Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

Second Edition

Compendium Method TO-16

Long-Path Open-Path Fourier Transform Infrared Monitoring Of Atmospheric Gases

Center for Environmental Research Information
Office of Research and Development
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Method TO-16
Acknowledgements

DISCLAIMER

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1. Scope

1.1   Fourier transform infrared (FT-IR) spectroscopy used for open-path monitoring of atmospheric gases is undergoing a vigorous development and growth period. Until now the developmental effort and the most of the data acquisition have been performed by highly trained individuals experienced in the fields of instrument development and spectroscopy. In the future, operators trained at the technician level will be required to perform the operation routinely. This method is intended to address that need. Specifically, the method is intended to allow trained technicians to acquire data in a standardized way and to process that data to obtain atmospheric gas concentrations. The primary intent is that the results will be obtained in a consistent fashion.

1.2 This method is intended for the use of an FT-IR system that acquires data using a long, open air path and does not require the acquisition of a sample for subsequent analysis. The system produces data that is a time sequence of the path-averaged atmospheric concentrations of various gases. Because the FT-IR can potentially measure the concentration of a large number of atmospheric gases, this method does not address the requirements for measuring a particular gas or a set of gases. Rather, it is intended to be a generalized method.

1.3 The method is intended to be instrument independent in that it discusses the processing of spectra so that gas concentrations can be obtained. The primary geometric configurations of FT-IR instruments that are commercially available are the monostatic configuration and the bistatic configuration. These configurations are shown schematically in Figures 1 and 2. This method can be used to process data from either of these types. It is assumed that the FT-IR is under computer control and that the controlling software will allow the manipulation of the spectra. This method is specifically designed to process spectra that will be analyzed by the commonly called classical least-squares technique. If the classical least-squares technique is to be used, the spectra must be processed in a specific way, and this document describes the steps of that processing. Although there are other ways to analyze the spectra, such as partial least squares, iterative least squares, spectral subtraction, principal component analysis, and peak height and peak area calculations, the use of these techniques requires that the spectra be processed in a different way than is described here. While some of the procedures given here are applicable to the other analysis techniques, this method addresses only the classical least-squares technique.

1.4 The method is not intended as a tutorial for the use of the computer software or the instruments themselves. Inclusion of this type of explanation would make this document excessively long. When certain features from the software packages are called for, it is assumed that the user has read or can read the appropriate description in the specific manual. As far as the instruments are concerned, it is assumed that the operator has participated in instrument training provided by the specific instrument manufacturer and that this training has been sufficient to enable the operator to produce spectra and to save them on a disk.

1.5 Since this method in this document is considered to be a set of operational procedures, the document does not contain an in-depth explanation about the origin or the rationale for the inclusion of particular steps. For a more complete and rigorous discussion of the FT-IR technique, the user of this method is referred to EPA's *FT-IR Open-Path Monitoring Guidance Document* (1).

1.6 The intent of this document is to provide the operator with stepwise procedures producing concentration data from spectra taken with an FT-IR. To accomplish this, items such as background spectra, water vapor reference

spectra, and stray light are discussed. In keeping with the concept of a procedure, these quantities must be specified directly. However, the entire area of FT-IR remote sensing of the atmosphere is undergoing rapid change, and parts of these procedures will without doubt need revision in the future. Throughout this document the user must keep in mind that for each procedure in the TO-16 method there may be other equally valid procedures that are currently being used that are not described here.

1.7 Finally, a statement about computer automation of these procedures is in order here. The method does not address the problem of automation directly and implies that an operator is available to perform the individual steps. Some operational software packages already exist that incorporate many of these routines in an automatic way. It is felt that each procedure potentially can be automated, but the steps listed here are those that need to be incorporated in any automated procedure.

2. Summary of Method

2.1 For the purpose of this document the operation of an FT-IR remote sensor is divided into two parts. The first is initial data acquisition after the system has been set up by the manufacturer and the second is what is considered to be routine data acquisition. The first of these data acquisition periods is intended to produce data that will form the basis of a quality assurance data set. The second is devoted to the production of time sequences of atmospheric gas concentration data.

2.2 There are several items that need to be determined before the FT-IR system can be put into routine service. These items have been selected to determine how the system is functioning initially and include the shortest path length that will saturate the detector, the ambient black body radiation level for the bistatic configuration, the stray light inside the instrument for the monostatic configuration, and the return intensity as a function of distance. Beyond these steps there is a survey set of data that should be acquired. Data from this survey set will form the basis of the routinely monitored quality control checks for the instrument.

2.3 In addition to the FT-IR data it is required that the ambient temperature and the relative humidity be monitored on a continuous basis so that the water vapor concentration as a function of time can be determined. It is to be clearly understood that relative humidity measurements alone are not relevant to this operation but the amount of water is. These data should be acquired at the site where the FT-IR data is taken. Use of data taken at airports miles away is not appropriate.

2.4 The initial step in the procedure for determining the concentration data for various gases is the production of a set of interferograms, and it should be the interferograms that are saved as the primary data. The various procedures given in Section 8 of this document use the single beam spectrum that is created from the interferogram. A single beam spectrum taken with a monostatic system over a 414-m path length is illustrated in Figure 3. Various atmospheric constituents as well as a stray light component are pointed out. However, it is the interferograms that are considered the most important data. If they are not saved they cannot accurately be reproduced by simply performing the inverse Fourier transform. Once a set of target gases has been selected, the wave number regions to be used in the analysis are chosen. For the monostatic instrument geometry, the stray light component must next be subtracted from each single beam spectrum. For the bistatic case, the black body radiation spectrum must be subtracted from each single beam spectrum. One spectrum from this set is then chosen to be the background, or I_0, spectrum, and this can be turned into a synthetic background spectrum. A second spectrum is then used to create a water vapor reference spectrum, and all the remaining spectra are then

converted to absorbance spectra. All the spectra to be analyzed are then checked for wave number shifts. Finally, the absorbance spectra are analyzed by the classical least-squares technique.

2.5 It is suggested that, if possible, twice each day a short cell filled with a known quantity of gas should be inserted in the infrared beam, and four spectra should then be recorded. The instrument must be operating in exactly the same manner as it is when it is routinely acquiring data but this time with the cell. These spectra are analyzed in the same way as all other spectra, but for the particular gas in the cell. This data is then added to the appropriate control charts. No exact procedure for using this cell and no specifications for the cell are provided at this time within this document. Not all the instruments that are commercially available can accommodate a cell, and many gases cannot be easily used in such a cell.

2.6 A subset of each day's spectra is then selected and the following two items are determined: the root mean square (RMS) noise in three wave number regions and the return beam intensity at two wave numbers. The range of water vapor concentrations over the time period during which the subset of data was taken is calculated. These data are also then added to the appropriate control charts.

2.7 The remainder of the data can then be checked as described in Section 8 and then against the data quality objectives provided by the monitoring program.

