Standard Guide for
Open-Path Fourier Transform Infrared (OP/FT-IR) Monitoring of Gases and Vapors in Air[1]

This standard is issued under the fixed designation E 1865; 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 describes 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 *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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*
E 131 Terminology Relating to Molecular Spectroscopy[2]
E 168 Practice for General Techniques of Infrared Quantitative Analysis[2]
E 1421 Practice for Describing and Measuring Performance of Fourier Transform Mid-Infrared (FT-MIR) Spectrometers Level Zero and Level One Tests[2]
E 1655 Practices for Infrared, Multivariate, Quantitative Analysis[2]

3. Terminology

3.1 For definitions of terms relating to general molecular spectroscopy used in this guide refer to Terminology E 131. 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 (μgm^{-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.

3.2.10 *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.

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[1] This guide is under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and is the direct responsibility of Subcommittee E13.03 on Infrared Spectroscopy.
Current edition approved March 10, 1997. Published July 1997.
[2] *Annual Book of ASTM Standards*, Vol 03.06.
[3] The boldface numbers in parentheses refer to a list of references at the end of this guide.

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 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
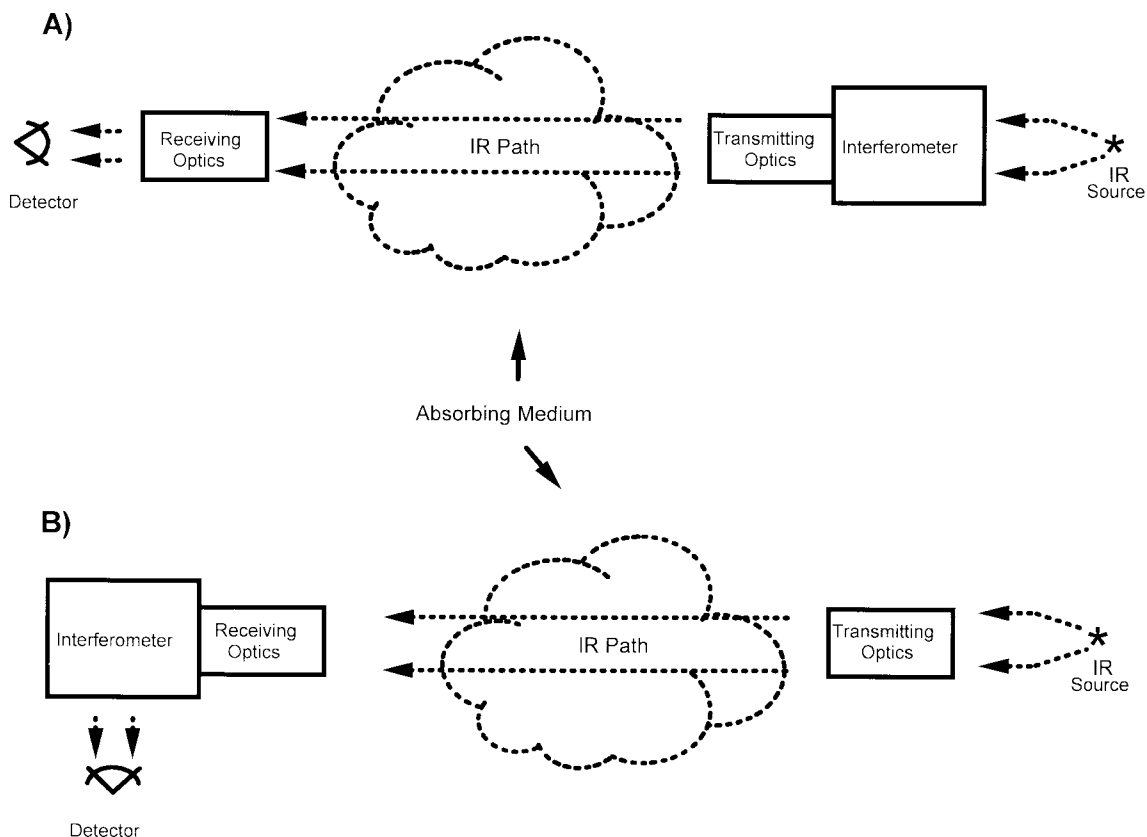
A)

B)

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

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**):

$$\frac{S}{N} = \frac{U_v(T) \cdot \theta \cdot \Delta v \cdot t^{1/2} \cdot \xi \cdot D^*}{(A_D)^{1/2}} \qquad (1)$$

where:

$U_v(T)$ = spectral energy density at wavenumber v from a blackbody source at a temperature T,
θ = optical throughput of the spectrometric system,
Δv = 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 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;
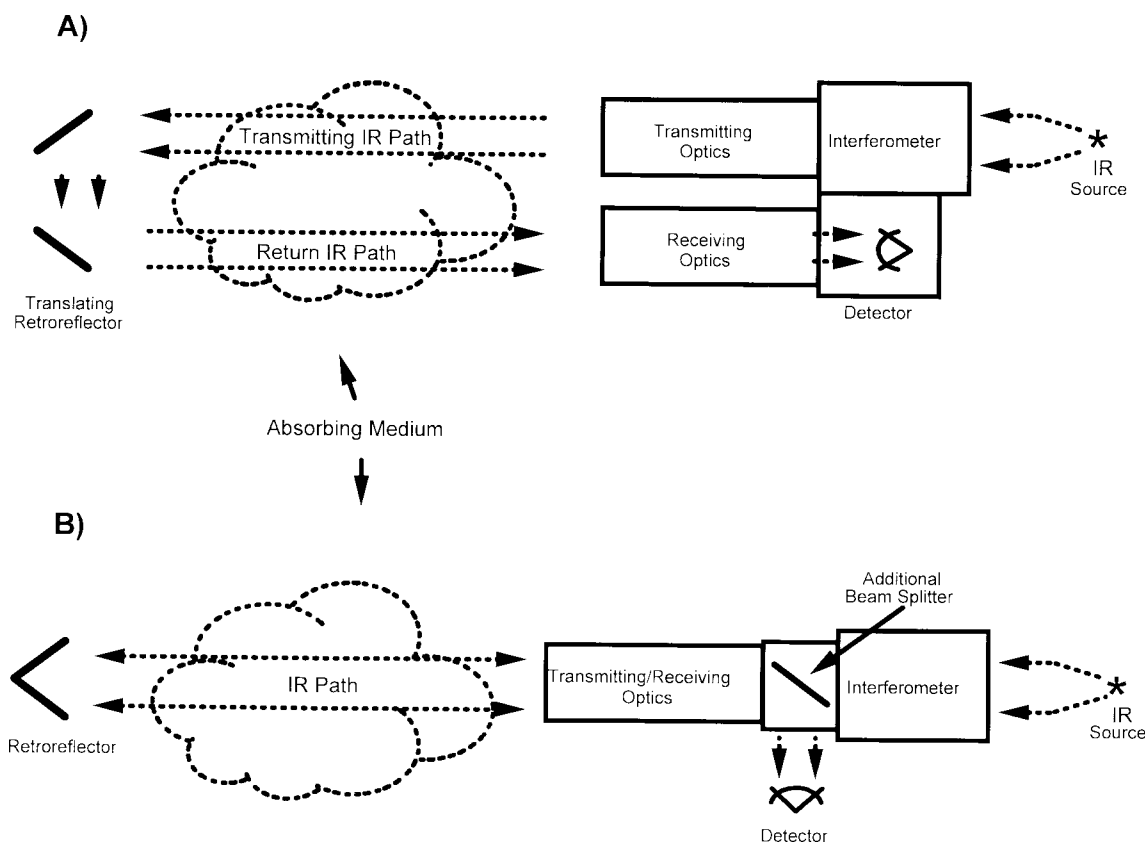
A)

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

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, Δv, 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 Δv by a factor of 2 (for example, changing the resolution from 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 Δv 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 Δv 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 Δv 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 Δv 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

