Standard Practice 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 1982; 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 practice covers procedures for using active open-path Fourier transform infrared (OP/FT-IR) monitors to measure the concentrations of gases and vapors in air. Procedures for choosing the instrumental parameters, initially operating the instrument, addressing logistical concerns, making ancillary measurements, selecting the monitoring path, acquiring data, analyzing the data, and performing quality control on the data are given. Because the logistics and data quality objectives of each OP/FT-IR monitoring program will be unique, standardized procedures for measuring the concentrations of specific gases are not explicitly set forth in this practice. Instead, general procedures that are applicable to all IR-active gases and vapors are described. These procedures can be used to develop standard operating procedures for specific OP/FT-IR monitoring applications.

1.2 *This practice 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 practice 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 Practices for General Techniques of Infrared Quantitative Analysis[2]
E 1421 Practice for Describing and Measuring Performance of Fourier Transform Infrared (FT-IR) Spectrometers: Level Zero and Level One Tests[2]
E 1655 Practices for Infrared, Multivariate, Quantitative Analysis[2]
E 1865 Guide for Open-Path Fourier Transform Infrared (OP/FT-IR) Monitoring of Gases and Vapors in Air[2]

2.2 *Other Documents:*

FT-1R Open-Path Monitoring Guidance Document[3]
Compendium Method TO-16–Long-Path Open-Path Fourier Transform Infrared Monitoring of Atmospheric Gases[4]

3. Terminology

3.1 For definitions of terms used in this practice relating to general molecular spectroscopy, refer to Terminology E 131.

3.2 For definitions of terms used in this practice relating to OP/FT-IR monitoring, refer to Guide E 1865.

3.3 For definitions of general terms relating to optical remote sensing, refer to the FT-IR Open Path Monitoring Guidance Document.

4. Significance and Use

4.1 An OP/FT-IR monitor can, in principle, measure the concentrations of all IR-active gases and vapors in the atmosphere. Detailed descriptions of OP/FT-IR systems and the fundamental aspects of their operation are given in Guide E 1865 and the FT-IR Open-Path Monitoring Guidance Document. A method for processing OP/FT-IR data to obtain the concentrations of gases over a long, open path is given in Compendium Method TO-16. Applications of OP/FT-IR systems include monitoring for gases and vapors 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. Instrumental Parameters

5.1 Several instrumental parameters must be chosen before data are collected with an OP/FT-IR system. These parameters include the measurement time, spectral resolution, apodization function, and zero filling factor. In some cases, the choice of these parameters might be limited by the parameters used to

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acquire and process the available reference spectra. Use the following procedures to select the instrumental parameters for each OP/FT-IR monitoring study.

5.2 *Measurement Time*—Determine the measurement time required to achieve the desired signal-to-noise ratio (S/N) at the selected resolution (see 5.3 and 6.7). Verify that this measurement time is appropriate for capturing the event being studied. If the measurement time is longer than the residence time of the plume in the path, the interferograms collected after the plume has exited the path will not contain spectral information from the target gas. Adding these signals in the interferogram domain to signals that contain information from the target gas will result in a dilution effect and can cause band distortions and nonlinearities. The variability in the water vapor concentration along the path can also limit the use of extensive signal averaging to improve the S/N. Measurement times from 1 to 5 min are typical for ambient monitoring, whereas shorter measurement times may be required for plume modeling studies.

5.3 *Resolution*—The choice of what spectral resolution to use while collecting OP/FT-IR data depends on the spectral characteristics of the target gases, the measurement time required to observe the pollutant plume, the concentrations of the target gases, the presence of interfering species, the choice of analysis method, and the data quality objectives of the monitoring study. This choice might be limited by the capabilities of the specific OP/FT-IR monitor used to collect data. Most commercially available, portable OP/FT-IR monitors are capable of producing spectra at a maximum resolution of 0.5 or 1 cm^{-1}, although instruments are available that will produce spectra at 0.125-cm^{-1} resolution. There is currently no consensus as to the optimum resolution to use while collecting field data. Most current practitioners use a resolution of either 0.5 or 1.0 cm^{-1}, although recent advances in instrumentation and data analysis techniques provide for the potential of using much lower resolutions. The choice of resolution can also affect other decisions that the operator must make before collecting or analyzing the data. For example, the spectral resolution affects the type of background spectrum that can be used, the method for generating a water vapor reference spectrum, and the choice of analysis method. The following steps can be taken to choose the best resolution for a particular application.

5.3.1 Examine reference spectra of the target gases and potential interfering species. If possible, acquire or obtain reference spectra of these gases at various resolutions. Determine the lowest resolution that resolves the spectral features of interest. Use this resolution as a starting point for future measurements.

5.3.2 If the appropriate facilities are available, develop calibration curves of the target gases at different resolutions. If an inadequate resolution is used, the relationship between the peak absorbance and concentration will not be linear. This relationship is also affected by the apodization function (see 5.4). If the compound of interest does not respond linearly with respect to concentration, a correction curve must be applied to the data during quantitative analysis.

5.3.3 Determine the effect of resolution on the other procedures involved with generating OP/FT-IR data, such as the creation of a synthetic background spectrum (see 10.3) and a water vapor reference spectrum (see 10.6.1) from the field spectra. These procedures rely on a series of subjective judgements, which require a visual inspection of the field spectra. The use of a higher resolution generally facilitates the ability of the operator to visualize the pertinent features of the field spectra.

5.3.4 Assess the resolution requirements of the analysis method. If the comparison (see 10.8.1) or scaled subtraction (see 10.8.2) method is used, the resolution should be sufficient to separate the spectral features of the target gases from those of the interfering species. If classical least squares (CLS) is used (see 10.8.3), a resolution higher than 4 cm^{-1} is generally required (**1**).[5] If partial least squares (PLS) is used (see 10.8.3), a resolution as low as 16 cm^{-1} may be sufficient (**2**).

Note 1—Most volatile organic compounds of interest in OP/FT-IR monitoring applications have absorption envelopes with full widths at half heights (FWHHs) of approximately 20 cm^{-1}. This observation would indicate that low-resolution spectra would be adequate for OP/FT-IR measurements. However, each OP/FT-IR spectrum will also contain features due to ambient gases, such as water vapor, carbon dioxide, carbon monoxide, and methane, which have FWHHs on the order of 0.2 cm^{-1} at atmospheric pressure. If low resolution measurements are made, the analysis method must be able to handle the spectral overlap and nonlinearities caused by an inadequate resolution of these atmospheric gases.

5.4 *Apodization*—Use the same apodization function that was used to process the reference spectra. If a choice of apodization function can be made, the Norton-Beer-medium function typically yields the best representation of the true absorbance as compared to Happ-Genzel or triangular apodization.

5.5 *Zero Filling*—Assuming that the field spectra were acquired at the same resolution as the reference spectra, choose zero-filling parameters that allow the data point density of the field spectra to match that of the reference spectra. In general, the original interferogram should be zero filled to the degree that the number of data points used in the Fourier transform is twice that in the original interferogram. No advantage is gained by zero filling by more than a factor of two for most applications.

6. Initial Instrument Operation

6.1 Several tests should be conducted before the OP/FT-IR monitor is deployed for a field study. These tests include measuring the electronic noise, the distance at which the detector saturates, the linearity of the system, the signal due to internal stray light or ambient radiation, the signal strength as a function of distance, and the random baseline noise. Use the instrumental parameters chosen in 5.2 through 5.5 for these tests.

6.2 *Measure the Electronic Noise*—Place a piece of opaque material in front of the detector element while the detector is operational, for example after the mercury-cadmium-telluride (MCT) detector has been cooled and has equilibrated. Record

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[5] The boldface numbers in parentheses refer to the references at the end of this practice.

the signal either as the interferogram or as a single-beam spectrum with the detector blocked. This signal represents the electronic noise of the system. The magnitude of this signal should be less than 0.25 % of the signal without the detector blocked, remain relatively constant over time, and decrease with the square root of the measurement time. If this signal is uncharacteristically large, an electrical component is most likely producing spurious noise. When this is the case, service of the system is indicated.

6.3 *Measure the Distance to Detector Saturation*—The distance at which the detector becomes saturated determines the minimum pathlength over which quantitative data can be obtained without making changes to the instrument. Evidence of detector saturation indicates that the detector may not be responding linearly to changes in the incident light intensity.

6.3.1 Set up the OP/FT-IR system with the retroreflector (monostatic configuration) or external, active IR source (bistatic configuration) at some predetermined distance, for example, 25 m, from the receiving telescope.

6.3.2 Align the system to maximize the detector output, which can be measured either as the peak-to-peak voltage of the interferogram centerburst or the intensity of a specific wavenumber in the single-beam spectrum. If the intensity of the single-beam spectrum is used, choose a wavenumber region that does not contain any absorption bands due to the target gases or atmospheric gases, such as water vapor.

6.3.3 Obtain a single-beam spectrum.

6.3.4 Examine the single-beam spectrum in the wavenumber region below the detector cutoff frequency. The instrument response in this region should be flat and at the baseline. An elevated baseline in this wavenumber region is due to nonphysical energy and indicates that the detector is saturated. 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. An example of an OP/FT-IR spectrum that exhibits nonphysical energy is given in Guide E 1865.

6.3.5 If nonphysical energy is observed in the single-beam spectrum obtained at the initial pathlength, increase the pathlength until the instrument response below the detector cutoff frequency is flat and at the baseline. This distance represents the minimum operating pathlength.

6.3.6 If the instrument response below the detector cutoff frequency is flat and at the baseline in the single-beam spectrum obtained at the initial pathlength, decrease the pathlength until nonphysical energy is observed in the single-beam spectrum. This distance represents the minimum operating pathlength.

6.3.7 If nonphysical energy is observed at the desired monitoring pathlength and the pathlength cannot be increased, attenuate the IR signal by placing a fine wire mesh screen in the modulated, collimated beam. Changing the gain of the detector preamplifier to lower the magnitude of the signal is not useful because the detector nonlinearity does not depend on gain.

NOTE 2—Determining the distance at which the detector becomes saturated is particularly important for MCT detectors. Detector saturation is not as severe a problem for thermal detectors, such as deuterated triglycine sulfate detectors.