3. Significance

3.1 VOCs enter the atmosphere from a variety of sources, including petroleum refineries, synthetic organic chemical plants, natural gas processing plants, and automobile exhaust. Many of these VOCs are acutely toxic; therefore, their determination in ambient air is necessary to assess human health impacts.

3.2 The environmental impacts from the release of airborne VOCs is a topic of great interest among air pollution scientists. It is important that measurement methods be developed to accurately assess the impact of airborne chemical emissions on the environment. Until now, traditional air sampling/analytical techniques (i.e., solid adsorbents, treated canisters, portable gas chromatographs, etc.) have been used to characterize emission impacts of airborne toxic chemicals in the environment.

3.3 The method of trace gas monitoring using FT-IR-based, long-path, open-path systems has a number of advantages that are significant over traditional methods. Some of these advantages are related to the path monitoring aspect of this method which, by its very nature, distinguishes the method from all point monitoring methods. The main advantages of these systems are the following:

- Integrity of the sample is assured since no sampling actually occurs.

- Multi-gas analysis is possible with a single field spectrum.

- Path-integrated pollutant concentrations are obtained.

- Spatial survey monitoring of industrial facilities is possible if scanning optics are used.

- Coadding of spectra to improve detection capabilities is easily performed.

• Rapid temporal scanning of line-of-sight or multiple lines-of-sight is possible.

• Monitoring of otherwise inaccessible areas is possible.

3.4 Applications include the monitoring of atmospheric gases along the perimeters of industrial facilities or, from an elevated, centrally located platform, monitoring over the industrial facility to infrared sources or retroreflectors placed along the facility edge. Other applications include monitoring (1) at hazardous waste sites during remediation or removal operations to provide warnings of high concentrations and to verify that back-to-work conditions have been achieved; (2) in response to accidental chemical spills or releases; (3) in workplace environments to develop concentration profiles at the worker level; and (4) in the ambient air for some compounds. It is theoretically applicable to the measurement of all gaseous compounds that exhibit absorption spectra in the mid-infrared region of the electromagnetic spectrum.

3.5 Significant advances have been made in recent years to develop the FT-IR systems into practical remote sensing tools, particularly in the understanding of the importance of water vapor interference associated with FT-IR methodology. As indicated in this method, the generation of a background spectrum for a given measurement and the generation of water vapor spectra to account to water vapor interference in mid-infrared measurements are features of the FT-IR measurement technique that deserve more attention. The significance of Compendium Method TO-16 is that it is the first such method to address all the features that are required to make a field measurement using FT-IR-based systems. As such, it provides a guide to field measurement as well as a basis for improvement and further consideration.

3.6 The ultimate significance of remote sensing with FT-IR systems is a matter of cost effectiveness and of technological advances. Technological advances are required in at least two important areas: (1) the improvement in the characteristics of the instrumentation itself and (2) the development of "intelligent" software. The software is required to improve the means for short-term adjustment of background and water vapor spectra to account for the continual variation of ambient conditions that can adversely affect the accuracy and precision of FT-IR based systems.

4. Applicable Documents

4.1 ASTM Standards

• Method D1356 *Definition of Terms Relating to Atmospheric Sampling and Analysis*.

4.2 EPA Documents

• *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air*, U. S. Environmental Protection Agency, EPA-600/4-83-027, June 1983.
• *Quality Assurance Handbook for Air Pollution Measurement Systems*, U. S. Environmental Protection Agency, EPA-600/R-94-038b, May 1994.
• *Open-Path Monitoring Guidance Document*, U. S. Environmental Protection Agency, EPA 600/4-96-040, April 1996.

5. Definitions

*[**Note**: This section contains a portion of the glossary of terms from the guidance document (1) for remote sensing that is applicable to Compendium Method TO-16. When possible, definitions of terms have been drawn from authoritative texts or manuscripts in the fields of remote sensing, air pollution monitoring, spectroscopy, optics, and analytical chemistry. In some cases, general definitions have been augmented or streamlined to be more specific to long-path, open-path monitoring applications and to Compendium Method TO-16. These definitions were intended to remain scientifically rigorous and still be generally applicable to the variety of FT-IR open-path remote-sensing issues that must be addressed by the operator.]*

5.1 Absorbance—the negative logarithm of the transmission. $A = -\ln(I/I_0)$, where I is the transmitted intensity of the light and I_0 is the incident intensity. Generally, the logarithm to the base 10 is used, although the quantity I really diminishes exponentially with A.

5.2 Apodization—a mathematical transformation carried out on data received from an interferometer to alter the instrument's response function. There are various types of transformation; the most common are boxcar, triangular, Happ-Genzel, and Beer-Norton functions.

5.3 Background Spectrum—1. With all other conditions being equal, that spectrum taken in the absence of the particular absorbing species of interest. 2. Strictly, that radiant intensity incident on the front plane of the absorbing medium. 3. A spectrum obtained from the ambient black body radiation entering the system. This background must be considered in FT-IR systems, in which the IR beam is not modulated before it is transmitted along the path. For FT-IR systems that do not use a separate source of infrared energy, the background is the source of infrared energy.

5.4 Beer's Law—Beer's law states that the intensity of a monochromatic plane wave incident on an absorbing medium of constant thickness diminishes exponentially with the number of absorbers in the beam. Strictly speaking, Beer's law holds only if the following conditions are met: perfectly monochromatic radiation, no scattering, a beam that is strictly collimated, negligible pressure-broadening effects (2,3).

5.5 Bistatic System—a system in which the receiver is some distance from the transmitter. This term is actually taken from the field of radar technology. For remote sensing, this implies that the light source and the detector are separated and are at the ends of the monitoring path.

5.6 Fourier Transform—a mathematical transform that allows an aperiodic function to be expressed as an integral sum over a continuous range of frequencies (4). The Fourier transform of the interferogram produced by the Michelson interferometer in an FT-IR is the intensity as a function of frequency.

5.7 FT-IR—an abbreviation for "Fourier transform infrared." A spectroscopic instrument using the infrared portion of the electromagnetic spectrum. The working component of this system is a Michelson interferometer. To obtain the absorption spectrum as a function of frequency, a Fourier transform of the output of the interferometer must be performed. A brief overview of the FT-IR is provided in *FT-IR Theory* (5). An in-depth description of the FT-IR can be found in *Fourier Transform Infrared Spectrometry* (6).

5.8 Intensity—the radiant power per unit solid angle. When the term "spectral intensity" is used, the units are watts per steradian per nanometer. In most spectroscopic literature, the term "intensity" is used to describe the power in a collimated beam of light in terms of power per unit area per unit wavelength.

5.9 Interference—the physical effects of superimposing two or more light waves. The principle of superposition states that the total amplitude of the electromagnetic disturbance at a point is the vector sum of the individual electromagnetic components incident there. For a two-component system of collinear beams of the same amplitude, the mathematical description of the result of addition is given by $I(p) = 2I_0(1 + \cos[A])$, where I_0 is the intensity of either beam, and A is the phase difference of the two components. The cosine term is called the "interference term" (7,8). See also "Spectral Interference."