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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, CO_2, and H_2O, which have sharp spectral features (FWHH $\approx$ 0.1 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 CO_2 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, CO_2, and water vapor, a resolution of 0.5 cm^{-1} was required to quantify arsine, diborane, and phosphine with a CLS algorithm. 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, 2, 4, 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 to 1815 cm^{-1} and 3550 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 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
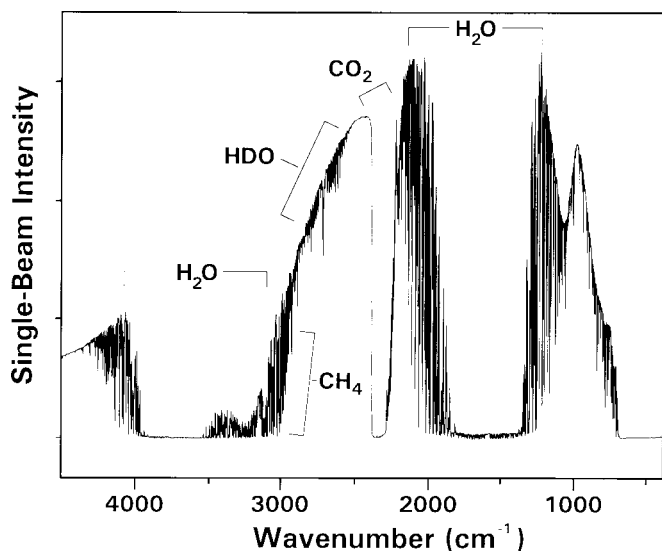
FIG. 3 Single-Beam OP/FT-IR Spectrum Along a 414-m Path with Regions of Typical Atmospheric Absorption Features Annotated

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 to 2550 cm^{-1}) and the R (2750 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 to 3900 cm^{-1} is opaque, again because of water vapor. At sufficiently long monitoring paths (approximately 50 m) spectral features of CO (2040 to 2230 cm^{-1}) and N_2O (2150 to 2265 cm^{-1}) should be observed in the single-beam spectrum. As in tests described in Practice E 1421, the intensity of the single-beam spectrum should be recorded for different regions, for example, near 990, 2500, 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 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 confused with an absorption band due to CO_2 near 668 cm^{-1}. The distance at which the nonphysical energy appears represents the minimum pathlength over which it is possible to operate without making changes to the instrument. A test for determining the ratio of the nonphysical energy to the maximum energy in the single-beam spectrum is given in Practice E 1421. If significant nonphysical energy is observed at the desired monitoring pathlength, it is possible to attenuate the IR beam, for example, by using a fine wire mesh screen to cover the aperture. As a last resort, it is possible to rotate the retroreflector or the IR source to lower the signal strength and minimize the nonphysical energy. Also, it is not useful to simply change the gain of the detector preamplifier to lower the apparent beam intensity, because the detector nonlinearity does not depend on gain.

8.4 *Signal Strength as a Function of Distance*—In OP/FT-IR systems, the IR beam is collimated before it is transmitted along the path. However, the beam will diverge as it traverses the path. The size of the IR source determines the divergence of the beam. Once the diameter of the beam is larger than the retroreflector (monostatic system) or the receiving telescope (bistatic system), the signal strength will diminish as the square of the distance. The need to determine the relationship between signal strength and distance is twofold. First, at some distance the system noise will become an appreciable part of the signal. Secondly, extraneous radiation can produce measurable signals in OP/FT-IR systems. For example, monostatic systems with the configuration depicted in Fig. 2(B) that use an additional beamsplitter have some signal contribution due to internal stray light. In bistatic systems that use an unmodulated, external IR source (Fig. 1(B)), ambient radiation contributes to the total signal. In both systems, the strength of the signal should be maintained above the signal due to either stray light or ambient radiation. To
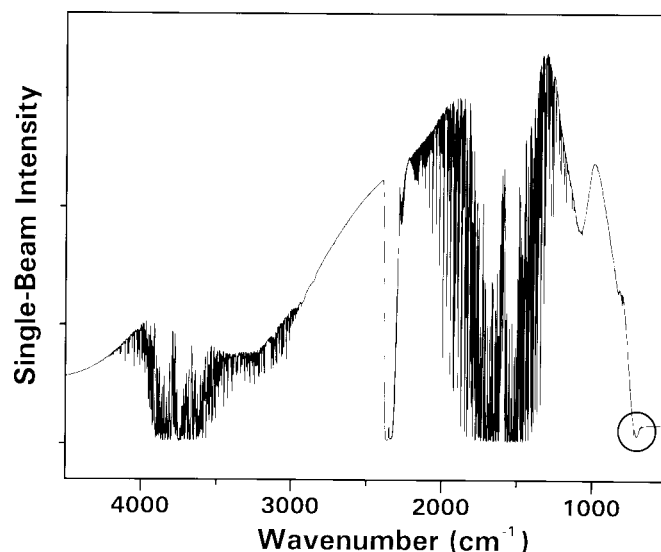

FIG. 4 Single-Beam OP/FT-IR Spectrum Recorded at a 20-m Total Path-length. The Nonphysical Energy Annotated in the Encircled Area Indicates Detector Saturation

determine the signal strength as a function of distance, start with the retroreflector or the IR source at the minimum working distance as determined in 8.3, then move the retroreflector or IR source back by some distance and record the magnitude of the signal. For this test, the signal strength can be determined by measuring either the peak-to-peak voltage of the interferogram or the intensity of the single-beam spectrum at a specific frequency. If the single-beam intensity is monitored for this test, a wavenumber region that does not contain water-vapor-absorption bands should be used.

8.5 *Determination of the Signal Due to Internal Stray Light and Ambient Radiation*—As shown in 8.2, single-beam spectra recorded with an OP/FT-IR monitor may exhibit non-zero signal intensities in wavenumber regions in which the atmosphere is totally opaque. This non-zero response can be attributed to either internal stray light or ambient radiation depending on the configuration of the OP/FT-IR monitor. Internal stray light is most likely to be a problem in monostatic systems that use a single telescope to transmit and receive the IR beam (see Fig. 2(B)). As discussed in 6.1.2, this configuration requires an additional beamsplitter to direct the return IR beam to the detector. This beamsplitter also diverts about 50 % of the IR energy before it is transmitted along the monitoring path. A portion of this diverted IR energy can be reflected by surfaces within the instrument housing and sensed by the detector without traversing the monitoring path. Ambient radiation mostly affects bistatic systems in which the active IR source is separated from the interferometer and detector (see Fig. 1(B)). In principle, all radiation collected by the receiving telescope is modulated by the interferometer and sensed by the detector. Because the IR radiation from the active IR source is not modulated as it propagates along the monitoring path in this type of system, there is no way to distinguish it from other IR sources in the field of view of the telescope. Therefore, the detector response in this type of bistatic system represents a composite of radiation from various IR sources. The presence of stray light or ambient radiation causes errors in the photometric accuracy and ultimately errors in the concentration measurements. Errors due to stray light or ambient radiation can be larger than those caused by other instrumental sources of error, such as source flicker. In general, if uncorrected for, the presence of stray light or ambient radiation always causes the concentration to be underestimated. For example, if stray light represents 10 % of the total return signal, the resulting calculated concentration will be approximately 10 % lower than the actual concentration. The relative effect of stray light or ambient radiation increases as the return signal decreases and is amplified at low values of transmittance (high values of absorbance). However, the effect of stray light and ambient radiation is not uniform across the range of absorbance values typically encountered in OP/FT-IR measurements. Therefore, even if the field spectra are corrected for either stray light or ambient radiation, the accuracy of the concentration measurements may still be affected. Thus, the relative contributions of stray light or ambient radiation to the total signal should be minimized. In bistatic systems, efforts to make the ambient background as consistent as possible should be made. Hot objects, objects that may undergo temperature differences

during the monitoring period, and the sky should not be in the field of view of the instrument during data acquisition. In monostatic systems, an excessive amount of internal stray light indicates either a design or an alignment problem in the transfer optics. Correction of excessive stray light problems may require action by the manufacturer of the instrument.