6.4 *Linear Response*—There are two types of nonlinearity that can affect OP/FT-IR data: detector nonlinearity and nonlinearity in absorbance. Evidence of detector nonlinearity can be observed by conducting the tests described in 6.3, although the absence of nonphysical energy in the single-beam spectrum does not guarantee that the detector is operating linearly. Some MCT detectors exhibit nonlinear response even when there is no evidence of detector saturation. The OP/FT-IR system can also exhibit nonlinearity in the change in absorbance with respect to changes in concentration due to the convolution of the instrumental line shape function with the spectral data. The choice of apodization function affects the severity of this nonlinearity. If a multipoint calibration is used in the data analysis, this type of nonlinearity can be accounted for. However, many OP/FT-IR systems rely on a single-point calibration. When this type of calibration model is used, the absorbance of the reference spectra should match the absorbance of the field spectra as closely as possible. The linearity of the system can be checked by using one of the following methods: analyzing polymer films of different, known thicknesses; using a dual-chambered gas cell; or attenuating the beam with wire screens of different, known mesh sizes.

6.4.1 *Polymer Films*—Acquire spectra of polymer films of different thicknesses to test the linearity of the OP/FT-IR system.

6.4.1.1 Collect a single-beam spectrum over the monitoring path without the polymer film in the beam. Use this spectrum as the background spectrum.

6.4.1.2 Insert a polymer film of known thickness into the IR beam and obtain a single-beam spectrum. Create an absorption spectrum from this spectrum by using the background spectrum acquired in 6.4.1.1.

6.4.1.3 Replace the first polymer film with another film of a different, known thickness and obtain a single-beam spectrum. Create an absorption spectrum from this spectrum by using the background spectrum obtained in 6.4.1.1.

6.4.1.4 Measure the absorbance maxima of selected bands in the two absorption spectra acquired in 6.4.1.2 and 6.4.1.3. Choose absorption bands that are not saturated. Perform this test on several absorption bands in different regions of the spectrum.

6.4.1.5 Compare the absorbance value of the selected band in the spectrum of one polymer film to that measured in the other. The ratio of the absorbance values of the two different films should be equal to the ratio of the film thicknesses.

NOTE 3—If the thickness of the polymer film used to test the linearity of the system is not known it can be calculated by using Eq 1:

$$b = \frac{1}{2n} \frac{N}{(v_1 - v_2)} \qquad (1)$$

where:
b = thickness of the sample,
n = refractive index of the sample,
N = number of interference fringes in the spectral range from v_1 to v_2,
v_1 = first wavenumber in the spectral range over which the fringes are counted, and

v_2 = second wavenumber in the spectral range over which the fringes are counted.

6.4.2 *Dual-Chambered Gas Cell*—Use a dual-chambered gas cell containing a high concentration of the target gas to test the linearity of the system. This cell should be designed with two sample chambers that differ in length by a known amount and are coupled so that each chamber contains the same concentration of the target gas (3).

6.4.2.1 Fill the dual-chambered cell with dry nitrogen at atmospheric pressure and insert it into the IR beam.

6.4.2.2 Acquire a single-beam spectrum along the monitoring path. Use this spectrum as the background spectrum for the chamber that is in the IR beam.

6.4.2.3 Reposition the cell so that the other chamber is in the IR beam, and acquire a single-beam spectrum along the monitoring path. Use this spectrum as the background spectrum for that chamber.

6.4.2.4 Fill the cell with a high concentration of the target gas. The absolute concentration of the target gas does not need to be known with this method.

6.4.2.5 Acquire single-beam spectra alternatively with each chamber positioned in the IR beam. Create absorption spectra by using the appropriate background spectrum for each chamber.

6.4.2.6 Measure the absorbance maxima of selected bands in the two spectra created in 6.4.2.5. Choose absorption bands that are not saturated. Perform this test on several absorption bands in different regions of the spectrum.

6.4.2.7 Compare the absorbance value measured with one chamber to that measured with the other. The ratio of the absorbance values measured with the two separate chambers in the beam should be equal to the ratio of the lengths of the chambers.

6.4.3 *Wire Mesh Screens*—Insert a wire screen of a known mesh size in the IR beam and record the signal. Remove this wire screen, insert another screen of a different, known mesh size in the beam, and record the signal. The ratio of the signals obtained with the two different screens should be equal to the ratio of the mesh sizes of the screens.

Note 4—Linearization circuits are available to minimize the problem of detector nonlinearity. These linearization circuits may not perform adequately for all detectors.

6.5 *Measure the Signal Due to Internal Stray Light or Ambient Radiation*—Single-beam spectra recorded with an OP/FT-IR monitor can exhibit a non-zero response in wavenumber regions in which the atmosphere is totally opaque. If the detector has been determined to be responding linearly to changes in the incident light intensity, this non-zero response can be attributed to either internal stray light or ambient radiation. 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. Ambient radiation mostly affects bistatic systems in which an unmodulated, active IR source is separated from the interferometer and detector. The presence of internal stray light or ambient radiation causes errors in the photometric accuracy and, ultimately, errors in the concentration measurements. The magnitude of the instrument response due to internal stray light or ambient radiation determines the minimum useful signal that can be measured with the OP/FT-IR system.

6.5.1 *Measure the Internal Stray Light*—In monostatic systems that use a single telescope to transmit and receive the IR beam, point the telescope away from the retroreflector or move the retroreflector out of the field of view of the telescope and collect a single-beam spectrum. This spectrum represents the internal stray light of the system and is independent of the pathlength. Record this spectrum at the beginning of each monitoring program or whenever optical components in the system are changed or realigned. An example of an internal stray light spectrum is given in Guide E 1865.

Note 5—Internal stray light can also be caused by strong sources of IR radiation 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 and cause an unwanted signal from reflections inside the instrument.

6.5.2 *Measure the Ambient Radiation*—In bistatic systems, which use an unmodulated, active IR source that is separated from the interferometer and detector, block or turn off the source and collect a single-beam spectrum. This spectrum is a record of the IR radiation emitted by the objects in the field of view of the instrument. Because this spectrum depends on what objects are in the field of view, it also depends on the pathlength. Thus, the ambient radiation spectrum must be acquired each time the pathlength is changed or whenever different objects come into the field of view. A recommended schedule for recording the ambient radiation spectrum has not been determined for all situations. However, recording an ambient radiation spectrum once every half hour is typical for most applications. An example of an ambient radiation spectrum is given in Guide E 1865.

Note 6—The ambient radiation spectrum recorded by an OP/FT-IR monitor is a composite of the various IR sources in the field of view of the instrument, such as gray body radiators, emission bands from molecules in the atmosphere, and the instrument itself. Because the ambient radiation spectrum is temperature dependent, its relative contribution to the total signal will vary. This variation will most likely be greater than any other source of instrumental noise. The ambient radiation spectrum will be different for each site and can also change with varying meteorological conditions throughout the day. For example, cloud cover can attenuate the atmospheric emission bands.

6.6 *Measure the Signal Strength as a Function of Pathlength*—In OP/FT-IR systems, the IR beam is collimated before it is transmitted along the path, but diverges as it traverses the path. 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 pathlength.

6.6.1 Start with the retroreflector or the external IR source at the minimum pathlength as determined in 6.3. Record the magnitude of the signal either as the peak-to-peak voltage of the interferogram centerburst or as the intensity of the single-beam spectrum at a specific wavenumber. Once the initial measurement has been recorded, move the retroreflector or IR source some distance away from the receiving telescope, for example, 25 m, and record the magnitude of the signal. Continue this procedure until the signal decreases as the square of the monitoring pathlength. Extrapolate the data to determine

the distance at which the magnitude of the signal will reach that of the random noise (see 6.7), internal stray light, or ambient radiation. This distance represents the maximum pathlength for that particular OP/FT-IR monitor.

Note 7—In bistatic systems, the relative contribution of the ambient radiation to the total signal increases as the signal from the active IR source decreases. As the signal from the active IR source approaches zero, there may be apparent shifts in the peak intensity of the single-beam spectrum.

6.7 *Determine the Random Baseline Noise of the System*— Set up the instrument at a pathlength that is representative of that to be used during the field study. Collect two single-beam spectra sequentially. Do not allow any time to elapse between the acquisition of these two spectra. Create an absorption spectrum from these two spectra by using one spectrum as a background spectrum. Which spectrum is used for the background is not important. Measure the random noise as the root-mean-square (RMS) noise (**4**). 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. The RMS noise should be determined in wavenumber regions that are not significantly impacted by water vapor, for example, 958–1008 cm^{-1}, 2480–2530 cm^{-1}, and 4375–4425 cm^{-1}. Record the value of the RMS noise for future reference.

7. Logistical Concerns and Ancillary Measurements at the Monitoring Sites

7.1 *Logistical Concerns*—Several logistical concerns must be addressed at each monitoring site before the OP/FT-IR monitor is deployed in the field. Consideration must be given to power requirements, mounting and support requirements, and climate control. Some ancillary measurements should also be made.

7.1.1 *Power*—Supply the required electrical power to the spectrometer. In bistatic systems with a remote IR source, an additional source of power must be provided if an electrical outlet is not available. Some IR sources can operate off a portable 12-V power supply, such as a car or marine battery. The output of the battery must be stabilized for quantitative measurements.

7.1.2 *Mounting and Support*—For short-term field studies, the spectrometer, the retroreflector, or the remote IR source are typically mounted on transportable tripods with swivel heads that allow for vertical and horizontal adjustments. For permanent installations, a more rigid mounting system can be used. In either case, the OP/FT-IR monitor should be isolated from vibrations.

7.1.3 *Climate Control*—Although some OP/FT-IR systems might be designed to withstand the elements, some effort should be made to protect the optical and electrical components of the system from rain and other forms of moisture, corrosive gases, and extreme cold or heat.

7.1.3.1 Spectrometers with hygroscopic internal optics, such as KBr beamsplitter, must be purged with a dry, inert gas or hermetically sealed to prevent moisture from damaging the optics. As an alternative, ZnSe optical components can be used.