5.10 Interferogram—the effects of interference that are detected and recorded by an interferometer; the output of an FT-IR and the primary data that is collected and stored (6,8).

5.11 Interferometer—any of several kinds of instruments used to produce interference effects. The Michelson interferometer used in FT-IR instruments is the most famous of a class of interferometers that produce interference by the division of an amplitude (9).

5.12 Light—strictly, light is defined as that portion of the electromagnetic spectrum that causes the sensation of vision. It extends from about 25,000 cm^{-1} to about 14,300 cm^{-1} (4).

5.13 Minimum Detection Limit—the minimum concentration of a compound that can be detected by an instrument with a given statistical probability. Usually the detection limit is given as 3 times the standard deviation of the noise in the system. In this case, the minimum concentration can be detected with a probability of 99.7% (10,11).

5.14 Monitoring path—the actual path in space over which the pollutant concentration is measured and averaged.

5.15 Monostatic System—a system with the source and the receiver at the same end of the path. For FT-IR systems, the beam is generally returned by a retroreflector.

5.16 Reference Spectra—spectra of the absorbance versus wave number for a pure sample of a set of gases. The spectra are obtained under controlled conditions of pressure and temperature and with known concentrations. For most instruments, the pure sample is pressure-broadened with nitrogen so that the spectra are representative of atmospherically broadened lines. These spectra are used for obtaining the unknown concentrations of gases in ambient air samples.

5.17 Relative Absorption Strength—a term used exclusively in Compendium Method TO-16 to describe the relation of absorption due to interfering species to the absorption of the target gas.

5.18 Resolution—the minimum separation that two spectral features can have and still, in some manner, be distinguished from one another. A commonly used requirement for two spectral features to be considered just resolved is the Raleigh criterion. This states that two features are just resolved when the maximum intensity of one falls at the first minimum of the other (5,6). This definition of resolution and the Raleigh criterion are also valid for the FT-IR, although there is another definition in common use for this technique. This definition states

that the minimum separation in wave numbers of two spectral features that can be resolved is the reciprocal of the maximum optical path difference (in centimeters) of the two interferometer mirrors employed.

5.19 Retroreflector—the CIE (Commission Internationale de l'Eclairage) defines retroreflection as "radiation returned in directions close to the direction from which it came, this property being maintained over wide variations of the direction of the incident radiation." Retroreflector devices come in a variety of forms and have many uses. The one commonly described by workers in remote sensing uses total internal reflection from three mutually perpendicular surfaces. This kind of retroreflector is usually called a corner cube or prismatic retroreflector (12).

5.20 RMS Noise—this quantity is actually the statistical quantity rms deviation. In Compendium Method TO-16 the rms noise (deviation) is calculated by using a least squares fit to the baseline. Because of this calculation, the rms noise in Compendium Method TO-16 uses the quantity N-2 in the denominator rather than N-1 as normally described.

5.21 Single Beam Spectrum—that spectrum which results from performing the Fourier transform on the interferogram. It is not a transmission spectrum. The term "single beam" is a holdover from older instruments that were double beam instruments.

5.22 Source—the device that supplies the electromagnetic energy for the various instruments used to measure atmospheric gases. These generally are a Nernst glower or globar for the infrared region or a xenon arc lamp for the ultraviolet region.

5.23 Spectral Intensity—see Section 5.8.

5.24 Spectral Interference—when the absorbance features from two or more gases cover the same wave number regions, the gases are said to exhibit spectral interference. Water vapor produces the strongest spectral interference for infrared spectroscopic instruments that take atmospheric data.

5.25 Synthetic Background—a spectrum that is made from a field spectrum by choosing points along the baseline and connecting them with a high-order polynomial or short, straight lines. The synthetic background is then used to find the absorbance spectrum.

5.26 Wave Number—the number of waves per centimeter. This term has units of reciprocal centimeters (cm^{-1}).

6. Apparatus and System Requirements

6.1 Summary

   6.1.1 Compendium Method TO-16 is a procedure that deals with how spectra taken with an FT-IR are to be processed in order to obtain various atmospheric gas concentrations. General requirements for FT-IR instrumentation is being prepared by a committee of L'Organisation Internationale de Metrologie Legale (OIML) and will be available in the very near future.
   6.1.2 The instrument requirements listed here are limited to those that will define a rudimentary but operational system. The requirements are delineated into three categories: those of the FT-IR sensor itself (see

Section 6.2), the computer associated with it (see Section 6.3), and the software that allows for data analysis (see Section 6.4).

6.2 FT-IR Sensor Requirements

6.2.1 The system should be capable of making spectral absorption measurements along an open air optical path.

6.2.2 The system can be either of the monostatic or the bistatic geometry.

6.2.3 The system must be able to produce and save an interferogram and a single beam spectrum.

6.2.4 The system must be able to operate with a resolution of at least 1 cm^{-1} over the mid-infrared region (700–4200 cm^{-1}).

6.2.5 The system must be capable of acquiring data by co-adding individual interferogram scans in one-scan increments. As a minimum, the system must be able to acquire data from a one-scan interferogram to an interferogram made up of sufficient co-added scans so that at least 5-min concentration averages can be obtained.

6.2.6 The system must be able to perform the mathematical procedure of Fourier transformation on the interferogram, thereby producing a so-called single beam spectrum. The transform can be performed as part of post-acquisition processing or in quasi-real time. If performed in quasi-real time the process of transformation should not add significantly to the data acquisition time.

6.2.7 Although there is no agreed upon procedure for the use of a gas cell with these systems, the system may have provisions for installing an ancillary gas cell in the optical beam. If that is the case, the installation must allow for the entire beam to pass through the cell. The cell can be of any of several designs: short, either single or double pass; multi-pass capable of producing a relatively long optical path; or a multi-chambered cell with the individual chambers interconnected and in parallel with one another.

6.3 Computer Requirements

6.3.1 The computer must be capable of acquiring data in the form of interferograms with sufficient speed so that the system is able to operate in quasi-real time.

6.3.2 The computer must have provisions for storing of the data acquired in one 24-h period. The storage must accommodate the interferograms.

6.3.3 The computer must have sufficient RAM to operate the controlling software and the data manipulation software.

6.4 Software Requirements

6.4.1 The software must have provisions for manipulating the spectra so that all the individual procedures listed here can be accomplished.

6.4.2 The software must be able to perform the analysis for concentration using classical least squares.

7. Materials and Supplies

7.1 Only a small number of materials are required in addition to the basic instrument for this method. However, the basic instrument operation may have specific material requirements such as liquid nitrogen or nitrogen, etc. A listing of any specific instrument's requirement for material must be obtained from the manufacturer.