8.5.1 *Measurement of the Internal Stray Light*—As mentioned previously, the problem of modulated, internal stray light is most apparent in monostatic systems that use a single telescope to transmit and receive the IR beam and require an additional beamsplitter in the path (see Fig. 2(B)). The stray light in the instrument can be measured without regard to the distance to the retroreflector. To measure the stray light in this type of monostatic system, point the telescope away from the retroreflector or move the retroreflector out of the field of view of the telescope and collect a spectrum. A record of the stray light spectrum should be made and compared to the single-beam spectrum recorded at the selected working distance. An example of the relative contribution of stray light to the total signal in this type of monostatic system is given in Fig. 5. In this case, the magnitude of the stray light is approximately 6 % of the total return signal. Typically the stray light spectrum will overlap with the minima of the field single-beam spectrum in wavenumber regions in which the atmosphere is totally opaque. The fine structure in the stray light spectrum from 4200 to 2900 cm^{-1} and 2200 to 1100 cm^{-1} is absorption due to near-field water vapor. The percent contribution of stray light to the total signal, while it varies with wavenumber, is typically relatively constant over time, provided that the optical components or optical configuration of the system have not been altered. Therefore, a stray light spectrum can be acquired at the beginning of the monitoring period and updated as necessary. Stray light can also be caused by strong sources of IR energy that are in the field of view of the instrument. For example, the sun may be in the instrument's field of view during sunrise or sunset, which might give rise to an unwanted signal that comes
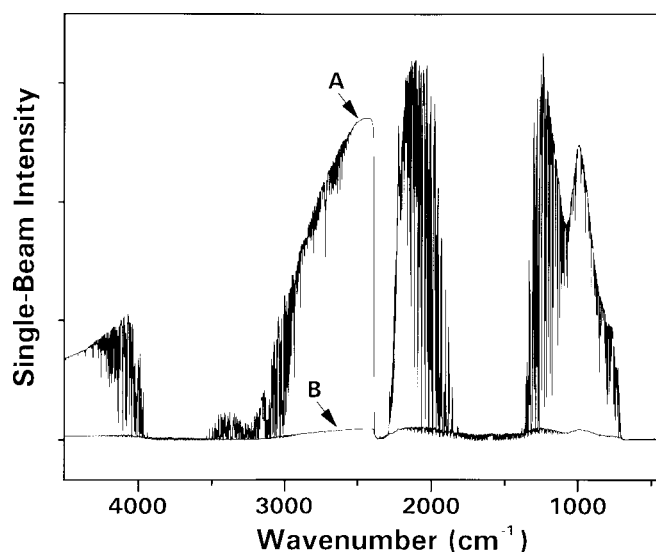

FIG. 5 Single-Beam OP/FT-IR Spectra Recorded with a Monostatic System over a 414-m Path with (*A*) the Telescope Directed at the Retroreflector and (*B*) the Telescope Slewed Away from the Retroreflector. Spectrum *A* Represents the Total Return Signal Whereas Spectrum *B* Represents the Signal Due to Stray Light

from reflections inside the instrument.

8.5.2 *Measurement of the Ambient Radiation*—For bistatic systems in which the active IR source is separated from the spectrometer (see Fig. 1(B)), the signal due to ambient radiation will be measured along with the signal from the active IR source. The signal due to ambient radiation can be measured by blocking or turning off the IR source. An example of the relative contribution of ambient radiation to the total signal in this type of bistatic system is given in Fig. 6. The spectrum obtained with the active IR source blocked or turned off is a composite of several IR sources in the field of view of the instrument, such as graybody radiators, the instrument itself, and emission bands from molecules in the atmosphere. The spectral distribution of a blackbody or graybody radiator depends on the temperature and emissivity of the object as described by Planck's law. The wavelength at which the power is a maximum varies inversely with temperature as described by Wien's displacement law. For example, the maximum intensity of a 300 K blackbody source would be observed at approximately 10 μm, or 1000 cm^{-1}. Therefore, the effect of ambient radiation is more pronounced in the fingerprint region, but is less significant above 2000 cm^{-1}. Because the spectrum due to ambient radiation is temperature-dependent, its relative contribution to the total signal will be variable. This variation will most likely be greater than any other instrumental source of noise. In addition, because the signal due to ambient radiation depends on what is in the field of view of the instrument, it will also depend on the distance between the IR source and the receiver. The spectral characteristics of the ambient signal can vary for different sites and can also change with changing meteorological conditions throughout the day. For example, if the clear sky is in the field of view of the instrument, emission bands from stratospheric gases, such as O_3 and CO_2, can be observed. These emission bands are generally not observed on cloudy days. Because the characteristics of the ambient signal can change, this signal must be

recorded on a more frequent basis than the stray light signal. Although a recommended schedule for recording the ambient spectrum has not been determined for all situations, an ambient spectrum is typically recorded once every half hour. This decision must be based on the site characteristics, meteorological conditions, the spectral region over which the analysis for the target gas is performed, and the data quality objectives of the study.

8.6 *Determination of the Random Noise of the System*—The random noise of the system can be determined from an absorption spectrum made from two single-beam spectra recorded sequentially. These spectra are to be taken under the same operating conditions and instrumental parameters as will be used during acquisition of the field spectra. There should be no time allowed to elapse between the acquisition of the two spectra. Once the two spectra have been acquired, an absorption spectrum should be made by using one of the two spectra as a background spectrum. Which spectrum is used for the background is not important. Determination of the random noise depends on the water-vapor concentration in the atmosphere, so the water-vapor concentration should also be monitored. The contributions of stray light and ambient radiation will be contained in these spectra. The random noise should be measured as the root-mean-square (RMS) noise. The actual wavenumber range over which the noise should be calculated will vary with the number of data points per wavenumber in the spectrum. A range of 98 data points is optimum for the RMS noise calculation **(14)**. For 1-cm^{-1} resolution with no additional zero filling, this means that the RMS noise measurement should be made over an approximately 50-cm^{-1} region. The RMS noise should be determined in wavenumber regions that are not significantly impacted by water vapor, for example 958 to 1008 cm^{-1}, 2480 to 2530 cm^{-1}, and 4375 to 4425 cm^{-1}. The magnitude of this noise should be measured periodically (at least daily) and plotted on a control chart to monitor the performance of the instrument. These tests are similar to those described in Practice E 1421.

8.7 *Determination of Wavenumber Shifts and Resolution Changes*—A test to determine if wavenumber shifts or changes in resolution have occurred should be conducted whenever the OP/FT-IR monitor has been moved to change the path, optical components in the system have been changed or realigned, or the instrument has been disassembled, shipped, or reassembled. Bands that are known to be singlets and that are always present in OP/FT-IR spectra can be used for this test. For example, water vapor has absorption bands at 1010, 1014, and 1017 cm^{-1} that will be in every spectrum as long as the product of the water vapor concentration and the pathlength is large enough. The bands at 1010 and 1017 cm^{-1} are actually doublets and cannot be resolved at 1-cm^{-1} resolution. The band at 1014 cm^{-1} is a singlet and can be used as a check for wavenumber shifts and resolution. Wavenumber shifts can also be measured by using the HDO bands in the 2720-cm^{-1} region, or with other absorption bands in the higher wavenumber region of the spectrum. Measurements at the high wavenumber region (short wavelength) are more sensitive to changes in the instrument, such as interferometer misalignment, than are those made in the lower wavenumber region (long wavelengths). The
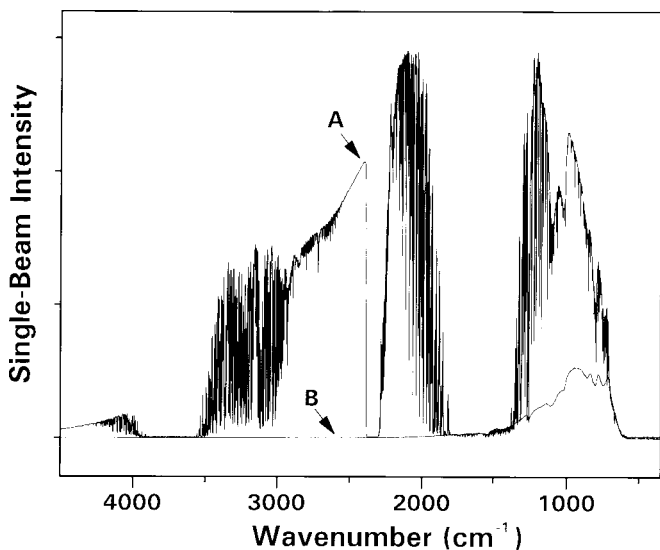

FIG. 6 Single-Beam OP/FT-IR Spectra Measured with a Bistatic System over a 207-m Path with (*A*) the IR Source On and (*B*) with the IR Source Off. Spectrum *A* Represents the Total IR Signal Whereas Spectrum *B* Represents the Signal Due to Ambient Radiation

HITRAN database **(15)** can be used as a guide to determine the positions of the water vapor bands, as well as bands for other atmospheric constituents. For any particular instrument, the band assignment may be slightly different because of the instrument's geometry, but it should not shift over time. There are two possible methods for determining wavenumber shifts between two spectra. The first is to compare the peak maxima in absorbance of the selected bands on the computer monitor. A more sensitive method is to subtract the second absorption spectrum from the first. For this test, the bands in the spectra being subtracted must be of the same intensity or they must be scaled to the same intensity prior to the subtraction operation. After subtraction, wavenumber shifts will result in a feature that appears to be the first derivative of the band shape. If a change in resolution has occurred, but there is no peak shift, the result will appear to have the shape of an "M" or a "W," depending on which of the two spectra contains the broader band. If there are no changes in the band from spectrum to spectrum, then the result of subtraction will be random noise.

