factor of 2. This results in an additional decrease in the S/N by one-half, which requires increasing the measurement time by another factor of 4 to obtain the original S/N . Thus, for high-resolution FT-IR spectrometers operating under variable throughput conditions, the total measurement time is increased by a factor of 16 when $\Delta\nu$ is decreased by a factor of 2. The preceding discussions apply only to the effect of resolution on the baseline noise level. Resolution may also affect the peak absorbance of the bands being measured. For a weak and narrow spectral feature whose full width at half height (FWHH) is much less than the instrumental resolution, the peak absorbance will approximately double on decreasing $\Delta\nu$ by a factor of 2. Assuming this band was measured under constant-throughput conditions, its S/N would be the same for measurements taken at the higher and lower resolution settings, provided the measurement times are equal. For weak, broad spectral features whose peak absorbance does not change as a function of resolution, acquiring data at a higher resolution will only increase the baseline noise.

7.4.2 Effect of Resolution on Quantitative Analyses—The determination of target gas concentrations by OP/FT-IR spectrometry depends on the linear relationship between IR absorbance and concentration as given by Beer's law. This linear relationship is observed only when the spectrum is measured at a resolution that is equal to or higher than the FWHH of the band. The measured spectrum is the convolution of the instrument line shape function and the true band shape. As a result, if the FWHH of the band is narrower than the instrumental function, the measured spectrum will vary only approximately linearly with concentration. For example, Spellicy et al (4) have shown that the absorbance for a single Lorentzian band with a FWHH of 0.1 cm^{-1} is linear with concentration only when measured at a high resolution, for example, 0.01 cm^{-1} . Deviation from linearity would most likely be observed in small molecules such as HCl, CO, CO₂, and H₂O, which have sharp spectral features (FWHH $\approx 0.1\text{ cm}^{-1}$). For larger molecules, such as heavy hydrocarbons that exhibit broader IR bands with contours of approximately 20 cm^{-1} , the linear relationship between absorbance and concentration is more likely to be followed at lower resolution.

NOTE 3—The effect of resolution on quantitative OP/FT-IR measurements has been addressed by several groups, although a consensus on what resolution is generally applicable has not yet been reached. The optimum resolution to use is influenced by the choice of quantitative analysis method. For example, if the scaled subtraction method is used, high-resolution spectra can be used to advantage. Bittner et al (7) used scaled subtraction to detect 5 ppb of benzene over a 100 m path. Spectra recorded at 0.125 cm^{-1} resolution allowed the narrow benzene band at 674 cm^{-1} to be separated from the strong CO₂ absorption bands. If a multivariate analysis method is used, the absorption bands of the target gas and interfering species do not need to be completely resolved. However, the degree of spectral overlap does seem to affect the accuracy of some multivariate techniques, such as classical least squares (CLS). For example, Strang et al (8) used a closed-path FT-IR system equipped with a 20.25 m multipass cell to monitor organic vapors and metal hydrides in simulated workplace environments. Because of spectral overlap with other target analytes, CO₂, and water vapor, a resolution of 0.5 cm^{-1} was required to quantify arsine, diborane, and phosphine with a CLS algo-

rihm. Also, only the 0.5 cm^{-1} resolution measurements exhibited a linear relationship for all concentrations of diborane studied. Strang and Levine (9) also observed little difference in the detection limits estimated for these compounds at resolutions of 0.5 cm^{-1} , 2 cm^{-1} , 4 cm^{-1} , and 8 cm^{-1} . However, diborane and phosphine were difficult to quantify at 8 cm^{-1} resolution because of an insufficient number of data points to define the absorption band used for quantification. In a laboratory study using a 5 cm cell, Marshall et al (10) found that, for selected volatile organic compounds (VOCs), the specificity and the accuracy of the CLS results deteriorated as the resolution was degraded. Childers and Thompson (11) used CLS to analyze a set of digitally created mixtures of spectra acquired on a bench-top FT-IR system equipped with a 0.5 cm gas cell. In this study, the CLS algorithm accurately quantified target analytes that exhibited spectra with overlapping sharp features, even when the bands used for analysis were not fully resolved. Because the spectral mixtures were created digitally, Beer's law was always upheld. However, a failure to identify all of the overlapping components in a mixture resulted in a bias and an increase in the error in the CLS analysis. The accuracy of the CLS analysis was also not affected by resolution for spectra with overlapping broad features. However, the magnitude of the errors in the CLS analysis was related to the number of data points per wavenumber in the spectra. Therefore, the errors in the CLS analysis increased as the resolution degraded, if the degree of zero filling was the same at each resolution. The magnitude of the errors in the CLS analyses also increased proportionally with baseline noise. Other multivariate techniques, such as partial least squares (PLS), may be superior to CLS in dealing with nonlinearity due to low resolution and severe spectral overlap. Griffiths et al (12) have suggested that because many VOCs of interest have band contours roughly 20 cm^{-1} wide, a low spectral resolution should be adequate for OP/FT-IR measurements. The authors found that the PLS standard error of calibration and standard error of prediction were at a minimum for measurements of VOC mixtures made at 16 cm^{-1} resolution. A low-resolution OP/FT-IR monitor based on this premise is currently being developed and evaluated.