7.2 A set of gases may have to be purchased in order to acquire spectra with a cell. This set of gases is intended to allow the operator to determine the precision and accuracy of the data obtained from the field spectra, but at the present time no procedure using a cell has been developed. The specific gases required are dependent on the particular monitoring program. If necessary, the gases can be purchased as pure gases, which are then diluted with nitrogen for use, or they can be a mixture of gases that are properly mixed at purchase. The dilution step can be quite cumbersome and it is recommended that appropriate mixtures of gas be acquired directly whenever possible. The required concentrations of the gases are dependent on the anticipated concentration of the target gas in the atmosphere and the ratio of the actual path length used to the length of the cell. Many applications will require that these gases be purchased with certifications traceable to the National Institute of Standards and Technology.

7.3 The only other material that may be required is a set of screens of varying mesh that will be used when determining whether the system is responding linearly. This screening can be regular aluminum window screen or made of other opaque metallic materials. The size of the mesh is not really important, but the screen should be large enough to cover the entire beam. The mesh itself should be chosen so as to change the transmitted intensity by an easily measured amount (on the order of 25% or more). The screen must not be made of any plastic materials as they transmit infrared energy. This in itself is not a problem but the plastic materials introduce absorbance at specific wave numbers and may not provide the desired result.

8. Standard Procedures for Processing of Infrared Spectra

8.1 Summary

The specific procedures that are required to produce atmospheric gas concentration data are included in this section. They start with the general operations procedure that describes how the other individual procedures should follow one another.

8.2 Suggested Order of Generation of FT-IR Concentration Data

8.2.1 This section provides the FT-IR operator with a systematic approach to the generation of FT-IR concentration data. These procedures are recommended for operators with little experience with FT-IR operation. As the operator gains more experience with the production of FT-IR concentration data, he may want to reorder the sequence of events to better fit his experimental schedule.

8.2.2 Assumptions

8.2.2.1 Compendium Method TO-16, in general, does not describe the general planning that is necessary to conduct a field program. It is felt that each data acquisition program is different and all programs cannot be covered in depth with a single procedure. For example, the time for acquiring a single spectrum can vary from a single scan of a few seconds up to a half hour. The actual time required for any one program is dependent on that program and therefore is not discussed further in this procedure. Much of the planning for the acquisition of data is connected to the generation of a detailed quality assurance/quality control (QA/QC) program plan, and this method is not considered to be such a plan. Section 9 presents individual items that should be addressed as a minimal quality assurance effort. The procedures in Section 8 cover only the production of concentration data.

8.2.2.2 It is also assumed that water vapor concentration data for the data acquisition period is available. This method does not discuss how to acquire that data, however. The water vapor concentration data is used for post-analysis review and for some of the QA/QC checks.

8.2.2.3 From this point on, it is assumed that the individual spectra have already been acquired. It is assumed that the interferograms have been converted to single beam spectra. It is further assumed that no other data manipulation has occurred.

8.2.3 The suggested order for the production of concentration data utilizing FT-IR is given below.

- Selection of wave number regions for analysis in the presence of interfering species (see Section 8.3).

- Generation of a background spectrum (see Section 8.4).

- Production of a water vapor reference spectrum (see Section 8.5).

- Subtraction of stray light or black body radiation (see Section 8.6).

- Generation of an absorbance spectrum (see Section 8.7).

- Correction for spectral shifts (see Section 8.8).

- Analysis of field spectra for concentration (see Section 8.9).

- Post-analysis review of the data (see Section 8.10).

8.3 Selection of Wave Number Regions for Analysis in the Presence of Interfering Species

8.3.1 Purpose. This section instructs the operator on how to select the wave number regions that are to be used in the analysis of field spectra. This section includes the process of working with interfering species because the absorbance spectrum of any one particular gas frequently overlaps with the absorbance of another species. This section also provides the operator with a measure of the strength of the interference.

8.3.2 Assumptions. One of the most important requirements when utilizing classical least squares as an analysis technique is the identification of all possible compounds whose absorption spectrum can interfere with the absorption feature being analyzed. It is therefore imperative that the operator has as complete knowledge as he can of the compounds that are expected to be present during the measurement period. The assumption made here is not only that this knowledge exists but that reference spectra for all the potentially present compounds also exist. The operator should be aware that absorption spectra from unexpected chemical compounds may appear during the data acquisition phase and that these must be accounted for in the analysis for the most accurate data.

8.3.3 Additional Sections Referenced. Section 9.2 is referenced in this section.

8.3.4 Methodology. While FT-IR spectra can in fact be acquired before it is known exactly what wave number region to use for any particular gas in the analysis, this is never a good idea. If on-line analysis is a requirement then the wave number regions must be selected first.

When starting, the operator must be aware that this is likely to be an iterative procedure and some wave number regions may be rejected in the process. The selected wave number region can be quite narrow, but there are some dangers in selecting a very narrow region. It is best if the operator at first selects the entire absorbing band structure, using the end points as the 1% absorbance values relative to the peak. If narrowing the wave number region becomes necessary, the operator should be aware that the selected wave number region should always encompass the largest possible range in absorbance.

This procedure starts by an examination of the absorption spectrum of the target gas and selection of the absorption feature that has the highest absorption coefficient and is outside the strong absorption regions of water vapor and carbon dioxide. The wave number region to use is the region that is covered by the entire peak under study. It is not necessary to include any wave number region whose relative absorbance is less than 1% of the peak. The absorption coefficient is calculated and the expected absorbance is calculated by using the anticipated concentration at the site. This absorbance is compared to the noise equivalent absorbance obtained from Section 9.2. If the expected absorbance is not 3 times higher than the noise equivalent absorbance, then that wave number region should be rejected. It is likely that if the anticipated absorbance does not meet this criterion then measurement of that particular gas will have to be rejected because the remaining absorption coefficients will be too small.

If that test is passed the procedure continues. The absorption features of all the other gases known to be present at the measurement site are then compared to the target gas for possible interferences. If the total interference is thought to be too strong, the wave number region is rejected and the process is started over with a different absorption feature. If all of the features in the target gas are rejected, the gas concentration cannot be measured by FT-IR.

To calculate the absorption coefficient for any particular feature, the operator must measure the absorbance of the feature being used at the peak of the feature. This is done by using the reference spectrum. Then by using the expression $\alpha = A/cl$ the absorption coefficient α is determined. The A in this expression is the peak absorbance measured from the reference spectrum, and the cl is the concentration–path length product also obtained from the reference spectrum.

Once α is obtained, an estimate of the peak absorbance can be made as follows. Use the expression $A = \alpha cl$, where the c is the anticipated concentration at the site and l is the anticipated path length. The c and the l used here must have the same units (e.g., ppm, meters) as the reference spectra. The calculated A is then the anticipated peak absorbance at the site.

To judge whether a particular gas is a possible interfering species, a comparison of the absorption features must be made. This is initially done by simply comparing the spectra of all the other compounds known to be present at the site with the absorption feature under study. If any overlap between the two spectra exists the gas must be considered an interfering species.