9. Monitoring Site Considerations

9.1 *Overview*—There are two types of monitoring programs for which field-site requirements must be discussed. One type of program is a long-term effort with the instrument placed in a permanent position. The second type is a short-term program designed to take data at a site for a period from a few days to a few weeks. The short-term program is more flexible in that the path configuration can be based on the meteorological conditions at the time of the monitoring program. Long-term monitoring programs must be designed to allow for changes in the direction of the path as dictated by changing meteorological conditions. The United States Environmental Protection Agency (USEPA) has prepared a set of changes to Part 58 of Chapter 1 of Title 40 of the *Code of Federal Regulations* (40CFR58)[4] that define the appropriate ambient air monitoring criteria for open-path monitors **(16)**. These amendments specifically address the monitoring of the criteria pollutant gases O_3, CO, NO_2, and SO_2. The amendments are significant in that they describe how the path is to be chosen in terms of obstructions and height above the ground. They also describe the appropriate positioning of the path in relation to buildings, stacks, and roadways.

9.2 *Selecting the Pathlength*—Several factors must be considered when selecting the pathlength. These factors include (*1*) instrumental parameters, such as the *S/N* of the system, the divergence of the IR beam, and the distance at which the detector saturates; (*2*) the characteristics of the target gases, such as anticipated concentrations and known absorptivities; (*3*) the presence and concentrations of interfering species; (*4*) meteorological data, such as wind direction and speed; and (*5*) physical constraints, such as the area of the emission source, the extent of the plume, and the availability of electrical power and suitable sites to accommodate the instrument and peripherals.

9.2.1 *The Longest Path*—There are several factors that influence the determination of the longest usable path. The signal strength decreases with an increase in pathlength. The reason for this is twofold. First, the IR energy is absorbed by molecules in the beam. Secondly, at some point along the path, the signal strength will decrease in proportion to the inverse square of the pathlength. The minimum acceptable signal should always be some factor above the signal due to noise, stray light, or ambient radiation. The criterion for what is considered to be the minimum acceptable signal will depend on the data quality objectives of the monitoring study. The maximum total pathlength may also be determined by the presence of interfering species. Consider, for example, the water vapor band at 1014 cm^{-1}, which has an absorbance of approximately 0.01 at a total pathlength of 30 m when the water vapor pressure is 1333 Pa (10 torr). If an absorbance of 1 is considered the maximum quantifiable value allowable for this band and it interferes in the region of analysis for the target gas, then the maximum usable pathlength is about 3 km. For gases that are distributed homogeneously along the path, the atmosphere will be considered optically dense at some pathlength. Then for these gases that distance is the maximum usable pathlength.

9.2.2 *Shortest Path Requirements*—The shortest path may be dictated by the distance at which the detector becomes saturated. Assuming that the instrument is operating linearly at any potential distance, the shortest path for the target gas can be calculated from the absorbance measured in a reference spectrum of the target gas, a knowledge of the minimum measurable absorbance, and the assumption that reciprocity holds. First, the minimum concentration that is to be measured must be chosen. Then, by using the minimum detectable absorbance, the minimum path can be calculated as follows.

9.2.2.1 Measure the absorbance at the appropriate wavenumber for the target gas from a reference spectrum from either a spectral library or data base (see 12.3). Record the concentration-pathlength product at which this spectrum was taken.

9.2.2.2 Calculate the absorptivity, *a*, for this gas by using the following equation:

$$a = A_r/b_r c_r \qquad (2)$$

where:
A_r = absorbance of the reference spectrum at a specified wavenumber,
b_r = pathlength at which the reference spectrum was measured, and
c_r = concentration of the reference standard.

9.2.2.3 Assume a minimum concentration that will be measured.

9.2.2.4 Set the minimum detectable absorbance at 3 times the RMS baseline noise as measured under normal operating conditions.

9.2.2.5 Calculate the minimum usable path (b_m) from the following:

$$b_m = A_m/ac_m \qquad (3)$$

where:

A_m = the minimum detectable absorbance determined in 9.2.2.4,
c_m = the minimum concentration assumed in 9.2.2.3, and
a = the absorptivity calculated in 9.2.2.2.

9.2.3 *Short Path Versus Long Path*—As shown in 9.2.2, the selection of the pathlength begins by calculating the minimum usable pathlength from Beer's law. If a retroreflector is used, the physical path can be half the optical path determined previously. This is advantageous when plumes of finite size are being measured because the pathlength may be chosen to be close to the physical extent of the plume. For homogeneously distributed gases, the path can be made longer with some advantage. But for plumes of finite extent, making the path longer than the width of the plume is detrimental. This is because the OP/FT-IR measurement actually determines the path average concentration, and if a portion of the path has zero concentration, there is a dilution effect. In practice, it is judicious to have the pathlength nominally longer than the width of the plume to account for slight variations in the plume over time. Another reason for choosing a path that is as short as possible is to minimize the effects of spectral interferences. For long-term monitoring programs with permanent installations, the only real option is to place retroreflectors or IR sources (depending on the instrument configuration) at various distances and switch from one to the other periodically or on some predetermined schedule. Some versions of OP/FT-IR monitors incorporate a scanning system that facilitates this procedure. Currently, almost no research has been done to define the optimum pathlength for various conditions. Thus, selection of the pathlength must be repeated for each individual monitoring program.

9.2.4 *Prevailing Winds*—Many applications involving OP/FT-IR monitoring depend on the wind to transport the pollutants being emitted by a source and deliver them to the monitoring path. Knowledge of the prevailing winds is important when setting up the path for long-term monitoring programs, but may be much less important for short-term programs. The short-term program usually demands that the operator be prepared to change the path configuration when the wind changes. For either the long-term or the short-term program, the ideal situation is to have more than one retroreflector or IR source. This capability allows the path direction and length to be altered in response to changes in the wind direction without having to transport the instrument itself. As mentioned previously, some versions of OP/FT-IR monitors incorporate a scanning system that allows the direction of the beam to be changed rapidly. Another way to deal with changes in wind direction is to use a plane mirror to reflect the beam so that the path encompasses the perimeter of the source. When emission rates need to be calculated from data taken with an OP/FT-IR system, the wind direction and speed must be known. The direction of the path with respect to the wind must also be known. A knowledge of the historical prevailing winds is of little use for this task. When emission rates are required, the wind speed and direction as a function of position and time (that is, the wind field) at the path must be measured directly.

9.2.5 *Slant Path Versus Horizontal Path*—Path orientation is important because the wind is the primary mode of transportation of the gases being monitored. A direct comparison between a slant path and a horizontal path cannot be made due to uncertainties in the wind field and the variability in the target-gas concentrations. Wind speed and direction can change dramatically over small regions when measured close to the ground. This is true not only because of the changing terrain but also because the motion of the air (a wind) must at least approach zero at the surface. There is some indication that the concentration contours of gases become very complex with altitude, at least in part because of turbulence. There are no data in the OP/FT-IR literature that describe the variation of concentration with altitude.

9.3 *Changing the Path*—If the plume from a source is being monitored and the wind changes direction, the path should be changed so that it encompasses the plume. Changing the path, however, should be done in accordance with some predetermined criteria that consider the ramifications of the change. For example, if the concentrations of fugitive emissions crossing a fence line are being monitored, there is little point in changing the direction of the path. Other than to account for changes in the wind direction, a change in the pathlength should be considered only for purposes of taking a background spectrum or when spectral interferences from compounds, such as water vapor, become so strong that the absorption due to the target gases is completely masked.

9.4 *Logistical Concerns*—Many logistical concerns will be site specific and will vary for each monitoring program. These concerns may also be different for permanent installations or short-term monitoring programs. Consideration must be given to power requirements, mounting requirements, shelter, and climate control. Some provision must be made to supply the required electrical power to the spectrometer. In bistatic systems with a remote IR source, an additional source of power must be provided. Some systems can operate off of a portable 12-V power supply, such as a car or marine battery. For quantitative work the output of the battery must be stabilized. For short-term field studies, the spectrometer, the retroreflector, or the remote IR source are typically mounted on transportable tripods. For permanent installations, a more rigid mounting system can be used. In either case, care should be taken to isolate the OP/FT-IR monitor from vibrations. The OP/FT-IR system should be protected from the elements. Exposure of the retroreflector, remote IR source, telescopes, and other optical components to corrosive gases should be limited. If exposure of the optical components to a corrosive environment cannot be avoided, some type of system to purge the surface of the optical components should be devised to minimize this exposure. Spectrometers with hygroscopic internal optics, such as a KBr beamsplitter, must be purged with a dry, inert gas or hermetically sealed to prevent moisture from damaging the optics. An alternative is to use ZnSe optical components. The spectral response of many spectrometers is sensitive to changes in ambient temperature. For example, the shape of the single-beam spectrum can change dramatically with changes in temperature. Also, in some instruments, the interferometer will not scan at ambient temperatures below 5°C. Therefore, in permanent installations, the temperature inside the shelter for the spectrometer should be controlled. For short-term field

studies, the spectrometer can be covered in some type of heated, insulating material.