7.5 Zero-Filling—The fast Fourier transform of a normal interferogram generates spectral points of regular intervals. When the interferogram contains frequencies that do not coincide with the frequency sample points, the spectrum resembles a "picket fence." Extending the interferogram synthetically with zeros added to the end will increase the density of points in the spectrum and reduce the picket fence effect. Zero filling improves only the digital resolution, and not the spectral resolution. Normally, some multiple (for example, 2, 4, etc.) of the original number of data points is added to the interferogram. One order of zero filling, which is two times the original number of data points, is usually appropriate. The picket fence effect is less extreme if the spectral components are broad enough to be spread over several sampling positions. It should be noted that zero filling does increase the file size and, therefore, the time required for data processing.

7.6 Apodization—The finite movement of the interferometer mirror truncates, or cuts off, the true interferogram. This, in effect, multiplies the interferogram by a boxcar truncation function. This function may cause the appearance of side lobes on both sides of a narrow absorption band. The corrective procedure for eliminating these side lobes is called apodization. Apodization is done by multiplying the interferogram by a mathematical function. Typical apodization functions include triangular, Happ-Genzel, and Norton-Beer functions. Apodization affects the spectral resolution, the peak absorbance, and the noise of the spectrum. The absorbance of narrow or strong bands will be most affected by the choice of apodization function. In general, the bands in a spectrum computed with no apodization will be more intense than bands computed from the

same interferogram after applying an apodization function. Apodization also degrades resolution slightly. In general, to obtain the optimum S/N for spectra of small molecules with resolvable fine structure, the use of no apodization is preferable if side lobes from neighboring intense bands do not present an interference. If side lobes are present and interfere with either qualitative or quantitative analyses, apodization becomes necessary. For broad absorption bands, the measured absorbance is about the same in apodized and unapodized spectra. Overall, the greatest noise suppression will be obtained with the strongest apodization function, but the spectral resolution and band intensities will be greatest for weaker apodization functions (6). The choice of apodization function also may affect the quality of fit in multivariate analysis techniques. The same apodization function should be used for the sample spectra as was used for the reference spectra. Also, the same apodization function should be used for spectral data that are to be exchanged from one instrument to another for comparative purposes.

7.7 Guidance for Selecting Instrumental Parameters—Although a stepwise protocol that specifies instrumental parameters is not yet available for OP/FT-IR monitoring, the operator should have an appreciation for the effect that the instrumental parameters have on spectral measurements. Grasselli et al (13) have published criteria for presenting spectra from computerized IR instruments, with an emphasis on FT-IR measurements. The authors established recommendations and guidelines for reporting experimental conditions, instrumental parameters, and other pertinent information describing the acquisition of FT-IR spectra. These guidelines should be followed when reporting OP/FT-IR data. The following guidelines should be taken into account when choosing the optimum instrumental parameters for OP/FT-IR measurements. The parameters may need to be optimized for the specific experiments planned, taking into consideration the goals of the monitoring study.

7.7.1 Measurement Time—First, determine the measurement time required to achieve the desired S/N at the selected resolution. Then determine if this is an appropriate measurement time to capture the event being studied. If the measurement time is longer than the event being studied there will be a dilution effect. Nonlinearities and band distortions might be observed due to adding a changing signal in the interferogram domain.

7.7.2 Resolution—Although there is currently no consensus among workers in the discipline of OP/FT-IR monitoring as to the optimum resolution to be used to collect field data, the following steps can be taken to choose the best resolution for a particular application.

7.7.2.1 Consider the bandwidths of the absorption features used to analyze for specific target gases. If the absorption bands of the target gases are broad, there may be no need to acquire high-resolution spectra. When this is the case, no additional information will be gained, and the measurements will have poorer S/N and will require longer data collection, longer computational times, and larger data storage space. The analyst must be aware, however, that the spectral features of atmospheric constituents such as CO_2 , H_2O , and CH_4 can be

completely resolved only at a resolution of 0.125 cm^{-1} or better. Because these compounds are in every long-path spectrum and often overlap with the target analyte, access to high-resolution data may be required to visualize the spectral features of the target gas and to identify interfering species. This information can then be used to develop the analysis method.