To judge the strength of any interfering species the absorption coefficients of the interfering species must be calculated as above and an estimate of the anticipated absorbance at the measuring site made. In measuring the correct absorbance to use for the interfering species, the operator should use the highest absorbance of the interfering species spectrum within the overlapping wave number region. Note that the actual peak absorbance of the interfering gas may very well fall outside the overlap region. The absorption coefficient and the anticipated absorbance at the site for the interfering species is then determined exactly as described above. Then the fractional overlap of the spectra must be determined and the estimated impact on the actual measurement is made.

To determine the fractional overlap, measure the wave number region of the overlap in the spectra and then divide that by the entire wave number region selected for the target gas. The measurement should be made by using the 1% relative absorbance wave numbers of the interfering species.

To estimate the strength of the overlapping absorbing feature, multiply the fractional overlap of the interfering species by the anticipated absorbance at the site (for the interfering species). Then divide that product by the

anticipated absorbance at the site for the target gas. The total interfering strength is then the sum of all the strengths for the individual interfering species.

The classical least squares technique is a very powerful tool for analysis and can determine the presence of very small quantities of gas in the presence of a fairly large interference. While no hard rule can be given, the operator should be concerned and at least attempt to find another wave number region if the total strength of the interfering species is more than 5 times the anticipated absorption of the target gas at the site.

If the operator rejects the wave number region, then the process is repeated with the next highest absorption coefficient and so on until a suitable wave number region is found. The operator is advised to record a table of these wave number regions in a permanent notebook for the specific gases that he is working with. It is likely that these calculations will have to be done only once for any particular target gas.

8.3.5 Procedure

8.3.5.1 Examine the reference spectrum of the target gas and select the absorbance feature with the highest absorbance that is outside the strong absorbance of water and carbon dioxide.

8.3.5.2 Record the wave number region using the relative 1% absorbance peaks as the end points.

8.3.5.3 Calculate the absorption coefficient α using the peak absorbance.

8.3.5.4 Calculate the anticipated absorbance at the field site using the α from Section 8.3.5.3, the concentration anticipated at the field site, and the path length anticipated at the field site.

8.3.5.5 Compare the result of Section 8.3.5.5 with 3 times the RMS noise calculated from Section 9.2.

8.3.5.6 Compare the absorbance spectra of all the gases known to be present in the atmosphere at the site. Record any overlaps with the selected region.

8.3.5.7 Calculate the following.

8.3.5.7.1 The absorption coefficient α of the interfering species using the peak absorbance in the overlap region.

8.3.5.7.2 The fractional overlap.

8.3.5.7.3 The anticipated strength of the interfering species.

8.3.5.7.4 The sum of the interfering strengths.

8.3.5.8 Accept or reject the wave number region.

8.3.5.9 If necessary repeat Sections 8.3.5.1 through 8.3.5.8 with the next highest absorbance peak.

8.4 Generation of a Background Spectrum

8.4.1 Purpose

8.4.1.1 This section instructs the operator on how to generate a background spectrum that can then be used as I_0 in Beer's law. A background spectrum can be generated by several methods. These methods are (a) the upwind background, (b) the cross-path background, (c) the zero target gas background, and (d) the synthetic background. The first three backgrounds are generally used with no further processing, but the synthetic background has to be made. Each is briefly discussed below.

8.4.1.2 Since the synthetic background is the only one that requires computer processing, it is the one for which the actual steps are given in this procedure.

8.4.2 Assumptions

8.4.2.1 The wave number regions for the analysis have previously been chosen.

8.4.2.2 Field spectra have been acquired, and one of them is to be used for a synthetic background.

8.4.2.3 Software is available that allows a synthetic background to be made.

8.4.3 Additional Sections Referenced. No other sections are referenced.

8.4.4 Methodology. In the derivation of Beer's law, one calculates how much the intensity of the infrared source diminishes as the energy traverses an absorbing medium. To calculate the concentration of the gas, the operator must compare the initial intensity obtained in the absence of the target gas with the measured intensity obtained when the target gas is present. This initial intensity is called the background, and it is the response of the instrument to the infrared source in the absence of any absorbance due to the target gas. A variety of phenomena are responsible for the shape of the background curve. A number of these phenomena are related to the instrument, but the predominant atmospheric process that shapes the background is the absorbance due to water vapor.

If any absorbance due to the target gas remains in the background, the absolute values of the gas concentration cannot be measured. In this case, only values relative to the concentration in the background will be obtained.

The upwind background is one that is predominantly used at smaller sites, where it is fairly simple to move the system from one side to another. Once the wind direction is known, the system is set up so that the path is along the upwind side and a spectrum that is to be used as a background is acquired. This procedure is normally done twice a day (morning and evening), and these spectra are generally used as backgrounds with no further processing.

The argument is made that an upwind background will contain only target gas concentrations from upwind sources. The remaining downwind field spectra will then give correct values from gases at the site alone. While this is a valid argument, it is not a very strong argument for the use of an upwind spectrum, and any variability in the upwind sources may erroneously be interpreted as variability of the target gas concentration at the site itself. Also to be noted when using such a spectrum is that it may not be valid for the entire time period the operator intends. As the water vapor concentration changes, the curvature of the baseline in the spectra changes also. This will give rise to high error bars (as calculated from classical least squares) and to variability in the target gas concentration that follows that of water. When that occurs, this background (or any background) may no longer be valid.

The cross-path background is taken with an optical path placed along one side of the site and with the wind velocity parallel to it. This background is generally used when the geometry of the site allows it, and it supposedly has no target gas concentration. This type of background may also pose some unwanted problems. If the wind is very light, then the gases from the site can indeed diffuse into the optical path. Target gas concentrations from elsewhere may be present, and interpretation may present the same problems described above.

Some researchers have obtained a background spectrum by simply waiting long enough for the gas concentration to go to zero. This method will not work for gases that are always present in the atmosphere, such as methane or carbon monoxide. This procedure may be used if there is sufficient time in the program for the waiting period and if real-time analysis is not an immediate requirement, but it is not clear whether the water vapor concentration will be in a satisfactory range. Also, the operator should not expect any one background to remain valid for more than a few days, and then a new background must be obtained.

If the measurement program merely requires a "yes" or "no" response to the question of whether a compound is present, then any spectrum that is taken may possibly be used for a background. If possible, the operator should use a spectrum that has a minimum of the target gas, but that is not necessary if the analysis software allows negative numbers. (Note that it is the difference of the concentration in the two spectra that will be measured.)

If, however, the absolute values of the concentration of the target gas in the optical path are required by the measurement program and no applicable spectrum can be found that is void of the target gas absorption, a synthetic background must be used. A synthetic background is one that is made from a single beam field spectrum, and it may have some of the target gas in it. Once a field spectrum has been selected, a new baseline is made to replace all the absorbance features in the wave number region used for analysis with a new curve that resembles the instrument baseline as closely as possible. This new baseline is made by connecting the data points along the original baseline with straight line segments, or by some other appropriate fitting procedure, thereby removing any absorbance features. The difficulty with this method is knowing where the baseline actually is. No points within any absorbance feature of the original spectrum can be used. A portion of a field spectrum and the synthetic background made from it by connecting the data points with very short straight line segments is illustrated in Figure 4. The original field spectrum has absorption lines due to water vapor in it.