9.5 *Ancillary Measurements*—There are several reasons why some ancillary measurements must be made when taking data with an OP/FT-IR monitor. One reason is the requirement to take data that can be used for QA/QC purposes. Another reason is that many programs will require a record of ancillary data, such as wind speed and direction. Also, the amount of water vapor in the atmosphere should be monitored because there are currently too many unanswered questions about the effect of water vapor on quantitative analysis methods. By far, water vapor represents the strongest spectral interference, and unless it is measured separately, questions may arise when the target gas concentration data are interpreted. The ambient pressure should also be recorded. At any one monitoring location a small change in ambient atmospheric pressure may be observed. In some cases, the data may have to be corrected for these changes, for example, when acquiring data at a high altitude, where the atmospheric pressure can be significantly different from that at sea level. Guidance for selecting and setting up the instruments for making meteorological measurements can be found in a USEPA handbook (**17**). Although this handbook does not directly address open-path measurements, it does provide useful information about meteorological instrumentation and measurements.

NOTE 4—A measurement of relative humidity is not satisfactory for use in OP/FT-IR monitoring. The actual partial pressure of water vapor must be found. If relative humidity is measured, then the temperature must also be measured so that the partial pressure of water can be calculated by consulting the Smithsonian psychrometric tables. These tables can be found in the CRC Handbook of Chemistry and Physics (**18**).

10. Background Spectra

10.1 *Need for a Background Spectrum*—The physical law that governs the determination of the target gas concentration is Beer's law. This law is defined in terms of absorption spectra, which in OP/FT-IR monitoring are calculated from a single-beam field spectrum and a single-beam background spectrum. In conventional FT-IR systems there is no background spectrum taken simultaneously with the sample spectrum to null the spectral features due to the IR source, beamsplitter, detector, and interfering species in the path. To remove these background spectral features, the single-beam sample spectrum is divided by a single-beam background spectrum, or I_0 spectrum. This operation generates a transmittance spectrum. The absorption spectrum is then calculated by taking the negative logarithm of the transmittance spectrum. Ideally, the background spectrum is collected under the same experimental conditions as those for the sample spectrum, but without the target gases present. However, in OP/FT-IR monitoring it is not possible to obtain the I_0 spectrum directly because the target gas cannot be removed from the atmosphere. There are currently five methods for obtaining I_0. These methods are based on obtaining synthetic, upwind, short-path, averaged, and iterative background spectra.

10.2 *Synthetic Background Spectra*—Synthetic background spectra can be generated by selecting data points along the envelope of a single-beam field spectrum and then fitting a series of short, straight lines to the selected points. The data points selected should not be on an absorption band or on the continuum produced by unresolved absorption bands. Synthetic I_0 spectra can be made that cover only selected wavenumber regions, or they can be made to cover the entire wavenumber range of the FT-IR system. An example of a synthetic spectrum is shown in Fig. 7. Some care must be used when synthetic I_0 spectra are generated so that distortions are not introduced into the intensity function. The final spectrum that is produced must follow the curvature of the single-beam spectrum from which it is made and cannot have artificial dips or peaks. Creation of a synthetic background spectrum over wavenumber regions that contain broad spectral features can be difficult. This method seems to work best when analyzing for compounds with narrow spectral features. A less subjective method for generating a synthetic background spectrum fits a series of segmented polynomial curves to a field single-beam spectrum (**19**).

10.3 *Upwind Background Spectra*—For short-term monitoring efforts, the path is generally chosen to be perpendicular to the wind field. If the area of the source is relatively small and its upwind side is accessible, an upwind I_0 spectrum can be acquired. A usable background spectrum can also be acquired by taking data along the side of the source as long as the wind is not blowing across the source area and transporting the emissions across the path used for the I_0 spectrum. Another technique for acquiring an upwind background spectrum is to wait until the wind shifts so that the monitoring path is along an upwind side of the pollutant source. This works well for isolated sources, but if there are other local sources emitting pollutants, this method can lead to errors in identifying and quantifying what is being emitted from the source under study. There are some advantages, however, to taking upwind background spectra this way. First, it is likely that sources are not isolated and the chemical species of interest are emanating from several locations. The compounds entering the area being investigated are thus included in the upwind background spectrum. Therefore, the measured concentrations of the target
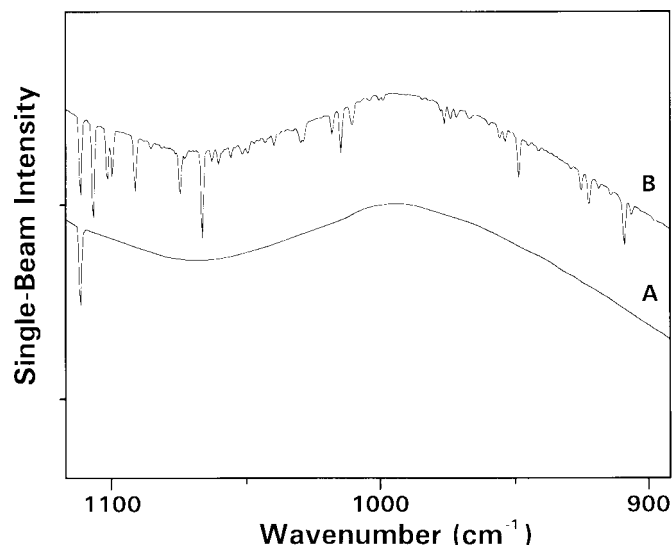
FIG. 7 Example of a Synthetic Background Spectrum (*A*) That was Created from the Single-Beam Spectrum (*B*). The peak at 1111 cm^{-1} was Intentionally Left in as a Point of Reference

gases can be attributed to the local source. There are also some disadvantages to using upwind background spectra. It is difficult to take upwind and downwind spectra frequently if the system has to be moved from one side of the source area to another. Generally, an upwind background spectrum is taken once at the beginning of the daily monitoring period and once at the end. If the configuration can be set up so that the path is on the side of the source area, a second retroreflector or IR source can be used, and the I_0 spectrum can be taken frequently without having to transport the entire system from one place to another.

10.4 *Short-Path Background Spectra*—Another possible technique for obtaining the I_0 spectrum is to bring the retroreflector or IR source close to the receiving telescope. This effectively eliminates the absorption caused by the target gases and minimizes the absorption caused by interfering species, such as water vapor. One problem with this method is that the detector can be saturated at short paths because too much IR radiation is incident on the detector element (see 8.3). Necessary checks for a short-path background spectrum include inspection of the spectral region below the detector cutoff frequency for nonphysical energy, comparison of the curvature in the short-path spectrum with the curvature of the field spectra, and determination of wavenumber shifts or resolution changes. One difficulty with obtaining a short-path background is deciding on an appropriate distance for placing the retroreflector or IR source. In addition to the potential for detector saturation, there is a second difficulty with monostatic systems. In monostatic systems the retroreflector will subtend different angles when it is positioned at different distances from the receiving telescope. If the interferometer does not have a Jacquinot stop, the retroreflector may be the actual optical field stop of the instrument. Changing the pathlength can cause distortions in the spectrum. When the pathlength is increased, the retroreflector subtends smaller angles, and the instrument uses different cones of light. This problem can be overcome by placing a field stop in the instrument so that it uses a smaller field of view than the smallest anticipated from the retroreflector. However, placement of field stops in the optical train of the instrument is a job for the manufacturer, and can't be done without potentially causing other problems. If two retroreflectors or IR sources are available, measurement of a short-path background is fairly easy to perform, provided that the concerns mentioned previously are addressed. The OP/FT-IR monitor can be pointed first to one retroreflector and then the other quite easily with some regularity.

10.5 *Averaged Background Spectra*—When the experimental conditions are fairly constant over a measurement period, it is possible to average several single-beam field spectra that have been taken over this time to create an I_0 spectrum. These spectra must have been analyzed and found to not contain any measurable concentration of the target gas. This average I_0 can then be used for the entire data set for that period. However, the experimental conditions often do not remain constant enough to allow averaging to be performed. The water-vapor concentration is changing most of the time, and so is the concentration of carbon dioxide. If other sources are in the area, the concentrations of the gases emanating from them are not likely

to be constant. If any of these gases are also being monitored, the use of an average I_0 will not give a true background spectrum that is representative of the entire monitoring period.