7.7.2.2 Determine if interfering species are present. If the comparison or scaled subtraction method is used for quantitative analysis (see 12.4), the resolution should be sufficient to separate spectral features of the target gases from those of interfering species.

7.7.2.3 Acquire reference spectra of the target gases. If the specific target gases are known before beginning the monitoring study, reference spectra of the compounds of interest should be obtained at various resolutions. By comparing the spectra recorded at different resolutions, the operator can determine the lowest resolution measurement that still resolves the spectral features of interest. This resolution setting should be used as a starting point for future measurements. If it is not possible to record the reference spectra, the operator should consult reference libraries to determine the resolution required to characterize the target analyte.

7.7.2.4 Develop calibration curves of the target gases. If an inadequate resolution is used, the relationship between absorbance and concentration will not be linear. This relationship is also affected by the apodization function. Calibration curves covering the concentration range of the target gases expected in the ambient measurements should be developed at different resolutions and with the use of different apodization functions to determine the optimum settings. If the compound of interest does not respond linearly with respect to concentration, a correction curve will need to be applied to the data during quantitative analysis.

7.7.2.5 Determine the effect of resolution on the other procedures involved with generating OP/FT-IR data, such as creation of a synthetic background and water-vapor-reference spectrum. These procedures rely on a series of subjective judgements based on the visual inspection of the field spectra. Choices made in these procedures can be facilitated by using a higher resolution.

7.7.3 Zero Filling and Apodization—In general, a zero filling factor of 2 should be used when processing the original interferograms. Triangular and Happ-Genzel apodization functions are commonly used in OP/FT-IR monitoring, although Griffiths et al (12) have indicated that a Norton-Beer medium function actually gives a better representation of the true absorbance. In all cases, however, the same parameters should be used to collect the field spectra that were used to record the reference spectra. The choice of apodization function may be limited by this requirement. If spectra from a commercial or user-generated library are to be the reference spectra for quantitative analysis, then the parameters that were used to generate those reference spectra should be used to collect the field spectra. Otherwise, errors in the concentration measurement will occur.

8. Initial Instrument Operation

8.1 The assumption made for the following discussion is that the manufacturer has set up the OP/FT-IR system and it is performing according to specifications. The tests outlined in this section should be performed before actual field data are recorded. Many of the tests involving the initial instrument setup are similar to those proposed for use in the quality assurance/quality control (QA/QC) procedures presented in Section 13 of this guide.

8.2 *The Single-Beam Spectrum*—The operator should become familiar with the features that are expected to be present in a typical single-beam spectrum. A single-beam spectrum acquired along a 414 m optical path at a nominal 1 cm⁻¹ resolution is shown in Fig. 3. There are several features in the spectrum that should be noted. First, the IR energy in the regions from approximately 1415 cm⁻¹ to 1815 cm⁻¹ and 3550 cm⁻¹ to 3900 cm⁻¹ is totally absorbed by water vapor. For a given pathlength, the width of the region for complete absorption varies as the amount of water vapor in the atmosphere changes. The strong absorption in the region from approximately 2235 cm⁻¹ to 2390 cm⁻¹ is due to carbon dioxide. The atmosphere is always opaque in this wavenumber region, even over short paths. The opaque regions represent the baseline of the single-beam spectrum and they should always be flat and register zero. Any deviation from zero in these regions indicates that something is wrong with the instrument operation. For example, the opaque regions are slightly elevated in Fig. 3. This is due to internal stray light. This point is discussed in more detail in 8.5. When the monitoring path is sufficiently long (for example, 200 m) or the water vapor partial pressure is high enough, for example, 1333 Pa (10 torr), an absorption band should be noticeable at 2720 cm⁻¹. This band is the Q-branch of deuterated water (HDO) and it is also possible to observe the P (2700 cm⁻¹ to 2550 cm⁻¹) and the R (2750 cm⁻¹ to 2850 cm⁻¹) branches. The spectral region around 3000 cm⁻¹ is also strongly impacted by water vapor,

although it is not opaque. The absorption features of methane are also in this region. The atmosphere from 3500 cm⁻¹ to 3900 cm⁻¹ is opaque, again because of water vapor. At sufficiently long monitoring paths (approximately 50 m) spectral features of CO (2040 cm⁻¹ to 2230 cm⁻¹) and N₂O (2150 cm⁻¹ to 2265 cm⁻¹) should be observed in the single-beam spectrum. As in tests described in Practice E1421, the intensity of the single-beam spectrum should be recorded for different regions, for example, near 990 cm⁻¹, 2500 cm⁻¹, and 4400 cm⁻¹, to form a basic set of data about the instrument's operation. Regions that are not impacted significantly by water vapor should be chosen. Along with this information, the operator should record the pathlength and water-vapor concentration.