7.1.3.2 Water vapor can condense on optical components, such as the retroreflector, that are exposed to the atmosphere. Some method to prevent this condensation, such as heating the component slightly above the dew point, must be implemented.

7.1.3.3 If exposure of the optical components to a corrosive environment cannot be avoided, devise some type of system to purge the surface of the optical components to minimize this exposure.

7.1.3.4 The spectral response of the spectrometer can be sensitive to changes in ambient temperature. In some instruments, the interferometer will not scan at ambient temperatures below 5°C. In permanent installations, the temperature inside the shelter that houses the spectrometer should be controlled and monitored. For short-term field studies conducted in cold-weather climates, the spectrometer should be covered with some type of heated, insulating material.

7.2 *Ancillary Measurements*—Make continuous, real-time measurements of the following parameters: temperature, relative humidity, barometric pressure, and wind velocity. These measurements should be recorded and archived with some type of automated data logger. Guidance for selecting and setting up the instruments for making meteorological measurements is given in a United States Environmental Protection Agency (USEPA) handbook (**5**). Although this handbook does not directly address open-path measurements, it provides useful information about meteorological instrumentation and measurements.

Note 8—A measurement of relative humidity is not satisfactory for use in OP/FT-IR monitoring. The actual partial pressure of water vapor must be determined. If relative humidity is measured, then the temperature must also be recorded so that the partial pressure of water can be calculated by consulting the Smithsonian psychrometric tables. These tables can be found in the *Handbook of Chemistry and Physics* (**6**).

8. Selecting the Monitoring Path

8.1 The monitoring path can be selected once the location of the pollutant source is known, pertinent meteorological data are available, and specific target gases have been chosen for the monitoring program.

8.2 *Orient the Path*—Determine the direction of the prevailing winds. Set up the monitoring path downward of the pollutant source and perpendicular to the wind field. Unless there is a specific need to do otherwise, the path should be horizontal to the ground because the concentration contours of the target gases can vary with altitude. An example of a possible orientation of the monitoring path relative to the pollutant source area is given in Fig. 1.

Note 9—The USEPA has amended Part 58 of Chapter 1 of Title 40 of the Code of Federal Regulations (40 CFR58) that define ambient air monitoring criteria for open-path monitors (**7**). These amendments describe how the path is to be chosen with respect to obstructions and height above the ground. They also describe the appropriate positioning of the path in relation to buildings, stacks, and roadways.

8.3 *Select the Pathlength*—Choose the pathlength to maximize the percentage of the plume from the pollutant source that is interrogated by the IR beam. The pathlength should be nominally longer than the width of the plume to account for variations in the plume over time. For homogeneously distributed gases, the path can be made longer, if needed, to increase

Upwind
FT-IR ☐ ◄— Background Path —► ⟩ Retroreflector

Prevailing
Wind
↓

**Source
Region**

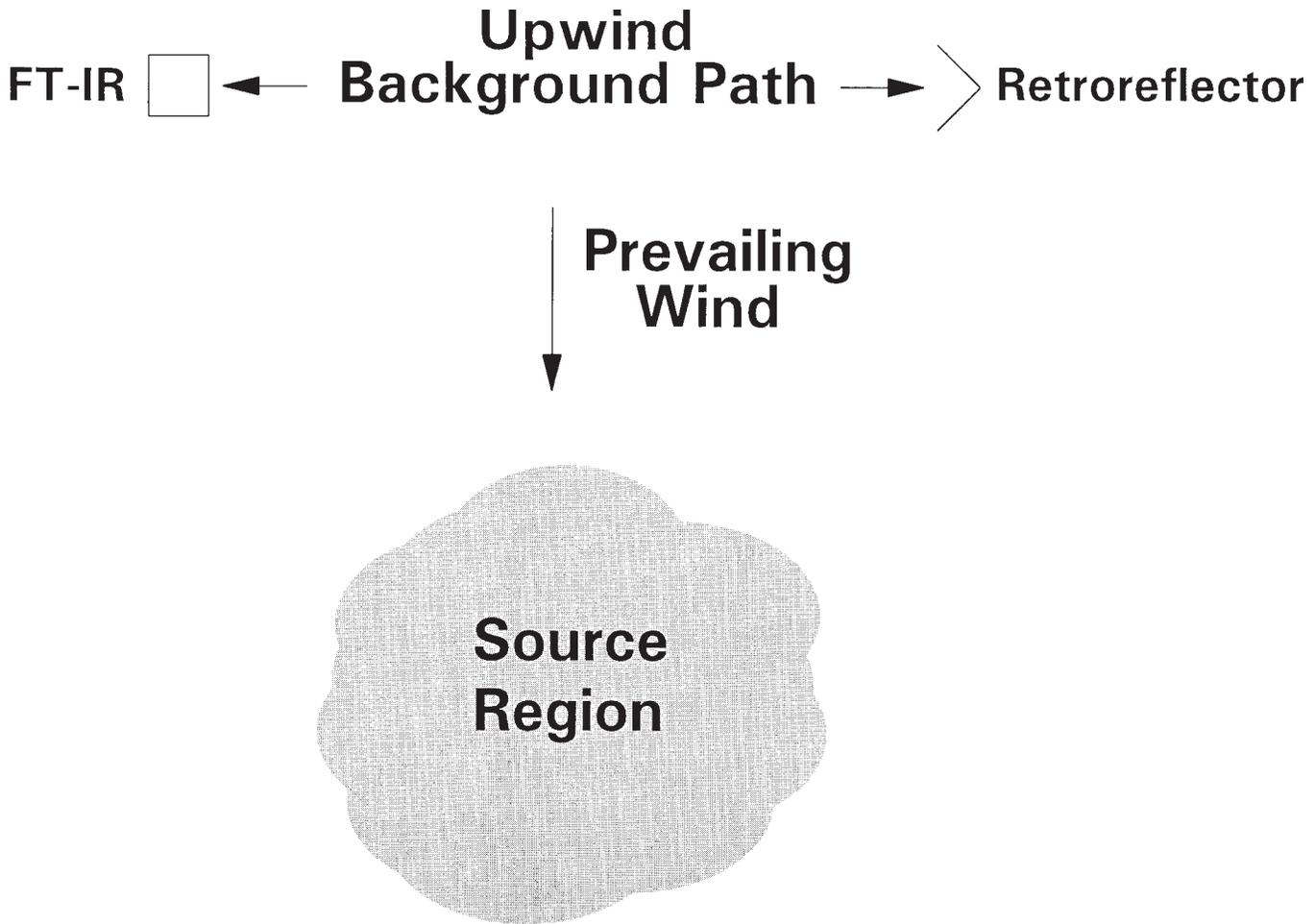FT-IR ☐ ◄— **Primary Data Path** —► ⟩ Retroreflector

FIG. 1 Possible orientations of the monitoring paths relative to the direction of the prevailing wind and the pollutant source for primary data collection and for an upwind background spectrum.

the measured absorbance. For plumes of finite extent, making the path longer than the width of the plume is detrimental because the OP/FT-IR monitor measures the path-averaged concentration. If part of the path has zero concentration, then there is a dilution effect. In some applications, the pathlength might be determined by logistical concerns, such as the availability of electrical power and suitable sites to accommodate the instrument and peripherals.

NOTE 10—The actual dimensions of the plume are difficult to define. Some models assume that the concentration profile of the plume can be described by a Gaussian function. The boundaries of the plume, however, may not be known prior to selecting the monitoring path.

8.3.1 *The Longest Pathlength*—The longest pathlength for a particular OP/FT-IR system was determined in 6.6.1 as the distance at which the total signal approaches the signal due to the system noise, internal stray light, or ambient radiation. For target gases and interfering species that are distributed homo-

geneously along the path, the atmosphere is optically dense at some pathlength. This distance represents the maximum pathlength for that gas and can be determined as follows.

8.3.1.1 Measure the absorbance of the analytical band of the target gas or interfering species from a reference spectrum. See 10.2 for procedures for choosing an analytical band. Record the concentration—pathlength product at which the reference spectrum was taken.

8.3.1.2 Calculate the absorptivity, a, for this gas by using Eq 2.

$$a = A_{ref}/b_{ref} C_{ref} \qquad (2)$$

where:
A_{ref} = absorbance of the reference spectrum at a specified wavenumber,
b_{ref} = pathlength at which the reference spectrum was measured, and

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c_{ref} = concentration of the reference standard.

8.3.1.3 Estimate the concentration of the target gas or interfering species from preexisting monitoring data or from ancillary measurements.

8.3.1.4 Select a maximum allowable absorbance value, based on the requirements of the analysis method.

8.3.1.5 Use Eq 3 to estimate the pathlength that would yield the maximum allowable absorbance value at the estimated concentration.

$$b_{max} = A_{max}/ac_{est} \qquad (3)$$

where:
A_{max} = the maximum allowable absorbance selected in 8.3.1.4,
c_{est} = the concentration estimated in 8.3.1.3, and
a = the absorptivity calculated in 8.3.1.2

The value of b_{max} calculated in Eq 3 is the longest allowable pathlength for measuring that particular target gas or interfering species.

8.3.2 *The Shortest Pathlength*—The shortest pathlength may be dictated by the distance at which the detector becomes saturated as determined in 6.3. If the instrument is operating linearly at any potential pathlength, the shortest pathlength for the target gas can be calculated as follows.

8.3.2.1 Measure the absorbance of the analytical band of the target gas from a reference spectrum. Record the concentration—pathlength product at which this spectrum was taken.

8.3.2.2 Calculate the absorptivity, a, for this gas by using Eq 2.

8.3.2.3 Estimate a minimum concentration that will be measured.

8.3.2.4 Set the minimum detectable absorbance at three times the RMS baseline noise as measured under normal operating conditions (see 6.7).

8.3.2.5 Calculate the minimum pathlength by using Eq 3, and the values of the absorptivity, minimum concentration, and minimum detectable absorbance found in 8.3.2.2 through 8.3.2.4, respectively.