Selecting the points for the baseline for a synthetic background may be quite difficult when large wave number regions are used or when the curvature of the baseline is high. This is a problem with the wave number region used for the analysis of ozone, for example.

8.4.5 Procedure

8.4.5.1 From the set of available spectra, select one spectrum by using the following criteria.

8.4.5.1.1 The target compound concentration should be near a minimum.

8.4.5.1.2 The interfering species concentration should be at a minimum.

8.4.5.1.3 The vapor pressure concentration should be in the mid range of water vapor concentrations during the period for which the background is to be used.

8.4.5.1.4 The return intensity at 987 cm^{-1}, 2520 cm^{-1}, and 4400 cm^{-1} should be normal for this instrument and for the particular path length used.

8.4.5.2 Once the candidate spectrum has been selected, use the available software to create a synthetic background.

8.5 Production of a Water Vapor Reference Spectrum

8.5.1 Purpose. This section instructs the FT-IR operator on how to create a water vapor reference spectrum from a single beam field spectrum. Absorption due to water vapor represents an interference to the spectral region of the target gas, and these interferences must be accounted for in whatever analysis routines that are finally used. Water vapor presents the predominant absorption features in the spectra acquired by the FT-IR, and the operator can expect it to interfere with the target gas spectrum. It is essentially impossible to create a water vapor reference spectrum in the laboratory by using a cell because the concentrations required are not normally attainable, and measuring the amount of water vapor in the cell is very difficult. Therefore, the water vapor reference spectrum has to be made from the acquired field spectra. Fairly large changes in the atmospheric concentrations of water vapor can occur rapidly, and that generally implies that a new water vapor reference spectrum has to be created.

8.5.2 Assumptions

8.5.2.1 The wave number regions for the analysis of the remaining spectra have previously been chosen.

8.5.2.2 Field spectra have been acquired, and one of them is to be used for a water vapor reference spectrum.

8.5.3 Additional Sections Referenced. Activities and evaluations performed in Section 8.4 are referred to in this section.

8.5.4 Methodology. The first step in the process of creating a water vapor reference is the selection of a single beam spectrum from the set available. The selection is based on a number of criteria. During the process, any absorbance due to the target gas must be subtracted from the water vapor reference. This can be done in a

number of ways, but until the operator gains some familiarity with the FT-IR analysis process, it is best to do this by starting with a spectrum that contains a reasonable amount of the target gas and any other interfering species. In this way it may be possible for the operator to see the absorbance feature and do the subtraction interactively. Otherwise, the concentration of the target gas needs to be measured by using an analysis routine and then subtracted by using the library reference spectrum.

There is also some argument that can be made to specifically acquire a spectrum with a large number of scans and to use that as a water vapor reference spectrum. The large number of scans ostensibly gives a smaller noise value. This argument is not generally true with the FT-IR systems because the calculated RMS noise is not usually generated by the system electrical noise. The majority of the calculated RMS noise seems rather to be the result of slight changes in the water vapor concentration and other atmospheric constituents from one spectrum to the other.

From the set of available spectra, one spectrum must be selected by using the following criteria.

- The target compound concentration should not be near a minimum. As the operator gains more experience at creating a water vapor reference he may want to minimize the target gas absorption if possible.

- The interfering species concentrations should not be near minima.

- The vapor pressure concentration should be in the mid range of water vapor concentrations during the period for which this particular water vapor reference spectrum is to be used. It should be remembered that many of the water vapor lines may be saturated as far as the instrument response is concerned. That implies that the time period that can be covered with any one water vapor spectrum must be carefully chosen. However, at the present time no explicit guidance concerning the length of time that a single water vapor reference is valid can be given. Perhaps the best advice is to compare the curvature of the baselines of the single beam spectra. If that is changing rapidly, a new water vapor reference spectrum may have to made.

- The return intensity at 987 cm^{-1}, 2520 cm^{-1}, and 4400 cm^{-1} should be normal for this instrument and for the particular path length used. Any spectrum that has been acquired in foggy or rainy conditions should not be used.

The last criterion is included as a check to determine that the instrument is operating correctly.

Once the candidate spectrum has been chosen, it must be turned into an absorption spectrum by using the background spectrum created in Section 8.4.

The new water vapor absorbance spectrum must now be analyzed for the presence of absorbance due to the target gas. To accomplish this, the normal analysis procedure can be used if an older version of the water vapor reference spectrum already exists. It is likely that using the older water vapor reference will result in somewhat higher error bars from the analysis. At the present time this can be ignored. The results of this analysis should be zero, but it can give a positive result if there is an absorbance due to the target gas in the newly created water vapor reference. If a positive value exists then that amount of the target gas must be subtracted from the water vapor reference spectrum. The exact procedure to use for the subtraction process will depend on the software that the operator has.

If no other water vapor reference exists, the following procedure must be used. A set of 15 pairs of spectra must be acquired with the FT-IR. They should be taken so that no time elapses between them. They should be acquired with the same number of scans and the same resolution as the newly created water vapor reference spectrum. The individual 15 pairs are used to create 15 absorbance spectra. These spectra should not contain any of the target compound absorbance because they have been taken back-to-back, and it is hoped that each will contain the same amount of the target gas absorption. These spectra must then be analyzed for the target compound by using the newly created water vapor reference.

The average value of the results of this analysis should be zero. If it is not but some positive or negative bias exists, some amount of the target compound absorbance is still in the water vapor reference spectrum.

There are two possibilities to consider if a bias exists. The first is that the baseline of the newly created water vapor reference is not quite correct, and the second is that some of the target compound must be subtracted from the newly created reference spectrum. (This can give rise to either a negative or a positive bias.) At the present time no procedure exists to correct for curvature of the baseline. If the operator decides that baseline curvature is the primary problem, then there is little that he can do to correct the problem.

If a bias exists that is not from a baseline curvature then the operator must subtract some of the target gas from the newly created water vapor reference. If an interactive software mode for subtraction exists, the subtraction can be done in an interactive mode using the target gas reference spectrum as the subtrahend. If an interactive software mode is not available, the target gas reference can be used as follows. The target gas reference spectrum can be multiplied by an appropriate factor and the result subtracted from the newly created water vapor reference. The path length at which the water vapor reference spectrum was acquired is known and the target gas concentration is known in parts per million from the analysis above. The reference spectrum absorbance is given in terms of parts per million meters. So the operator must divide the absorbance of the spectrum by the path length in meters and by the ratio of the concentrations (reference/calculated). The resulting spectrum can then be subtracted from the created water vapor reference.

Repeat the analysis procedure and this process until the target gas concentration is zero.