8.3 *Distance to Detector Saturation*—One of the first pieces of information to obtain with an OP/FT-IR monitor is the pathlength at which the detector becomes saturated. For permanent installations in which the pathlength is fixed or predetermined this should be a parameter specified to the manufacturer. The distance at which the detector becomes saturated is particularly important for mercury-cadmium-telluride (MCT) detectors that are currently used in OP/FT-IR systems. Detector saturation is not as severe of a problem for thermal detectors, such as deuterated triglycine sulfate detectors, which may be used in OP/FT-IR systems in the future. The operator should pay particular attention to the spectrum in the wavenumber region below the detector cutoff. For the MCT detector used to generate Fig. 3, the detector cutoff occurs between 600 cm⁻¹ and 700 cm⁻¹. The spectrum below the detector cutoff frequency should be flat and at the baseline. If the spectrum has an elevated baseline in this wavenumber region, the detector may be operating in a nonlinear manner. If this is the case, nonphysical energy will appear well below the detector cutoff as the retroreflector or IR source is brought closer to the receiving optics. An example of this is given in Fig. 4 for a single-beam spectrum recorded at a 20 m pathlength. The minimum of this artifact is not to be

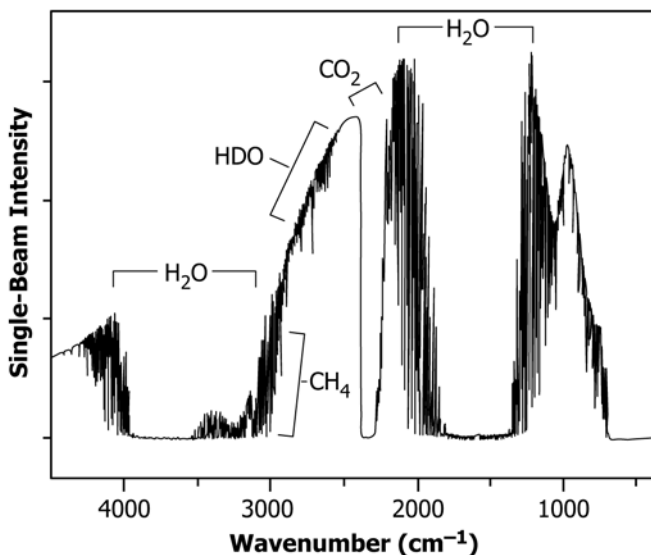


FIG. 3 Single-Beam OP/FT-IR Spectrum Along a 414 m Path with Regions of Typical Atmospheric Absorption Features Annotated

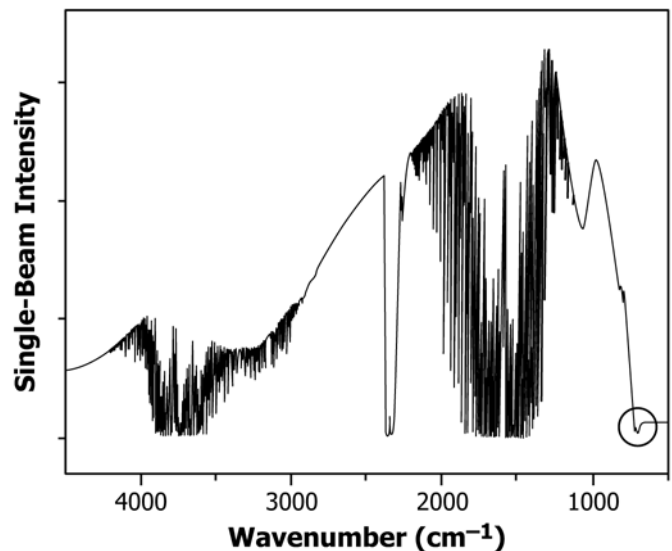


FIG. 4 Single-Beam OP/FT-IR Spectrum Recorded at a 20 m Total Pathlength. The Nonphysical Energy Annotated in the Encircled Area Indicates Detector Saturation