8.4 *Estimate Detection Limits*—The method detection limit (MDL) in units of the concentration—pathlength product, for example ppm-m, can be estimated by using Eq 4.

$$(bc)_{min} = A_{min}/a \qquad (4)$$

where:
A_{min} = minimum detectable absorbance, for example, three times the RMS baseline noise, and
a = the absorptivity, as calculated in 8.3.1.2

To obtain the MDL of homogeneously distributed gases in units of concentration, for example ppb, divide the value of $(bc)_{min}$ by the pathlength. Examples of estimated detection limits for several hazardous air pollutants and common atmospheric gases are given in Annex A1 (see Table A1.1). This table can be used during the planning phase of a field study to determine if measurements of selected target gases are feasible at a particular monitoring site for a given monitoring pathlength. This procedure is also applicable to estimating the MDL for the comparison (see 10.8.1) or the scaled subtraction (see 10.8.2) analysis methods. Lower estimates of the MDL

may be obtained when mulivariate analysis methods (see 10.8.3) are used by calculating the standard error of measurement for the target gas in a spectrum in which the target gas is not present.

9. Data Acquisition

9.1 Perform the following steps to acquire the OP/FT-IR spectral data once the instrumental parameters have been chosen (see Section 5), initial performance tests have been completed (see Section 6), logistical concerns have been addressed (see Section 7), and the monitoring path has been selected (see Section 8).

9.2 *Align the Instrument*—Allow the system to equilibrate. Adjust the vertical and horizontal position of the receiving telescope, the retroreflector, or the external IR source to maximize the peak-to-peak voltage of the interferogram centerburst or the intensity of the single-beam spectrum at a specific wavenumber. Record the value of the maximum signal.

9.3 *Determine the Random Baseline Noise of the System*—Record the magnitude of the RMS noise as described in 6.7. Compare this value with historical data to determine that the instrument is performing within the data quality objectives of the study.

9.4 *Choose the Type of Data File*—Select the type of data file that is to be collected, for example, either a single-beam spectrum or an interferogram.

Note 11—The interferogram should be the type of raw data that is collected to allow for more choices in post-data acquisition processing.

9.5 *Acquire the Spectral Data*—Choose the number of data files to be collected and the intervals at which they are to be acquired, then start acquiring the data.

10. Data Analysis

10.1 The steps that are required to analyze OP/FT-IR field spectra include selecting the spectral region over which the analysis will be performed; generating a background spectrum; correcting the field spectra for internal stray light or ambient radiation; generating an absorption spectrum from the interferogram; obtaining the appropriate reference spectra; correcting the field spectra for wavenumber shifts; and choosing the analysis method.

10.2 *Select the Analysis Region*—Perform the following steps to determine the optimum region of the spectrum over which to perform the data analysis. This determination will be influenced by the choice of analysis method (see 10.8).

10.2.1 Find the most intense absorption band in a reference spectrum of the target gas. If the comparison (see 10.8.1) or scaled subtraction (see 10.8.2) method is used to analyze the data, choose this absorption band as the analytical band. If a multivariate analysis method, such as CLS or PLS (see 10.8.3), is used, then select the wavenumber region that encompasses the entire envelope of the most intense absorption band.

10.2.2 Measure the absorbance maximum of the band chosen in 10.2.1. Use Eq 2 to calculate the absorptivity of the target gas. Estimate the concentration of the target gas that is expected to be present at the monitoring site, then estimate the absorbance of the analytical band by using Eq 5:

$$A_{est} = abc_{est} \qquad (5)$$

where:

A_{est} = estimated absorbance of the target gas,
a = the absorptivity of the target gas,
b = the monitoring pathlength, and
c_{est} = the estimated concentration of the target gas.

If the estimated absorbance is lower than three times the RMS noise (see 6.7), this absorption band may be too weak to measure the target gas at the monitoring site by either the comparison or scaled subtraction methods. The use of weaker absorption bands might be appropriate when multivariate analysis methods are used because these methods have demonstrated the ability to extract quantitative information from apparent baseline noise.

10.2.3 If the most intense absorption band is in a region of the OP/FT-IR field spectrum that is optically opaque due to absorption by atmospheric water vapor or carbon dioxide, then return to 10.2.1 and select the next most intense absorption band.

10.2.4 Determine if the absorption band chosen in 10.2.3 is optically dense, or saturated at the monitoring pathlength. If this is the case, return to 10.2.1 and select the next most intense absorption band.

10.2.5 Determine if an interfering species other than water vapor or carbon dioxide is present that would prohibit the absorption band chosen in 10.2.4 from being used. If this is the case, return to 10.2.1 and select the next most intense absorption band. Proceed to the other data analysis procedures once a suitable absorption band has been found.

10.3 *Produce a Background Spectrum*—In conventional FT-IR spectrometry, a background single-beam spectrum is obtained in the absence of the sample of interest. The single-beam sample spectrum is divided by this background, or I_0, spectrum to create a transmittance spectrum. This operation, in effect, nulls out the spectral features due to the detector, IR source, beamsplitter, and other optical components. 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. The following methods can be used to produce an I_0 spectrum.

10.3.1 *Synthetic Background Spectra*—A software package that allows individual data points to be selected, deleted, or moved along the ordinate must be available to generate a synthetic background spectrum. An example of a synthetic background spectrum. An example of a synthetic background spectrum is given in Guide E 1865. To create a synthetic background spectrum, perform the following steps.

10.3.1.1 Select a single-beam spectrum with an intensity profile that matches the profile of the field spectra and that was acquired when the concentrations of the target gases and interfering species were at a minimum.

10.3.1.2 Select data points along the envelope of this single-beam field spectrum, matching the instrument response curve as closely as possible. Do not select data points on an absorption band or on the continuum produced by unresolved absorption bands.

10.3.1.3 Fit a series of short, straight lines or some other appropriate function to the selected points to generate a smooth curve that follows the profile of the original single-beam field spectrum. Do not introduce any distortions, artificial dips, or peaks into the intensity function.

10.3.1.4 An automated procedure that fits a series of segmented polynomial curves to a single-beam field spectrum can also be used as an alternative to producing a synthetic background spectrum manually (**8**).

NOTE 12—A resolution of 2 cm^{-1} or better is generally required to develop a synthetic background spectrum. At lower resolutions, the unresolved water vapor continuum interferes with the visualization of the true instrument response curve (see Fig. 2). A synthetic background spectrum is most effective when analyzing for target gases with narrow absorption features. This type of background spectrum is more difficult to develop for target gases with broad absorption bands, especially when low concentrations are to be measured.

10.3.2 *Short-Path Background Spectra*—A short-path background spectrum can be used when a synthetic background spectrum is not suitable, for example, during low-resolution measurements or when analyzing for target gases with broad absorption bands. The short pathlength that is used for this type of background spectrum effectively eliminates the absorption caused by the target gases and minimizes the absorption caused by interfering atmospheric species. An example of a short-path background spectrum is given in Fig. 2(C). Perform the following steps to produce a short-path background spectrum.

10.3.2.1 Position the retroreflector or external IR source close to the receiving telescope, and obtain a single-beam spectrum.

10.3.2.2 Inspect the short-path background spectrum in the spectral region below the detector cutoff frequency for non-physical energy.

10.3.2.3 Compare the intensity profile of the short-path spectrum with that of the field spectra.

10.3.2.4 Determine if wavenumber shifts or resolution changes have occurred between the field spectra and the short-path background spectrum.

10.3.2.5 If any anomalies are detected in 10.3.2.2 through 10.3.2.5, do not use the short-path background spectrum. Wire mesh screens can be used to attenuate the IR intensity, but the use of these screens may also introduce changes in the single-beam intensity profile.

NOTE 13—One problem with producing a short-path background spectrum is that the detector can be saturated as short pathlengths. Another difficulty arises when obtaining a short-path background spectrum with monostatic systems. In these systems, the retroreflector subtends 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. When this is the case, the retroreflector subtends smaller angles as the pathlength is increased, and the instrument uses different cones of light. Therefore, changing the pathlength can cause distortions in the spectrum. 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.

10.3.3 *Upwind Background Spectra*—If the area of the pollutant source is relatively small and its upwind side is accessible, an upwind I_0 spectrum can be acquired. An example of a possible orientation of the monitoring path for an upwind background spectrum is given in Fig. 1. Generally, the instrument must be transported to obtain an upwind background spectrum. This procedure is most often not applicable to
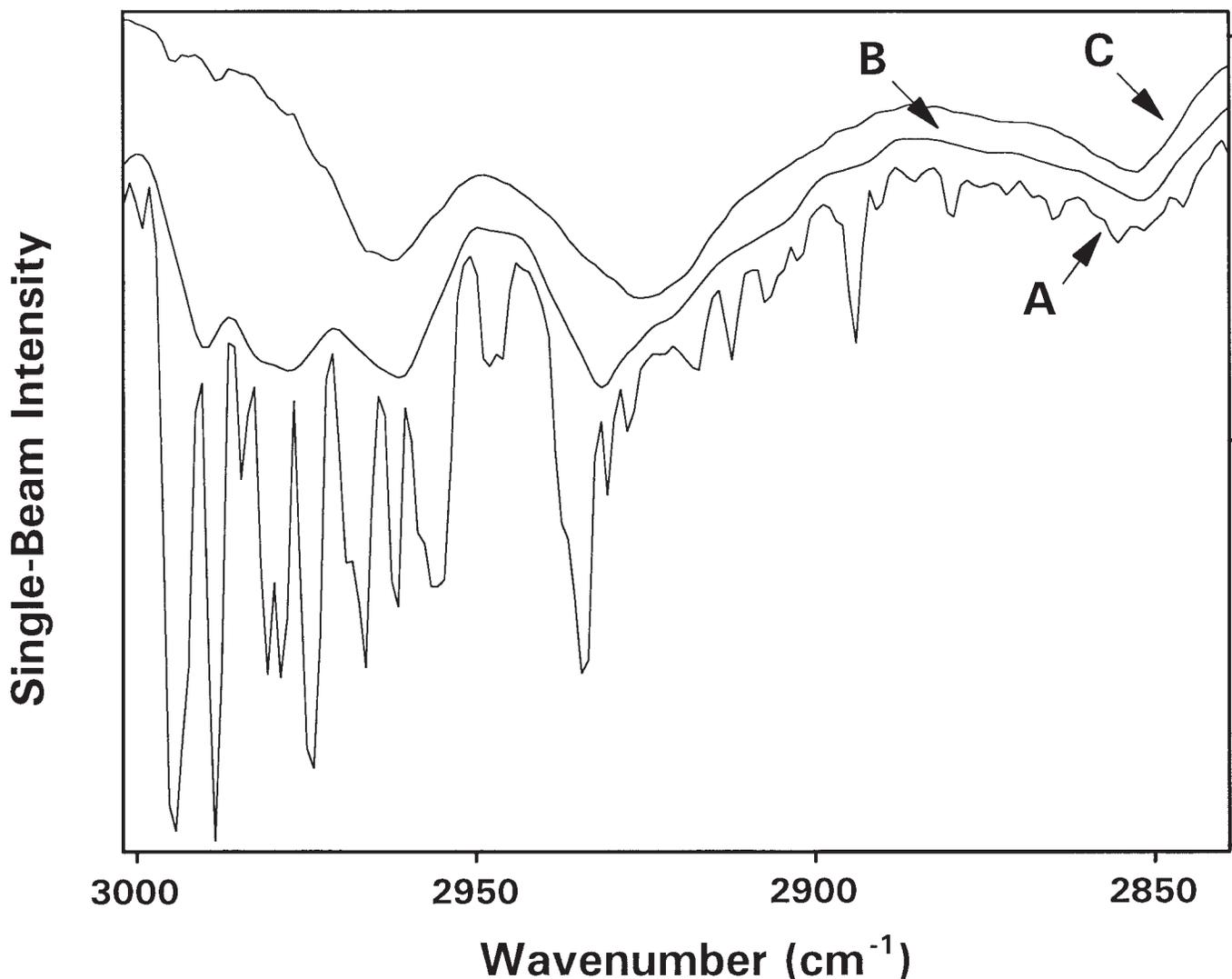
FIG. 2 Single-beam OP/FT-IR spectra collected at 2-cm^{-1} resolution representing: (A) a field spectrum acquired over a 200-m path; (B) a synthetic background spectrum; and (C) a short path background spectrum. The positions of the spectra are offset slightly on the ordinate for clarity.