10.6 *Iterative Background Spectra*—Another method for generating an I_0 spectrum from previously collected field data uses an iterative approach **(20)**. In this method, an initial I_0 spectrum is generated from one of the methods described previously or is selected from archived data. This I_0 spectrum is used to generate an absorption spectrum from a single-beam field spectrum. This absorption spectrum is then analyzed for the target gases. If any target gases are detected, they are subtracted in proportion to their concentration from this absorption spectrum. A single-beam spectrum is then recreated from the subtracted absorption spectrum by using the initial I_0 spectrum. The recreated single-beam spectrum, without the absorption features of the target gases, now becomes the I_0 for use with the next single-beam field spectrum collected. This process can be automated and repeated for each sequential field spectrum collected.

10.7 *General Advice About Background Spectra*—Acquisition of the I_0 spectrum represents one of the more difficult tasks associated with using an OP/FT-IR monitor. Little information has been published on the frequency at which a new background spectrum should be acquired. There is some evidence from experiments conducted with bench-top laboratory FT-IR systems that indicates that a new I_0 should be taken for each sample spectrum. There is also some evidence from long-term OP/FT-IR monitoring programs that indicates that a single I_0 can be used over an extended period of time with no detrimental effects. Neither of these observations has been corroborated by any in-depth study of the background spectra in OP/FT-IR monitoring. The decision to acquire a new background should be based on the data quality objectives of the study. In any case, whenever any optical component (IR source, mirrors, windows, etc.) is changed in the instrument, a new background must be acquired. All of the currently used methods for generating a background spectrum are fraught with difficulties. No one method is generally accepted as the best method for acquiring a suitable I_0 spectrum. There are few guidelines as to what represents a valid background spectrum for the production of accurate data. Perhaps the most important point is that the curvature of the background spectrum must be very similar to the curvature of the single-beam field spectra. Otherwise, abnormalities in the baseline of the generated absorption spectra can cause errors in the concentration analysis.

11. Water Vapor Reference Spectra

11.1 *Need for a Water Vapor Reference Spectrum*—Water vapor absorption bands are present in all regions of the mid-IR spectral region, and these bands interfere with the spectrum of almost every potential analyte. Because of this, the absorption features of water vapor must be accounted for during the analysis of field spectra. Some amount of the water-vapor absorption is accounted for if there is water vapor absorption in the background spectrum. However, when a synthetic background is used, all of the features due to water vapor will appear in the absorption spectrum. It is possible to account for the water vapor by considering it as an interfering species in

the analysis method. To do this, however, a water vapor reference spectrum must be available. Water vapor reference spectra are available commercially. However, these spectra are not generally suitable for use in the field for two reasons. First, the concentration-pathlength product at which the commercial reference spectra were recorded is too small. Secondly, the band shapes of these spectra typically do not match those of the field spectra because of slight differences in the instrument line shape functions of the laboratory FT-IR system used to record the reference spectra and the OP/FT-IR monitor used to record the field spectra.

11.2 *Water Vapor Spectra Considerations*—Any single-beam spectrum that exhibits a sufficient amount of water-vapor absorption in the wavenumber region of interest can be used for the production of a water vapor reference spectrum. Spectra taken at short pathlengths or during very dry periods may not be satisfactory. At some locations the water vapor partial pressure has been observed to change from a low of less than 133 Pa (1 torr) in the winter to a high of approximately 4400 Pa (33 torr) during the summer. Changes in the water vapor concentration of this magnitude, along with any instrument changes, may require that a new water-vapor spectrum be produced. Also, large changes in the water-vapor concentration across the beam can occur over short time frames in refineries and chemical manufacturing facilities where steam vents are present. To account for these potentially large changes in water-vapor concentrations along the path, a library of water-vapor spectra can be created from field data acquired under varying atmospheric conditions. It is the responsibility of the operator to determine when the water-vapor spectrum has to be remade, and no hard and fast rules on the frequency for creating a new spectrum are presently available. If the estimated detection limits or confidence levels of the analysis increase from one data set to another, a first step in determining the cause is to compare the water-vapor reference spectrum with the water vapor absorption features in the field spectra and to compare trends in the measured target gas concentrations with changes in water vapor concentration along the path. The primary concern for the production of a water vapor spectrum is that the final result must not contain any of the target gas. If the water vapor spectrum contains even a small amount of a target gas, the analysis will be in error by that amount. The ease with which the absorption features of the target gas can be removed from the water vapor reference spectrum depends on many instrumental factors, such as resolution, and the process can be quite time-consuming. The removal of the target gas absorption is done by spectral subtraction and requires great attention to detail. A suitable water-vapor spectrum can also be generated from spectral databases, such as HITRAN. The high-resolution bands calculated from HITRAN can be convolved with an appropriate instrument function to match the spectral bands in the field spectra. Care must be taken to maintain the proper band shapes and relative band intensities when manipulating the high-resolution data.

NOTE 5—In some applications, such as extractive or stack monitoring, which involve elevated temperatures, the water vapor reference spectrum must be acquired at the same temperature at which the field spectra are collected. The relatively small temperature differences experienced in ambient, open-path measurements do not significantly affect the relative intensities of the water vapor bands.

11.3 *General Process for the Production of a Water Vapor Spectrum*—The production of a water-vapor spectrum is a multi-step process. A general procedure that can be followed to produce a water vapor reference spectrum from field spectra is given as follows.

11.3.1 Select two single-beam spectra that will be combined into a water vapor absorption spectrum. The spectra selected in this step should be at the same resolution as the field spectra. The water-vapor spectrum should have the same or better *S/N* as the field spectra. The water-vapor concentration for these two spectra should be representative of the water-vapor concentration contained in the field spectra to be analyzed. Curvatures and any other special features of the baselines of these spectra should be the same as those of the field spectra baselines over the wavenumber regions of interest.

11.3.2 Use one of the spectra to create a synthetic background spectrum. Either of the two spectra selected in 11.3.1 can be used to create a synthetic background that is then used to create an absorption spectrum. The synthetic background must be created over the same wavenumber region as will be used for the final analysis. The wavenumber region can be larger than that used for analysis, but it cannot be smaller. If the analysis is to be done for more than one gas, the synthetic background should be created in the spectral regions of all the gases of interest at the same time. Otherwise, when the absorption spectrum is created, some or all of the water-vapor absorption will be ratioed out and the process will have to be started over. If an upwind I_0 is used here instead of a synthetic background, the apparent water-vapor absorption will be a result of the ratio of the two spectra. If the water vapor concentrations along the monitoring path and the upwind path are nearly the same, then the *S/N* of the water-vapor spectrum created in this way will be poor. Therefore, use of a synthetic background spectrum is recommended for this process.

11.3.3 Use the remaining spectrum (after 11.3.2) as the sample spectrum and the newly created synthetic background to create an absorption spectrum that is to be used as the water vapor reference spectrum.

11.3.4 Subtract a reference spectrum of the target gas from the absorption spectrum created in 11.3.3 to remove any absorption features due to the target gas.

11.3.5 Record two single-beam spectra back to back as was done in 8.6 in determination of the random noise. Create an absorption spectrum from these two spectra by using one of the spectra as the background. This spectrum should exhibit a flat, featureless baseline. Determine visually that no target gas is present in the absorption spectrum.

11.3.6 Analyze the spectra recorded in 11.3.5 for the target gas or gases by using one of the methods described in Section 12. If a multivariate analysis method is used, designate the newly created water vapor reference spectrum as an interfering species.

11.3.7 Steps 11.3.4-11.3.6 are an iterative process. The newly created water-vapor spectrum must be used in the analysis of other spectra. The results of these analyses must be examined to determine whether any of the target gas remains in

the water vapor reference spectrum. If the analysis yields a negative value for the target gas, some features due to that target gas remain in the water vapor reference spectrum. If the analysis yields a positive value for the target gas, features from the target gas were oversubtracted from the water vapor reference spectrum. In either case, the target gas reference spectrum must be scaled to the absorbance corresponding to the concentration value calculated by the analysis, and this amount of the target gas must be either added in or subtracted out of the water vapor reference spectrum. At this point the absorption spectra should be reanalyzed. These steps are to be repeated until the concentration values calculated by the analysis are near zero. Several back-to-back spectra should be analyzed in this way to determine if the concentration values are systematically or randomly distributed around zero.

12. Data Analysis

12.1 The analysis of OP/FT-IR data includes generating an absorption spectrum from the interferogram, developing or obtaining the appropriate reference spectra, and then applying the chosen analytical method to determine the concentration of the target gases.