8.5.5 Procedure

8.5.5.1 Select the single beam spectrum that is to be used for a water vapor reference using the criteria listed above.

8.5.5.2 Create an absorbance spectrum using the appropriate background spectrum.

8.5.5.3 Analyze the newly created water vapor reference for the target gas.

8.5.5.4 If necessary, subtract the proper amount of the target gas absorption from the water vapor reference.

8.5.5.5 Reanalyze the water vapor spectrum.

8.5.5.6 Repeat Sections 8.5.5.3 through 8.5.5.5 until the target gas concentration is zero.

8.6 Subtraction of Stray Light or Black Body Radiation

8.6.1 Purpose. This section instructs the operator how to subtract the stray light or black body radiation measured by the instrument from the field spectra. This procedure can be used by operators using either the monostatic or the bistatic instrument configurations. The subtraction for either configuration is performed by using single beam spectra.

8.6.2 Assumptions. Assumptions. For both the stray light component and the black body radiation component measurement the instrument must be operating at its equilibrium conditions. That is, the FT-IR must have been allowed to warm up. As long as the operating conditions are not changing rapidly, the spectra should be acquired by using a large number of scans so as to provide a good signal-to-noise ratio. Since these spectra have to be subtracted from the field spectra, noise will be added to the analysis, and a longer acquisition time minimizes the electrical noise. Acquiring data for up to one half hour is satisfactory. Not much is gained in the signal-to-noise ratio by acquisition times longer than that.

8.6.3 Additional Sections Referenced. No other sections are referenced.

8.6.4 Methodology. The procedure for subtracting stray light is primarily to be used for the removal of a spurious signal from FT-IR instruments using the monostatic configuration with a second beam splitter. While it is possible to have scattered light that gives rise to unwanted signals in instruments using the other geometric configurations, this component is very difficult to measure and is considered to be a difficulty that the manufacturer has to deal with. This type of stray light subtraction will not be discussed further in this method. Instrument manufacturers strive to have the stray light as small as possible compared to the intensity returning from the retroreflector, but to remove it all can be a formidable task, and it should therefore be measured and subtracted. It is fairly simple to show mathematically that, whatever percentage of the return intensity the stray light intensity represents, that percent error will be carried through to the final result in the analysis. The presence of stray light can sometimes be detected visually in the single beam spectrum as is shown in Figure 3. Therefore, it has to be subtracted from the spectra if the errors in the data are to be minimized. The intent of the specific program may indicate it is not necessary to subtract the stray light spectrum from the field spectra; an example is when only the identification of compounds is necessary.

Once the stray light intensity is known and measured it should not change unless some component of the optical system is changed or reoriented. Therefore, the stray light spectral subtraction can easily become part of the routine analysis. Since the stray light component is generated inside the instrument, its intensity is not path-length dependent. This means that the stray light will change its intensity relative to the return intensity as the path length changes. It can easily be measured by simply slewing the instrument away from the retroreflector and acquiring a spectrum.

The need to subtract the black body radiation arises only in bistatic systems that have an unmodulated source at one end of the physical path. It is convenient to think that the black body radiation comes from the fact that the field of view of the receiving telescope is larger than the angle that the infrared source subtends; therefore, the instrument allows the infrared energy from the surroundings into the system. This is only partially true, and if the instrument is at the same temperature as the surroundings, the black body radiation can be thought of as coming entirely from the instrument enclosure. That is because all black body radiators at the same temperature radiate the same amount of energy per unit area. Therefore, the easiest way to measure the black body spectrum is to turn the source off and then acquire a spectrum.

There is an additional problem with the black body radiation curve that occurs when the instrument is pointed at the sky. When this situation occurs it is very likely that there will be an emission spectrum superimposed on the black body curve. The emission spectrum arises from several atmospheric gases and is quite variable. Even the smallest amount of cloud cover will dramatically change the intensity of this spectrum. That fact makes it almost impossible to subtract the emission spectrum totally. It is advisable to avoid pointing the instrument so that it has the sky in the field of view. If that cannot be avoided, the operator should be aware that higher than normal errors can occur in the data in the region below about 1050 cm^{-1}.

Small changes in the ambient temperature (10 °K) are not thought to be significant in the black body radiation, and thus one spectrum should be usable for an extended period. These spectra should be subtracted from the field spectra after the single beam spectra have been obtained. If the interferograms are subtracted and the single beam is then calculated, a different result is obtained. The reason for that is not fully understood at this time.

8.6.5 Procedure

8.6.5.1 Measure the stray light in the instrument by slewing the instrument off the retroreflector.

8.6.5.2 Subtract this spectrum from each single beam field spectrum before proceeding with the analysis.

8.6.5.3 Measure the black body radiation spectrum by turning the source off.

8.6.5.4 Subtract this spectrum from each single beam field spectrum before proceeding with the analysis.

8.7 Generation of an Absorbance Spectrum

8.7.1 Purpose. This section instructs the operator on how to generate an absorbance spectrum from the field spectra and an appropriately chosen background spectrum.

8.7.2 Assumptions. The following assumptions are made.

8.7.2.1 An appropriate background spectrum is available.

8.7.2.2 All the field spectra have been converted to single beam spectra.

8.7.2.3 All the field spectra have been corrected for stray light and the black body radiation if necessary.

8.7.3 Additional Sections Referenced. No other sections are referenced.

8.7.4 Methodology. Beer's law is the underlying physical law that governs the way the least squares analysis is performed. Mathematically, Beer's law is written as $I(\nu) = I_0(\nu)\exp(-\alpha CL)$. In order to calculate C, the concentration of the gas in the atmosphere, one must divide by I_0 and take the logarithm of the result. That gives $\ln(I_0/I) = \alpha CL$. The spectrum described by the term $\ln(I/I)$ is called the absorbance spectrum. The FT-IR analysis is actually done by using the logarithm to the base 10, but this is normally transparent to the operator.

All software packages that are available for least squares analysis allow the generation of an absorbance spectrum. The operator is generally asked to supply the background spectrum, but then the process is mathematically performed by the computer. It is important to understand that some correction may be necessary to the field spectra before they are converted to absorbance spectra.

8.7.5 Procedure. Use the available software to create the absorbance spectra.

8.8 Correction for Spectral Shifts

8.8.1 Purpose. This section instructs the operator on how to align two spectra so as to minimize the errors involved with spectral shifts.

8.8.2 Assumptions. The field spectra have been acquired and are in the single beam format. A water vapor reference that is to be used for analysis is available. A background spectrum has been prepared and is available for use. In order to check for a shift between the field spectrum and the reference spectrum, an absorbance spectrum must be used if the reference spectrum is an absorbance spectrum.

8.8.3 Additional Sections Referenced. No other sections are referenced.

8.8.4 Methodology. There are three ways that a spectral shift will affect the FT-IR data analysis. The first is when a spectral shift between the field absorbance spectrum and the water vapor reference spectrum exists. The second is when a spectral shift between the field absorbance spectrum and the library reference spectrum for the target gas exists. The third is when a nonsynthetic background is used and a spectral shift exists between the background and the field spectra. A spectral shift compared to the instrument may also be noticed when new reference spectra are purchased or produced on an instrument other than the one used for data acquisition. The

first two of these comparisons are done using absorbance spectra, but the third must be done with single beam spectra.