permanent installations. An upwind background spectrum is usually taken once at the beginning of the daily monitoring period and once at the end. Perform the following steps to produce an upwind background spectrum.

10.3.3.1 Determine the location of the pollutant source and the wind direction.

10.3.3.2 Set up the monitoring path along the upwind side of the pollutant source and acquire a single-beam spectrum.

10.3.3.3 Analyze the upwind background spectrum for the target gas. If any target gas is present in this spectrum, the concentrations measured when it is used as a background spectrum will be the difference between the concentration in the field spectrum and that in the background spectrum.

10.3.3.4 If the instrument cannot be transported, wait until the wind shifts so that the existing monitoring path is along an upwind side of the pollutant source and acquire the background spectrum.

10.3.4 *Averaged Background Spectra*—When the experimental conditions are fairly constant over the monitoring study,

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 not to contain any measurable concentration of the target gas. This average I_0 can then be used for the entire data set for the study.

10.3.4.1 Analyze a series of field spectra for the target gas.

10.3.4.2 If no target gas is detected in these spectra, average these spectra to produce a background spectrum.

10.4 *Correct the Single-beam Field Spectra for Internal Stray Light or Ambient Radiation*—Subtract the single-beam spectrum of internal stray light (monostatic systems) or ambient radiation (bistatic systems) from the single-beam field spectra (see 6.5.1 and 6.5.2). Do not rescale the ordinate of either spectrum before performing the subtraction. In monostatic systems, the same internal stray light spectrum can generally be used for an entire data set. In bistatic systems that are equipped with an unmodulated external IR source, use a source-off spectrum that was taken close in time, generally

within one-half hour, and under the same atmospheric conditions as the field spectra.

10.5 *Calculate the Absorption Spectrum*—Divide the single-beam field spectrum by the background spectrum produced in 10.3 to obtain a transmittance spectrum. Take the negative logarithm (base 10) of the transmittance spectrum to obtain the absorption spectrum. Use the absorption spectrum for all further data analysis.

10.6 *Obtain the Reference Spectra*—Producing reference spectra is an exacting undertaking and requires great attention to the experimental details. It is unlikely that most users of OP/FT-IR monitors will prepare their own reference spectra because spectral libraries are available commercially. The use should, however, be aware that the use of reference spectra that were not generated with the same instrument used in the field can lead to errors in the accuracy of the concentration measurements. The magnitude of these errors is difficult to assess. Even when the same resolution, zero filling, and apodization are used for the reference and field spectra, slight wavenumber shifts (see 10.7) and differences in the band width can be observed (see 11.2.5). Also, if a linear algorithm is used in the data analysis method, the concentration—pathlength product of the reference spectra should match as closely as possible that of the field spectra. One reference spectrum that the operator will most likely have to create, however, is a water vapor reference spectrum.

10.6.1 *Produce a Water Vapor Reference Spectrum*—A water vapor reference spectrum that is produced in the laboratory with a long-path cell typically does not have a concentration-pathlength product that is representative of that found in the field. Therefore, a water vapor reference spectrum must be developed by some other means. Perform the following steps to produce a water vapor reference spectrum from a field spectrum.

10.6.1.1 Select a single-beam field spectrum that has a water vapor concentration that is representative of the water vapor concentration in the field spectra.

10.6.1.2 Retrieve the background spectrum that was produced in 10.3.

NOTE 14—A synthetic or short-path background spectrum is required during the creation of a water vapor reference spectrum. If an upwind or averaged I_0 is used, the apparent water vapor absorption will be the ratio between the water vapor absorption in the field spectrum and that in the background spectrum.

10.6.1.3 Create an absorption spectrum from the two single-beam spectra selected in 10.6.1.1 and 10.6.1.2. The absorbance values of the water vapor bands should match those in the field spectra as closely as possible. The water vapor reference spectrum will be produced from this absorption spectrum.

10.6.1.4 Subtract a reference spectrum of the target gas(es) and any known interfering species from the absorption spectrum created in 10.6.1.3 to remove any absorption features that cannot be attributed to water vapor. The resulting spectrum is the water vapor reference spectrum. The following steps can be used to check the newly-created water vapor reference spectrum for the presence of absorption features due to the target gas(es) or interfering species.

10.6.1.5 Record a series of single-beam spectra back to back. Create a series of absorption spectra from these spectra. For each spectrum in the series, use the preceding spectrum as the background spectrum. For example, to create an absorption spectrum from the second spectrum in the series, use the first spectrum in the series as the background spectrum. Each spectrum should exhibit a flat, featureless baseline that is representative of the random baseline noise. Determine visually that no target gas is present in these absorption spectra.

10.6.1.6 Analyze the spectra recorded in 10.6.1.5 for the target gas(es) and interfering species by using one of the methods described in 10.8. If a multivariate analysis method is used, designate the newly-created water vapor reference spectrum as an interfering species. 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, scale the ordinate of the target gas reference spectrum to the absorbance corresponding to the concentration value calculated by the analysis, and either add in or subtract out this amount of the target gas from the water vapor reference spectrum. Reanalyze the series of absorption spectra. Repeat these steps until the concentration values calculated by the analysis method are near zero. Analyze several back-to-back spectra in this way to determine whether the concentration values are systematically or randomly distributed around zero.

10.6.1.7 A synthetic water vapor reference spectrum can be calculated from the HITRAN data base as an alternative to producing a water vapor reference spectrum from a field spectrum **(9)**. The output of the HITRAN data base can be convolved with the appropriate instrument line shape function to match the field spectra **(8)**.

10.6.2 *Produce Reference Spectra of the Target Gases*—If an adequate reference spectrum of the target gas is not available, the following general procedure can be used to produce one. Deliver a known concentration of the target gas into a closed IR cell. The use of multipass cells with relatively long pathlengths is recommended for this procedure. Use a pure sample of the target gas mixed with an inert gas such as nitrogen. The concentration of the target gas in the cell should yield a reference spectrum with a range of absorbance values that match as closely as possible those expected to be found in the field spectra. A continuous flow or a static method can be used. In either case, a total pressure of 1 atm should be maintained in the cell. Synthetic spectra of common atmospheric gases can also be generated from the HITRAN data base **(8, 9)**. 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.

10.7 *Correct for Wavenumber Shifts*—Software that allows the spectra to be shifted along the wavenumber scale must be available to correct the spectra for wavenumber shifts. To determine if a wavenumber shift has ocurred, compare the peak maxima in absorbance of selected bands from the field spectra with those of the reference spectra. Subtract one spectrum from the other. The bands in the two spectra being subtracted must

be of the same intensity, or they must be scaled to the same intensity prior to the subtraction operation. Wavenumber shifts will result in a feature in the difference spectrum that appears to be the first derivative of the band shape. Correct for these wavenumber shifts by shifting the reference spectra to match the field spectra. If there are no changes in the peak positions of the absorption bands in the field spectra as compared to the reference spectra, then the result of subtraction will be random noise and no wavenumber correction is required.

10.8 *Calculate the Concentration Values*—Several methods can be used to calculate the concentration values of target gases from OP/FT-IR spectra. General methods of IR quantitative analysis are given in Practice E 168. Quantitative methods in IR spectrometry can be classified as either univariate, in which a single absorption band or frequency is used, or multivariate, in which multiple absorption bands or frequencies are used. Two types of univariate methods, the comparison method and the scaled subtraction method, are used in OP/FT-IR monitoring. These methods usually require high resolution spectra when applied to OP/FT-IR data. Multivariate analysis methods can be used to advantage when the concentrations of several target gases are to be determined simultaneously, several interfering species are present, and the spectral features of the target gases overlap with those of the interfering species and other target gases. This situation is usually 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 CLS, inverse least squares, PLS, and principal components regression. The most common multivariate analysis methods used in OP/FT-IR monitoring are CLS and PLS. A complete discussion of these methods is given in Practice E 1655 and a review by Haaland (**10**). Several software packages allow OP/FT-IR data to be analyzed by some type of multivariate method. Because of the differences in these software packages, a detailed step-by-step procedure for their use cannot be given. However, some general considerations for CLS and PLS are discussed in 10.8.3. Each of the methods discussed below assumes that the single-beam field spectra were corrected for internal stray light or ambient radiation; an absorption spectrum has been created from the single-beam field spectra by using an appropriate background spectrum; and the absorption spectra were corrected for wavenumber shifts.