12.2 *Generation of the Absorption Spectrum*—A single-beam field spectrum is generated and recorded for each sampling period. A background spectrum is generated by one of the methods described in Section 10. A transmittance spectrum is then obtained by dividing the field spectrum by the background spectrum. The absorption spectrum is obtained by taking the negative logarithm of the transmittance spectrum. The absorption spectrum is used for all further data analysis.

12.3 *Generation of the Reference Spectrum*—A reference spectrum is usually generated by using a known concentration of gas in a closed cell. The cell is usually at least 1-m long, although it is preferable to use multipass cells with longer pathlengths. A pure sample of gas mixed with an inert gas such as nitrogen is used. The concentration of gas used to generate the reference spectrum should yield a range of absorbance values that match as closely as possible those expected to be found in the field measurements. The system can use a flowing stream of gas, but a total pressure of 1 atm should be maintained in the cell. The production of reference spectra is an exacting undertaking and requires great attention to the experimental details. It is unlikely that most users of the OP/FT-IR technique will prepare their own reference spectra because spectral libraries are available commercially. There is, however, no independent organization responsible for validating the accuracy of these spectral libraries. Synthetic spectra of the atmospheric gases can also be generated from the HITRAN data base or from high-resolution laboratory data. Reference spectra produced either in the laboratory or from spectral databases must be generated at the temperature and pressure at which the field measurements will take place.

12.4 *Analytical Methods*—After the reference spectra of the target gases are obtained, the appropriate wavenumber region for analysis must be selected. The selection should be based on an examination of the reference spectra and the type of analytical method chosen. Two issues must be addressed to make this selection. Ideally, the gas should have a high absorptivity in the selected region, and the region should be free of absorption bands from interfering species. If interfering species are present they must be identified and accounted for in the analysis method. Once an appropriate wavenumber region is selected, data analysis can proceed. The concentration of the unknown gas can be determined in three general ways, as described below: the comparison, scaled subtraction, and multivariate analysis methods. Each method uses a reference spectrum of the gas being investigated. General methods of infrared quantitative analysis are given in Practice E 168.

12.4.1 *Comparison Method*—One method of determining the concentration is to measure the absorbance at a particular wavenumber and compare it with the absorbance of the reference (*ref*) spectrum at the same wavenumber. Then, if reciprocity holds (as implied by Beer's law), the unknown (*unk*) concentration of the target gas is obtained as follows.

$$A_{ref}/A_{unk} = b_{ref}c_{ref}/b_{unk}c_{unk} \qquad (4)$$

Solving for the unknown concentration gives the following:

$$c_{unk} = c_{ref}b_{ref}A_{unk}/b_{unk}A_{ref} \qquad (5)$$

This concentration has the same units as that of the reference spectrum.

12.4.2 *Scaled Subtraction Method*—The scaled subtraction method is similar in principle to the comparison method. This method is particularly useful if there are spectral features due to interfering species that overlap with those of the target gas. However, for scaled subtraction to be successful, either the target gas or the interfering species should have at least one unique absorption band. High-resolution data can be used to an advantage with this method. Scaled subtraction can be done as follows. Most software packages allow two spectra to be subtracted interactively. In this case the reference spectrum should be subtracted from the field spectrum until the absorption maximum of the band of interest is zero. Once the subtraction is completed the software reports a scaling factor. This factor can be multiplied by the concentration used to generate the reference spectrum to obtain the concentration of the target gas in the field spectrum. There is some operator skill involved in subtracting spectra interactively; therefore, some practice in using this method is recommended before the actual field spectra are analyzed. Also, if there is an uncorrected frequency shift between the OP/FT-IR system and the spectrometer on which the reference spectra were measured, the scaled subtraction can give first derivative shaped residuals (see 8.7).

12.4.3 *Multivariate Analysis Methods*—Multivariate analysis methods can be used to advantage when the concentrations of several target gases are to be determined and several interfering species are present. This is the case most often encountered in OP/FT-IR monitoring, so some type of multivariate analysis method is generally preferred. There are several methods that are used to perform multivariate analyses of IR spectra, including Classical Least Squares (CLS), inverse least squares, Partial Least Squares (PLS), and principal components regression. The most common multivariate analysis methods used in OP/FT-IR monitoring are CLS and PLS. Brief discussions of these two methods are given in the following sections. For a more complete discussion of multivariate analysis methods the reader is referred to Practice

E 1655 and a review by Haaland **(21)**.

12.4.3.1 *Classical Least Squares (CLS)*—CLS is the most widely used multivariate method for analyzing OP/FT-IR data. The calibration model in CLS is Beer's law, in which absorbance is represented as a linear function of concentration. The CLS analysis finds the linear combination of reference spectra that minimizes the sum of squared differences between the field spectra and the linear combination of reference spectra. Because CLS uses the additive linear relationship between absorbance and concentration, the spectral features of the target gases and interfering species do not need to be resolved. Also, CLS is a full spectrum method that, in principle, can be used to analyze over the entire wavenumber range of the field spectrum. In practice, the CLS analysis is typically performed over smaller spectral regions, for example 100 cm^{-1}. A spectral region that contains minimal spectral overlap, absorption bands that adhere to Beer's law, and no baseline irregularities is generally chosen for the analysis. Several factors must be taken into account when developing a CLS method. First, all species that have absorption features in the analysis region must be included in the calibration set of reference spectra. Secondly, the CLS analysis assumes a linear relationship between absorbance and concentration. In practice, detector nonlinearities, inadequate spectral resolution, optically dense absorption bands, and poor baseline modeling can lead to deviations from Beer's law. Some of these effects may be accounted for in the calibration set of reference spectra and by assuming the appropriate baseline model. However, the CLS analysis should be performed in spectral regions where these nonlinearities are not severe.

12.4.3.2 *Partial Least Squares (PLS)*—PLS is a factor analysis method that, like CLS, is a full spectrum method. In PLS, the calibration spectra are decomposed into the product of two matrices. One matrix is the basis set of full-spectrum loading vectors and the other is a matrix of scores of the loading vectors for the field spectra. The loading vectors are analogous to the pure component reference spectra in CLS, whereas the scores can be modeled to be linear with concentration. The PLS method can be broken down into steps that separately involve CLS calibration and prediction followed by inverse least squares calibration. In the PLS prediction phase, a least-squares procedure is used to find the best fit of the loading vectors to the field spectrum. The scores of each loading vector yielding the linear least-squares fit to the field spectrum are then related to concentration with a separate inverse least-squares analysis. The PLS method is not restricted to a direct physical model, such as Beer's law. Thus, in PLS, the spectral data are modeled empirically, which often provides a better fit to the field data. Unlike CLS, the number of factors used in PLS is not restricted to the number of known species in the field spectra. Factors that correlate with the concentrations of the species in the field spectra and also account for the variance in the spectra are extracted by the PLS method. Therefore, PLS is often better suited for handling nonlinearities or other sources of variation in the field spectra due to baseline deviations, inadequate resolution, and severe spectral overlap. However, this greater flexibility is often gained at the expense of useful qualitative information. Also, in

comparison to CLS, the PLS method requires more extensive calibration. To date, PLS has been applied to OP/FT-IR data on a limited basis. However, Griffiths et al **(12)** have shown that PLS can be used to advantage when analyzing low-resolution spectra.

13. Quality Assurance and Quality Control

13.1 *Recommendations for Tests to be Included in a QA/QC Program for OP/FT-IR Monitors*—Development of a QA/QC program for OP/FT-IR monitoring should include, but not necessarily be limited to, the tests discussed as follows. These tests are designed to determine that the instrument is operating properly and producing good data. Some of these issues were discussed previously for the initial verification of instrument performance in Section 8, but can be used for routine QA/QC procedures as well. Other criteria for developing a QA/QC plan, such as siting criteria or chain of custody for data, should be addressed as warranted, but are not discussed here. General guidance for developing a QA/QC program is given in a USEPA document **(22)**. Two separate issues must be addressed in a QA/QC program. One issue is whether or not the instrument is working properly. The other issue is if the quantitative analysis method is producing the correct results. In addition to the tests described here, level zero and level one tests for measuring the performance of FT-IR spectrometers are given in Practice E 1421.

13.2 *Noise Measurements*—Measurements of two types of noise, instrumental electronic noise and random baseline noise, should be routinely taken.

13.2.1 *Electronic Noise*—The electronic noise should be recorded periodically by placing opaque material in front of the detector element while the detector is cooled. This signal is indicative of the noise, for example 60-Hz electrical noise, of the system with no detector signal. The magnitude of this signal should remain relatively constant and typically contributes less than 0.25 % of the total signal. If some electrical component of the system is producing spurious noise, it will become apparent from this measurement.