10.8.1 *Comparison Method*—Perform the following steps using the comparison method to calculate the concentration of the target gas.

10.8.1.1 Measure the absorbance of the analytical absorption band of the target gas in the field spectra (A_{fld}) and the reference spectrum (A_{ref}) at the same wavenumber.

10.8.1.2 Obtain the concentration (c_{tar}) of the target gas as follows.

$$A_{ref}/A_{fld} = b_{ref} c_{ref}/b_{tar} c_{tar} \qquad (6)$$

Solving for the concentration of the target gas gives the following.

$$c_{tar} = c_{ref} b_{ref} A_{fld}/b_{tar} A_{ref} \qquad (7)$$

The concentration of the target gas will be in the same units as that of the reference spectrum.

10.8.2 *Scaled Subtraction Method*—Perform the following steps using the scaled subtraction method to calculate the concentration of the target gas.

10.8.2.1 Subtract a reference spectrum of the target gas from the field spectrum until the absorption maximum of the analytical absorption band is zero.

NOTE 15—If there is an uncorrected wavenumber shift between field spectra and the reference spectra, the scaled subtraction can give first-derivative shaped residuals. If this is the case, correct the spectra for wavenumber shifts (see 10.7) and repeat the scaled subtraction.

10.8.2.2 Record the scaling factor required to perform the subtraction.

10.8.2.3 Multiply the concentration of the reference spectrum by the scaling factor to obtain the concentration of the target gas in the field spectrum.

10.8.3 *Classical Least Squares (CLS) and Partial Least Squares (PLS)*—In CLS, the calibration model 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. The PLS method is not restricted to a direct physical model, such as Beer's law. In PLS, the spectral data are modeled empirically, which often provides a better fit to the field data. Perform the following steps using either the CLS or PLS method to calculate the concentration of the target gas.

10.8.3.1 Inspect the absorption spectra for baseline abnormalities. If the baseline contains any unusual features, then consider using a different background spectrum (see 10.3) to recreate the absorption spectra. If the field spectra exhibit baseline variations that are not related to the concentration of the target gas or the interfering species, some type of baseline fitting procedure must be included in the CLS method. These baseline variations can be modeled in PLS.

10.8.3.2 Choose the analysis region (see 10.2). In principle, the entire wavenumber range of the field spectrum can be used. In practice, the CLS or PLS analysis is typically performed over smaller spectral regions, for example, 200 cm^{-1}. If CLS is used, choose a spectral region that contains the widest range of absorption bands that adhere to Beer's law. If the wavenumber region must be narrowed to eliminate interfering species, choose the region that will yield the largest possible range of absorbance values.

10.8.3.3 Identify the interfering species in the wavenumber region chosen for analysis (see 10.2). Include reference spectra of these interfering species in the calibration set. In CLS, all gases that have spectral features in the analysis region must be included in the calibration spectra.

10.8.3.4 Develop a set of calibration spectra from reference spectra of the target gases and interfering species. The S/N of the reference spectra should be high compared to the S/N of the field spectra. Some CLS software packages require that a series of spectral mixtures containing varying concentrations of the target gases and interfering species be developed. Other CLS packages use pure component reference spectra of the target gases and interfering species. The latter method essentially uses a single-point calibration, which most likely does not

account for deviations from Beer's law. Compared to CLS, the PLS method typically requires more extensive calibration. 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.

10.8.3.5 Perform the concentration analysis.

10.8.3.6 Inspect the residuals and the errors of the analysis. The spectral residuals can be viewed in some packages. This feature allows previously unaccounted for interfering species to be detected and identified. These interfering species can then be included in the calibration set, and the field spectra can be reanalyzed. Abstract spectra are generated by PLS, as opposed to the estimated pure-component spectra generated by CLS. Therefore, some qualitative information is lost during the PLS calibration.

10.8.3.7 If the residuals of the analysis are not within the data quality objectives of the study, examine the analysis method for the presence of uncorrected wavenumber shifts; interfering species that were not identified and included in the calibration set; or deviations from Beer's law due to detector nonlinearities, inadequate spectral resolution, optically dense absorption bands, or poor baseline modeling. 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.

11. Quality Control (QC) Procedures

11.1 Three separate issues must be considered when performing QC procedures on OP/FT-IR data: the performance of the OP/FT-IR system, the accuracy of the concentration values, and the precision of the measurements. Procedures for monitoring the performance of the OP/FT-IR system and for estimating the accuracy and the precision of the concentration values are given below. General guidance for developing a Quality Assurance/Quality Control (QA/QC) program for environmental monitoring applications is given in a USEPA document (11). An example of a USEPA audit of an OP/FT-IR program has also been described (12).

11.2 *Monitoring the Performance of the OP/FT-IR System*—Level zero and level one tests for measuring the performance of FT-IR spectrometers are given in Practice E 1421. Some tests for evaluating the performance of OP/FT-IR systems during initial instrument operation are given in 6.2-6.6. Many of these tests are also used to monitor the performance of the OP/FT-IR system. These tests include measuring the electronic noise, the random baseline noise, and the signal strength; inspecting the single-beam spectrum for nonphysical energy and changes in the intensity profile; and checking for wavenumber shifts and changes in resolution. These tests should be performed at least twice a day, at the beginning and at the end of the daily monitoring period. These tests can also be applied to archived data when reviewing or validating a data set. Plot the results from these tests versus time on a control chart to determine if any trends in the data exist.

11.2.1 *Electronic Noise*—Measure the electronic noise, as described in 6.2.

11.2.2 *Random Baseline Noise*—Measure the random baseline noise, as described in 6.7. Spectra taken at longer time intervals during the study can be analyzed in this manner to determine baseline stability or systematic noise.

11.2.3 *Signal Strength*—Measure the signal strength either as the peak-to-peak voltage of the interferogram centerburst or the single-beam intensity in a selected wavenumber region. If the interferogram is used for this measurement, also record the position of the zero peak difference. Note any unusual atmospheric conditions, such as fog, snow, or heavy rain, that might affect the signal strength.

11.2.4 *Single-Beam Spectrum*—Examine the single-beam spectrum for nonphysical energy and other evidence of nonlinear response. Measure the single-beam intensity in different wavenumber regions, for example, near 990, 2500, and 4400 cm^{-1}, to determine if the output power of the IR source, the transmitting or reflecting properties of the optics, or the alignment of the interferometer have changed.

11.2.5 *Wavenumber Shifts and Changes in Resolution*—Conduct the following tests to determine if wavenumber shifts or changes in resolution have occurred during the acquisition of each data set. These tests should also 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, and reassembled.

11.2.5.1 Select absorption spectra taken at different times during the study, for example, near the beginning, middle, and end of the study.

11.2.5.2 Compare the peak maxima in absorbance of selected bands to determine visually if a change has taken place between the spectra in the data set.

11.2.5.3 Subtract one absorption spectrum from the other. The bands in the two spectra being subtracted must be of the same intensity, or they must be scaled to the same intensity prior to the subtraction operation.

11.2.5.4 If a wavenumber shift has occured between the two spectra, the subtraction result will exhibit a feature that appears to be the first derivative of the band shape.

11.2.5.5 If a change in resolution has occurred, but there is no wavenumber shift, the subtraction result will exhibit a feature that has the shape of an *M* or a *W*, depending on which of the two spectra contains the broader band.

11.2.5.6 If there are no wavenumber shifts or changes in resolution, the result of subtraction will be random noise.

NOTE 16—Use absorption bands that are known to be singlets and that are always present in OP/FT-IR spectra. 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^{-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 changes in resolution. The HDO bands in the 2720-cm^{-1} region can also be used for these tests.

11.3 *Determining the Accuracy and Precision of the Concentration Data*—The accuracy and precision of the measured concentration values of the target gases depend on several factors, including the stability of the instrument; the choice of background spectrum; corrections for wavenumber shifts and

changes in resolution; corrections for internal stray light or ambient radiation; the accuracy of the reference spectra; and the presence of interfering species and how well they are accounted for in the analysis method. At the present time, there is no definitive way to assess the accuracy and precision of OP/FT-IR data. The accuracy and precision of the field measurements can be estimated by using either ambient gas concentrations or a short cell containing a known amount of the target gas.

11.3.1 *Ambient Gas Concentrations*—The concentrations of atmospheric gases, such as nitrous oxide and water vapor, can be used to estimate the accuracy and precision of the OP/FT-IR concentration data. Nitrous oxide and water vapor are detectable in most OP/FT-IR spectra, provided that the concentration—pathlength product is sufficient. Therefore, no additional spectra need to be acquired to use these gases for QC purposes. Also, no changes have to be made to the instrument to measure them. The concentrations of other atmospheric gases, such as methane, ozone, and carbon monoxide, are generally too variable or are too likely to be impacted by local pollutant sources to be used for QC purposes.

11.3.1.1 *Nitrous Oxide (N_2O)*—The average global concentration of N_2O is approximately 310 ppb. At any particular site, the concentration of N_2O should be relatively constant. Auto exhaust contains trace amounts of N_2O, so monitoring sites that are heavily impacted by automobile traffic may exhibit some variability in the ambient concentrations. Nitrous oxide exhibits an absorption envelope from 2155 to 2265 cm^{-1}. Absorption from atmospheric carbon dioxide interferes with the q-branch, so the p-branch from 2155 to 2225 cm^{-1} is generally used for the analysis. The measured concentration of N_2O should be near 310 ppb. If the field spectra have not been corrected for internal stray light or ambient radiation, the concentration value of N_2O will be low. The percent error in the concentration measurement will be approximately equal to the percentage of internal stray light or ambient radiation relative to the total signal. Other potential causes of errors in the N_2O concentration include an inadequate background spectrum, uncorrected wavenumber shifts, or a poor water vapor reference spectrum. A plot of the N_2O concentration versus time indicates the precision with which the OP/FT-IR measurements can be made. Variations in the N_2O concentration of more than ±10 % indicate that the instrument is not stable and corrective action should be taken.

NOTE 17—Although monitoring the ambient concentration of N_2O can indicate the accuracy and precision with which OP/FT-IR measurements can be made, measuring this gas does not directly assess the accuracy and precision of the concentrations of other species along the path. As stated previously, the accuracy and precision of the concentration measurement depend on many variables. For example, if a synthetic background spectrum is used, accurate measurements of N_2O indicate that the background spectrum is most likely valid over the spectral region used for the analysis, for example, from 2155 to 2225 cm^{-1}. However, this observation does not indicate that the background spectrum is valid, for example, for the analysis of ozone in the spectral region from 975 to 1075 cm^{-1}.

11.3.1.2 *Water Vapor*—Generally, water vapor will be the most concentrated species along the path. At concentration—pathlength products that are typically used in OP/FT-IR moni-

toring, water vapor exhibits absorption bands in most spectral regions of interest. In multivariate analysis methods, water vapor must be included as an interfering species for most target compounds. The water vapor concentration can also be determined from OP/FT-IR data by designating water vapor as a target gas in the analysis method. Although the water vapor concentration in the atmosphere is variable, it can be used to estimate the accuracy and precision of the OP/FT-IR measurements because it is measured independently during field studies. If the concentrations of water vapor measured over the spectral regions of interest do not agree with those determined by the calibrated, independent method, some problem exists with the OP/FT-IR measurements. Potential causes for errors in the water vapor concentrations measured by the OP/FT-IR monitor include an invalid background spectrum over the analysis region, an inaccurate water vapor reference spectra, uncorrected wavenumber shifts, unsubtracted internal stray light or ambient radiation, insufficient spectral resolution, and the presence of unaccounted for interfering species. As with the N_2O measurements, the measurement of the water vapor concentration does not give an absolute indication of the accuracy and precision for each target gas concentration. However, an accurate measurement of the water vapor concentration in each spectral region of interest indicates that the background spectrum, the water vapor reference spectrum, and the analysis method are valid for that spectral region, and that most likely the interfering species are accounted for correctly. An example of a comparison of the water vapor concentration along a 200-m path calculated from 0.5-cm^{-1} resolution OP/FT-IR data versus the water vapor concentration calculated from relative humidity and temperature measurements from a solid-state point monitor is given in Fig. 3

11.3.2 *Short Gas Cell*—A gas cell that contains a known concentration of the target gas or gases can be introduced into the IR beam to estimate the accuracy and precision of the OP/FT-IR measurements. The advantage of using a short gas cell 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. The short cell method has the disadvantage of attenuating the IR beam due to the transmitting and reflecting properties of the windows used in the cell. Therefore, the performance of the system is somewhat degraded when the cell is in place. Also, the intensity profile of the single-beam spectrum will be affected by the spectral characteristics of the cell. New background and water vapor reference spectra must be created for use when the cell is positioned in the optical path. Another problem with the use of short gas cells is that the concentration of the target gas in the cell must be large to obtain measurable absorption features. These high concentrations can lead to self-broadening effects and, in some cases, the formation of dimers. No standard procedures for using a short gas cell for accuracy and precision measurements have been developed to date. The general guidelines discussed below should be followed when designing and using a short gas cell for accuracy and precision measurements.

11.3.2.1 The cell should be designed with wedged windows to minimize interference fringing.
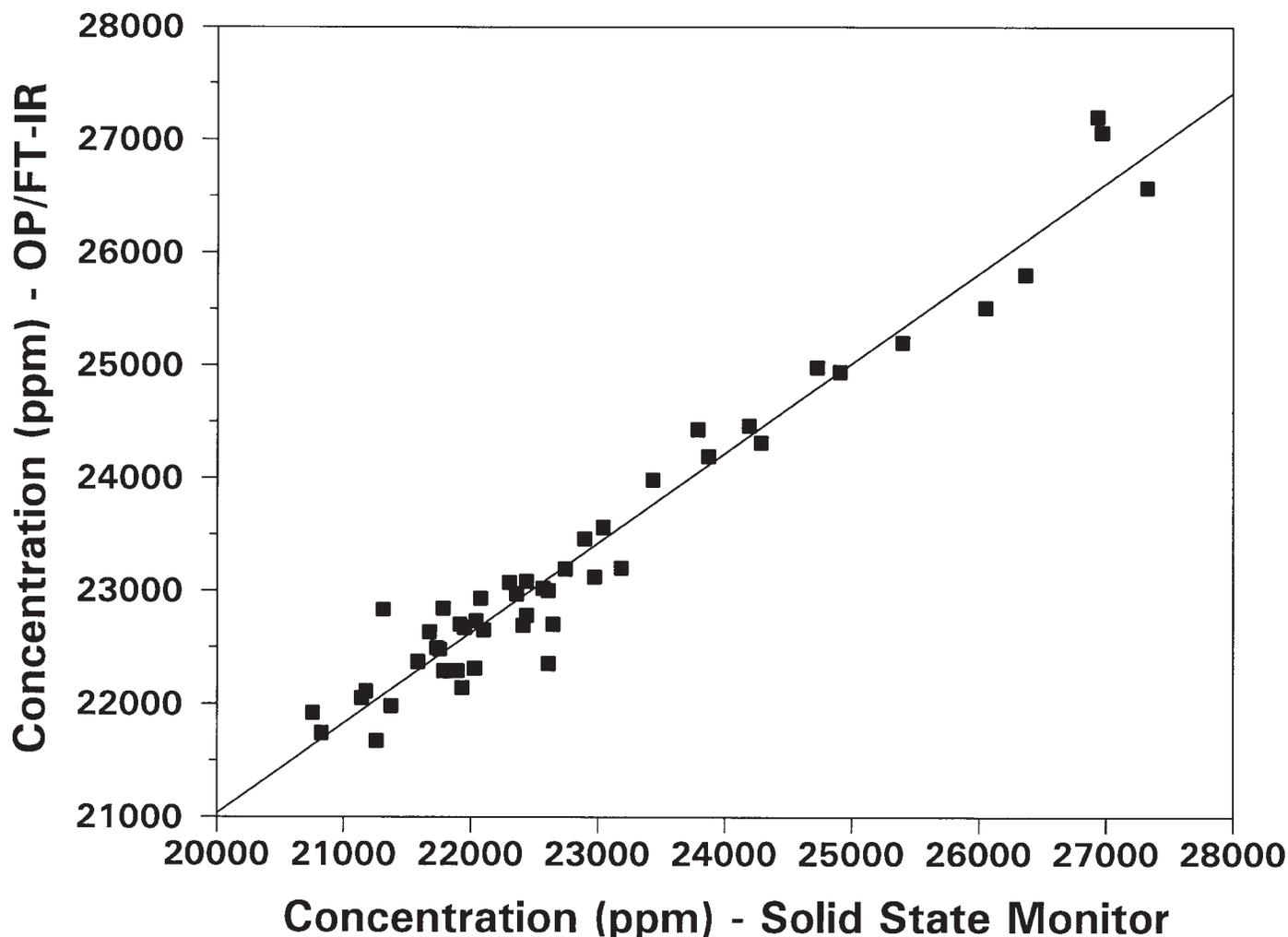
FIG. 3 Plot of the water vapor concentration over a 200-m path calculated from 0.5-cm^{-1} resolution OP/FT-IR data using a CLS analysis over the 2840–3240 cm^{-1} special range versus the water vapor concentration calculated from relative humidity and temperature measurements made with a solid-state point monitor.

11.3.2.2 The diameter of the windows should be large enough so that the entire IR beam interrogates the contents of the cell. This requirement usually dictates that the cell be placed somewhere in the optical path in which the IR beam is relatively small.

11.3.2.3 The pathlength of the cell should be as long as practically possible to allow for a measurable absorbance for a given concentration of gas. The vapor pressure of some gases is too low for adequate IR spectrum to be measured using a short, for example, 10 cm, cell. In general, the partial pressure of the target gas in the cell should not exceed approximately 9.3 kPa (70 Torr or 9.2×10^{-2} atm) for nonpolar compounds and 1.3 kPa (10 Torr or 1.3×10^{-2} atm) for polar compounds.

11.3.2.4 A continuous flow or static method can be used to fill the cell with the target gas or gases. In either case, the final pressure in the cell should be 1 atm.

11.3.2.5 The measurements with the cell should be done over the same pathlength and under the same conditions at which the field measurements are taken.

11.3.2.6 The QC measurements should be taken when the concentration of the target gas along the path is constant or near a minimum. Often, this condition will not be met during monitoring studies. Therefore, the concentration value measured by the OP/FT-IR monitor will be a combination of the concentration in the cell and that along the path. Fluctuations of the target gas concentration along the path will be reflected in the QC measurements.

11.3.2.7 Surrogate standards, such as SF$_6$, have been used with the short cell method during OP/FT-IR measurements. As with the ambient measurements of N$_2$O (see 11.3.1.1), the accuracy and precision determined for surrogate standards are valid for the surrogate standard only and not for all of the target gases.

11.3.2.8 Special precautions are necessary when analyzing polar compounds with a gas cell. Some polar compounds may adhere to or react with the cell walls or the transfer tubing. When this is the case, the concentration of the target gas in the

cell cannot be accurately determined. Therefore, proper passivation of the sampling apparatus and gas cell is necessary for the accurate sampling of polar compounds.

11.4 *Evaluate the Analysis Method*—Use the following procedures, as appropriate, to check the results of the analysis method.

11.4.1 Plot the concentration of the target gas(es) versus time. Examine the plots for any unusual trends. Some atmospheric gases follow a characteristic diurnal pattern, and that pattern should be evident for those particular gases. No negative excursions should be evident in the plots.

11.4.2 Examine the plots of concentration versus time for concentration spikes that cannot be attributed to a known pollutant source. If such a spike exists, examine the original spectra to verify the presence of the compound in question and its concentration. Subtract the appropriate absorption spectra of any interfering species from the field spectrum, and then compare the signature and absorbance values of the resultant spectrum to the reference spectrum of the target gas for the proper features and intensities.