13.2.2 *Random Baseline Noise*—Random baseline noise is measured by recording back-to-back spectra after the detector has been filled with liquid nitrogen and allowed to equilibrate. One spectrum is then divided by the other, and the absorption spectrum is calculated. The result is a spectrum of the random system noise. The RMS noise in absorbance units can then be calculated from these spectra. These spectra should be acquired by using the same instrumental parameters to be used during collection of field data. The RMS noise should be calculated in a spectral region that is devoid of absorption due to water vapor or other atmospheric gases. If not, changes in the concentrations of these ambient gases over the measurement time will influence the magnitude of the noise calculations. Noise measurements can also be taken over the spectral region chosen for analysis of a target gas to give an estimate of detection limits. For the baseline noise measurement, it is best to record these two spectra back to back, as passage of time between the two spectra might also include changes in atmospheric conditions or concentrations of species in the path. Spectra taken at longer time intervals during the study can be

ratioed in this manner to determine baseline stability or systematic noise.

13.3 *Stability of Instrument*—Several aspects related to the stability of the instruments can be measured. All of the measurements in the following discussion should be recorded on at least a daily basis and compared to existing data to establish that the instrument is performing properly.

13.3.1 *Noise Measurements*—The noise measurements described in 13.2 should be taken daily and recorded on a control chart to alert the operator of any changes or trends in the noise.

13.3.2 *Signal Strength*—The signal strength should be measured daily, or several times during the day. This can be measured either as the single-beam intensity in a selected wavenumber region or as the magnitude of the interferogram centerburst. At this time, the position of the zero peak difference of the interferogram should also be recorded, and the single-beam spectrum should be examined for evidence of system nonlinearity. The single-beam intensity should be measured in different wavenumber regions to determine if the characteristics of the IR source have changed or the interferometer alignment has changed. The high wavenumber portion of the spectrum will be most sensitive to interferometer misalignment and will show a decrease in intensity relative to the other wavenumber regions if changes have occurred. The signal strength also depends on atmospheric conditions. For example, fog attenuates the beam intensity. Thus, the atmospheric conditions must be noted when this measurement is taken. As with the noise measurements, the signal strength should also be plotted daily on a control chart. A decrease in signal could be related to a drop in the source intensity, misalignment of the external optics, misalignment of the interferometer optics, deterioration of the system optics, or a loss in the detector Dewar hold time.

13.3.3 *Wavenumber Shifts and Changes in Resolution*—The positions and FWHHs of selected absorption bands should be recorded and monitored as discussed in 8.7 to detect wavenumber shifts or changes in instrumental resolution.

13.4 *Accuracy and Precision*—The accuracy and precision of OP/FT-IR measurements are difficult to determine. Accuracy and precision can be estimated by using either ambient gas concentrations or a short cell containing a known amount of the target gas.

13.4.1 *Ambient Gas Concentrations*—The concentrations of atmospheric gases, such as CH_4 or N_2O, can be used to a certain extent for accuracy and precision measurements. These gases have an average global concentration of approximately 1.7 ppm and 310 ppb, respectively. They are always present in OP/FT-IR spectra, and no changes have to be made to the instrument to measure these gases. If the ambient concentrations of these gases are assumed to be constant, precision measurements can be made. For example, in one study, the concentration of N_2O measured continuously over a five-day period was found to vary by only ± 3.5 % of the mean value (**23**). On the other hand, CH_4 concentrations have been observed to change by a factor of 2.5 during a 5-h period. Therefore, care must be taken to account for possible local emission sources if ambient gases are used for QA/QC purposes. Although ambient gases such as N_2O can be used to

estimate the precision of OP/FT-IR measurements and to indicate that the instrument is working properly, accuracy is more difficult to determine. The accuracy of the concentration measurement depends on several factors, including the choice of analysis method, the type of background spectrum used, the presence of interfering species and how they are accounted for in the analysis method, and the accuracy of the reference spectra, including the water vapor reference spectrum. Therefore, for example, if the concentrations of N_2O are used for QA/QC purposes, the estimates of precision and accuracy are valid only for N_2O and will not necessarily be representative of the precision and accuracy for other target gases.

13.4.2 *Short Gas Cell*—An alternative approach to using ambient gases for QA/QC data is to insert a short gas cell that contains a known concentration of the target gas or gases into the IR beam. This method has the disadvantage of attenuating the IR beam due to the transmitting and reflecting properties of the windows used in the cell. The performance of the instrument is somewhat degraded and the intensity profile of the single-beam spectrum will be affected by the spectral characteristics of the cell. These factors might require that new background and water vapor reference spectra be created for use when the cell is positioned in the optical path. The advantage of the short gas cell approach is that a known quantity of target gas is in the path. If this quantity is accurately known and is constant, accuracy and precision measurements can be made. Standard QA/QC techniques using a short cell are currently under development.

13.4.3 *Effect of Stray Light and Ambient Radiation*—Stray light and ambient radiation can affect the quantitative results and must be accounted for as described in 8.5.

13.4.4 *Validity of Analysis Method*—In addition to determining the accuracy and precision of the instrumental measurements, the accuracy and precision of the method used for quantitative analysis must also be determined. In most cases, an automated software package is used to determine the concentrations of the target gases. These procedures can be checked manually by comparing the sample spectra to spectra of reference gases with a known concentration. Interactive subtraction procedures that yield a scaling factor for the reference spectrum can be used to verify the concentration measured by the software. In addition, the reference spectra can be scaled to the desired concentration and then added to the field spectrum. When the composite spectrum is then analyzed, the measured concentration should reflect the amount of reference gas added. Care must be taken in choosing the spectral regions used to analyze for each target gas. For example, the optimum region for analysis does not always encompass the entire absorption envelope. Possible interfering species must also be accounted for in the analysis method. The operator should also be aware that any time a concentration spike appears that cannot be immediately attributed to a known source, the actual spectral data should be examined to verify the presence of the compound in question and its concentration. This can be done by first subtracting the appropriate absorption spectra of any interfering species from the field spectrum. The signature and absorbance values of the resultant spectrum should then be compared to the reference spectrum

for proper features and intensities. Also, any time that the concentrations of the target gases seem to correlate with changes in water-vapor concentration, the spectra of the target gases should be examined to verify that the changes in concentration are real. If the concentrations of the target gases exhibit either positive or negative inflections with respect to changes in water-vapor concentration, the analysis method should be altered to alleviate the problem.

13.4.5 *Accuracy of Reference Spectra*—If the instrument is operating properly and a suitable analysis method is developed, the accuracy of the OP/FT-IR technique will ultimately be determined by the accuracy of the reference spectra. To date, no way of validating or certifying these reference spectra exists. The National Institute of Standards and Technology (NIST) is currently addressing this issue. The analyst can currently compare existing libraries to identify both qualitative and quantitative errors, although some proprietary libraries might not be accessible to all users.

13.5 *Completeness, Representativeness, and Comparability of the Data*—These requirements will vary with specific monitoring applications. Care must be taken to ensure that spectra are acquired frequently enough to account for the variability of the target gas concentration. Failure to do this will make it difficult to discern between real changes in the target gas concentration and possible variability in the OP/FT-IR measurements. If possible, the OP/FT-IR data should be initially compared to an established method. This can be difficult because the OP/FT-IR produces a path-averaged concentration, whereas most established methods use some type of point monitor. Some OP/FT-IR data have been compared to the canister method or other point monitors with success, however **(24)**. Although not exact, these comparisons can give the operator an idea if the OP/FT-IR measurements are within generally accepted values. If not, corrective action should be taken.

13.6 *Ancillary Measurements*—The type of ancillary measurements required will vary, depending on the type of study being conducted. For any OP/FT-IR measurements, the ambient temperature, water vapor concentration, ambient pressure, and wind velocity should be recorded. The operator should also be aware of the effect of changes in altitude on ambient pressure. If the instrument is housed in an enclosed environment, the temperature of that environment should also be recorded. It is also useful to record the temperature inside the spectrometer itself, especially in cold weather situations.

13.7 *Documentation*—As with any analytical methodology, a log of instrument use, downtime, and repairs, as well as notes regarding unusual observations, should be maintained. These notes can prove invaluable for analyzing data that appear to be abnormal. Records should be kept that are appropriate for the type of study being conducted. For example, the requirements for a research and development project may be different from the requirements for legally defensible data.

14. Keywords

14.1 air analysis; Fourier transform infrared; FT-IR; open-path monitoring; spectrometers

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