11.4.3 Examine the concentrations of the target gases for any correlation with changes in the water vapor concentration. If such a correlation exists, examine the original spectra 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, make the appropriate changes to the analysis method to alleviate the problem.

11.4.4 If an automated software package was used to calculate the concentration values, manually check these values by comparing the field spectra to spectra of reference gases with a known concentration. Use an interactive subtraction procedure that yields a scaling factor for the reference spectrum to verify the concentration measured by the software.

11.4.5 Choose an alternative spectral region or analytical absorption band over which to perform the data analysis. Compare the results from this analysis with those obtained over the primary analysis region.

11.4.6 Verify the accuracy of the reference spectra. To date, no way of validating or certifying the reference spectra exists. The National Institute of Standards and Technology (NIST) is currently addressing this issue (14). If possible, compare reference spectra obtained from different sources or data bases.

11.5 *Completeness of the Data*—Verify that the frequency of data acquisition was sufficient to account for the variability in the target gas concentration by examining the plots of concentration versus time. Gaps in the data during rapid changes in the target gas concentration may indicate that data were not taken at a frequent enough interval.

11.6 *Representativeness of the Data*—The concentration values determined by OP/FT-IR measurements represent the path—averaged concentration along the monitoring path. In some applications, such as fenceline monitoring, where the only concern is detecting fugitive emissions along the perimeter of the facility, the OP/FT-IR measurement will be representative of the desired end result. In other applications, such as characterizing the plume from an area source, measurements along multiple monitoring paths may need to be made. The concentrations measured over each of the monitoring paths can then be compared to determine which measurements are representative of the plume concentration.

11.7 *Comparability of the Data*—Compare the OP/FT-IR data to data obtained from an established method. As discussed in 11.3.1.2, comparing the water vapor concentration obtained from the OP/FT-IR data to that obtained by an independent method can be useful. 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. Bear in mind that the OP/FT-IR data represent path—averaged concentrations, which may not be directly comparable to data obtained with a point monitor.

11.8 *Documentation*—Maintain a log of instrument use, downtime, repairs, and observations regarding instrument performance, atmospheric conditions, or unusual occurrence at the monitoring site. The requirements for adequate documentation will depend on the nature of the monitoring program. For example, requirements for a research and development pilot study will be less stringent than those for a study producing legally defensible data.

12. Keywords

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

ANNEX

(Mandatory Information)

A1. ESTIMATED DETECTION LIMITS FOR SEVERAL HAZARDOUS AIR POLLUTANTS AND COMMON ATMOSPHERIC GASES

A1.1 See Table A1.1 for estimated MDLs of selected gases.

TABLE A1.1 Estimated Method Detection Limits (MDL) for Selected Gases[A]

Compound	Class[B]	v_{max}[C] (cm^{-1})	MDL[C] (ppb-m)	v_{max}[D] (cm^{-1})	MDL[D] (ppb-m)
acetaldehyde	caa	1761	2063	2729	6674
acetonitrile	caa	1463	8403	1042	46095
acrolein	pp,caa	1730	1297	958	4509
acrylic acid	caa	1726	639	1439	1326
acrylonitrile	pp,caa	954	3398	971	4548
ammonia	pp	967	620	931	718
benzene	pp,caa	673	266	3047	4449
bis-(2-chloroethyl)ether	pp,caa	1138	2157	767	4372
bromomethane	pp,caa	1306	11547	2983	12455
1,3-butadiene	caa	908	1445	1014	5719
2-butanone	pp,caa	1745	1483	1175	3224
carbon dioxide	ag	2361	637	668	608
carbon disulfide	pp,caa	1541	191	1527	266
carbon monoxide	cp	2173	4583	2112	5417
carbon tetrachloride	pp,caa	795	178	773	1027
carbon sulfide	caa	2070	240	2051	330
chlorobenzene	pp,caa	740	1341	1483	3980
chloroethane	pp,caa	1288	6744	677	6871
chloroform	pp,caa	772	359	1219	1927
chloromethane	pp,caa	732	6652	1459	9517
m-dichlorobenzene	pp	1581	1266	784	1305
o-dichlorobenzene	pp	749	1428	1462	5142
dichlorodifluoromethan	pp	1161	294	921	303
1,1-dichloroethane	pp,caa	705	2049	1060	3053
1,2-dichloroethane	pp,caa	731	1983	1237	6803
1,1-dichloroethene	pp	869	1241	793	1814
1,2-dichloroethene	pp,caa	864	5024		
dichloromethane	pp,caa	750	1174	1276	4113
1,1-dimethylhydrazine	caa	2775	1962	909	3774
ethylbenzene	pp,caa	2975	2031	697	2277
ethylene oxide	pp,caa	3066	987	872	3327
formaldehyde	caa	1745	1248	2802	2581
hexane	caa	2964	1023	1467	7710
hydrogen chloride	caa	2945	3164	2822	3620
hydrogen fluoride	caa	4038	578	3877	761

TABLE A1.1 Continued

Compound	Class[B]	v_{max}[C] (cm^{-1})	MDL[C] (ppb-m)	v_{max}[D] (cm^{-1})	MDL[D] (ppb-m)
hydrogen sulfide	caa	1293	535003		
isooctane	caa	2961	554		
methane	ag	3017	1597	1305	2998
methanol	caa	1033	1249	2982	5933
methylmethacrylate	caa	1169	1199	1748	1341
nitric oxide	ag	1894	4388	1843	6816
nitrobenzene	pp,caa	1553	852	1355	1049
nitrogen dioxide	cp,ag	1629	540	1599	742
nitrous oxide	ag	2213	932	1300	3946
ozone	cp	1054	2533	1040	3971
phosgene	caa	849	318	1832	667
phosphine	caa	2326	7699	992	12468
propionaldehyde	caa	1762	2305	2992	4107
propylene oxide	caa	3001	2838	837	4549
styrene	caa	695	1720	909	2908
sulfur dioxide	cp	1377	372		
sulfur hexafluoride	tracer	947	42	615	420
tetrachloroethene	pp,caa	915	708	781	2654
toluene	pp,caa	728	1632	3018	3583
1,1,1-trichloroethane	pp,caa	725	533	1088	1183
1,1,2-trichloroethane	pp,caa	742	1615	941	7933
trichloroethene	pp,caa	849	1173	944	1578
trichlorofluoromethane	pp	846	178	1084	634
vinyl acetate	caa	1225	688	1790	1327
vinyl chloride	pp,caa	942	2824	1620	3643
vinylidene chloride	caa	868	1669	1086	2501
m-xylene	pp,caa	768	1601	690	3825
o-xylene	pp,caa	741	1070	2949	5797
p-xylene	pp,caa	795	1765	2936	3340

[A] The MDLs were estimated by using Eq 4, with values of the absorptivity calculated from 1-cm^{-1} reference spectra with triangular apodization from a commercially-available spectral library **(13)** and a minimum detectable absorbance of 1×10^{-3}.

[B] Pollutant classification: priority pollutant (pp); criteria pollutant (cp); hazardous air pollutant from the 1990 Clean Air Act Amendment (caa); atmospheric gas (ag).

[C] Peak position and MDL for the most intense absorption band.

[D] Peak position and MDL for the second most intense absorption band in a different spectral region.

REFERENCES

(**1**) Childers, J. W., Russwurm, G. M., Thompson, E. L., Jr., and Phillips, B., "Resolution Revisited—Practical Considerations in Open-Path FT-IR Monitoring", *Proceedings of Optical Remote Sensing for Environmental and Process Monitoring*, VIP-55, Air & Waste Management Association, Pittsburgh, PA, 1996, pp. 167–178.

(**2**) Griffiths, P. R., "Open-Path Atmospheric Monitoring with a Low Resolution FT-IR Spectrometer", *Proceedings of Optical Sensing for Environmental and Process Monitoring*, VIP-37, Air & Waste Management Association, Pittsburgh, PA, 1996, pp. 274–284.

(**3**) Russwurm, G. M., Childers, J. W., and E. L. Thompson, Jr., "Quality Assurance Aspects of FT-IR Data Using a Short Cell and High Concentrations of Gases", *Proceedings of Optical Sensing for Environmental and Process Monitoring*, VIP-55, Air & Waste Management Association, Pittsburgh, PA, 1996, pp. 147–156.

(**4**) Mark, H., and Workman, J., *Statistics in Spectroscopy*, Academic Press, New York, 1991.

(**5**) U.S. Environmental Protection Agency, *Quality Assurance Handbook for Air Pollution Measurement Systems*, Vol. IV - Meteorological Measurements, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1989.

(**6**) *Handbook of Chemistry and Physics*, CRC Press, Cleveland, OH.

(**7**) *Federal Register* 60(194), 52315, 1995.

(**8**) Phillips, B., Moyers, R., and Lay, L. T., "Improved FTIR Open Path Remote Sensing Data Reduction Technique," *Proceedings of Optical Sensing for Environmental and Process Monitoring*, VIP-37, Air & Waste Management Association, Pittsburgh, PA, 1995, pp. 374–388.

(**9**) University of South Florida, *USF HITRAN-PC*, University of South Florida, Tampa, FL, 1993.

(**10**) Haaland, D. M., "Multivariate Calibration Methods Applied to Quantitative FT-IR Analysis," *Practical Fourier Transfrom Infrared Spectroscopy—Industrial and Laboratory Chemical Analysis*, Ferraro J.R., and Krisynan, K., eds., Academic Press, San Diego, CA, 1990, pp. 396–468.

(**11**) U.S. Environmental Protection Agency, *EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations*, Doc. No. EPA/QA/R-5, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1994.

(**12**) Childers, L. O., "The USEPA QA Auditor is Scheduled for a Visit. What Can I Expect?". *Proceedings of Optical Remote Sensing for Environmental and Process Monitoring*, VIP-55, Air& Waste Management Association, Pittsburgh, PA, 1996, pp. 127–138.

(**13**) *Infrared Spectra for Quantitative Analysis of Gases*, Infrared Analysis, Inc., Anaheim, CA.

(**14**) Quantitative Infrared Data Base, SRD-79, National Institute of Standards and Technology Gaithersburg, MD, Oct., Nov. 1998.