When a synthetic background is used, any spectral shift between the field spectrum (single beam) and the background spectrum (single beam) is irrelevant. That is because the synthetic background generation process does away with all spectral features of interest.

A question arises as to what sort of a shift is really important to the analysis. Some researchers discuss this in terms of absolute quantity of wave numbers. This is not really satisfactory because then apparently small shifts are important for some spectral features while at other times they are not. If a Gaussian shape is used to describe the absorption line shape, then it is possible to show mathematically that when the absorption feature of interest shifts by about 10% of the line width (FWHH), a 5% error occurs in the least-squares analysis. If a Lorentzian line is used to describe the actual line shape, the shift can be about 15% of the line width (FWHH) before a 5% error occurs when least-squares analysis is used. Experimentally, if a 5% error is acceptable, it is only seldom that line shifts will be important. However, if a 1% error is all that is allowed by data quality objectives, then the same calculations show that a 0.5% shift (FWHH) of the line is all that can be tolerated. This really implies that wave number shifts will probably not be important when broad absorption features (such as presented by ozone) are used but will be crucial for narrow absorption features (such as presented by carbon monoxide). The predominant spectral feature in the FT-IR open path field spectra is water vapor, and the pressure-broadened lines of water have a line width (FWHH) of about 0.2 cm^{-1}. Since water is the predominant feature, the errors produced by the classical least-squares technique will be primarily caused by how well water is handled in the analysis. That means that water vapor must always be checked for shifts.

Experience has shown that when a spectral shift occurs, the magnitude of the shift is different in the C–H (2900–3000 cm^{-1}) stretch region than it is in the fingerprint region. This implies that all line shifts are caused by some change in the interferometer and/or the system optics. If that is truly the case, then the shift is linear in wave number, and a linear correction must be applied when the correction is made throughout the field spectrum. Some computer software automatically identifies a wave number shift and then shifts the entire spectrum by the proper amount. If that software is available it should be used.

The best place to determine whether a shift has occurred is in the low-wavelength or high-wave-number end (in the region of the C–H stretch) of the spectrum. It may also be possible to automatically determine during the acquisition phase whether a shift has occurred and then shift each individual spectrum as it is being acquired. To do that, some known spectral feature present in every spectrum must exist. Thus it may be possible to select some water vapor line that is present in all the spectra covering a particular time period and compare all the spectra with that particular line. A shift of that kind guarantees that all the field spectra are aligned one to the other but does not automatically guarantee that the field spectra and the reference spectra will be aligned. At any rate, at the present time no such line has been agreed upon, and it may not be possible to select a single line for all occasions.

If shifting software is not available, two problems are presented to the operator. The first is how to recognize a shift and the second is how to correct for it over the entire wave number region.

Recognizing that a shift has occurred can be facilitated by subtracting one spectrum from another. If a small (less than the line width) shift has occurred, the difference will appear as an "S"-shaped curve. This kind of curve is closely related to the first derivative of the line shape if the shift is small. Determining the absolute magnitude of the shift can be a difficult task, and no simple mathematical relation exists between the features of the S-

shaped curve and the magnitude of the shift. At the present time, the best estimate of the magnitude of the shift is obtained from measuring the difference of the peak positions of the two lines. However, this is best done on spectra that have been interpolated to increase the number of data points. Or, if the operator so chooses, he may zero fill the interferogram by a factor of 2 or 4 in order to increase the number of data points.

Since the correction for a shifted spectrum is most likely linear in wave number, the shift must be done in steps if appropriate software is not available. A shift between the individual library reference spectra and the field absorbance spectra can be overcome because the library spectra can be individually shifted. It may also be possible (depending on the software available) to rename the water vapor reference spectrum so that there are two or three of them, each with its own shift, and then do all the analysis simultaneously. The same procedure can be used to overcome a shift between the field spectra and the background spectrum when a synthetic background is not used. However, if the shift is small (less than the data point spacing) but significant, then all the spectra may have to be interpolated or zero filled to correct for the shift.

 8.8.5 Procedure (applicable when shifting software is not available).

 8.8.5.1 Subtract the two spectra and examine the residual for an S-shaped curve. Do the background and the field spectra first because these have to be done with single beam spectra.

 8.8.5.2 Determine the magnitude of the shift by comparing the peaks of the individual lines.

 8.8.5.3 Shift one spectrum with respect to the other. This will have to be done in the target gas analysis regions and may have to be done several times.

 8.8.5.4 Create absorbance spectra from the field spectra and the background and repeat Sections 8.8.5.1 through 8.8.5.3.

 8.8.5.5 Perform a correction for shift to the water vapor reference spectrum, the reference spectrum, and the background if necessary. The field spectra should not be shifted, as this requires the most time.

8.9 Analysis of the Field Spectra for Concentration

 8.9.1 Purpose. This section instructs the user on the procedures used for the analysis of FT-IR absorbance spectra in order to produce gas concentration values.

 8.9.2 Assumptions. The spectra have been converted to absorbance spectra and all changes and corrections listed in the above sections have been made to them. A set of reference (library) spectra that includes the target gas, the interfering gases, and a water vapor reference is available for use. A software package that is capable of performing least squares analysis on the spectra is available.

 8.9.3 Additional Sections Referenced. No other sections are referenced.

 8.9.4 Methodology. There are a number of ways to analyze the spectra in order to obtain concentration data. These include peak height or peak area analysis, spectral subtraction, partial least squares, iterative least squares, principal component analysis, etc. While these methods are all usable, this procedure uses classical least squares as described mathematically by Haaland and Easterling (13). The use of classical least squares requires that the spectra be prepared in a specific way for the analysis to work efficiently and effectively. Thus the majority of Compendium Method TO-16 is concerned with preparation of the spectra.

It is likely that, when the other techniques cited above are used, the data will have to be prepared in a different manner. Under those conditions the steps of this procedure that deal with spectral preparation are not usable.

Whatever software is available to perform the classical least-squares technique, it must be able to perform the analysis of a single target gas in the presence of interfering species. It is only seldom that the range of wave numbers used for the analyses will be free of absorbances due to interfering species. This is particularly true of water, and the analysis routines must be able to perform a multiple linear regression of the field spectra.

There are a number of software packages that are in use that perform classical least-squares analysis of the spectra. These all have somewhat different user interfaces and operating conditions, but in all cases the mathematical algorithms are transparent to the user. Therefore, the software packages are not described in detail here. Since the classical least-squares analysis is a multiple linear regression, it must have certain items available for it to function. The items that are common to all available analysis packages include the target gas reference spectrum, the background (or I_0) spectrum, the water vapor reference spectrum, and whatever interfering gas reference spectra are necessary. Most software packages are, however, only available with the FT-IR instrument itself. The primary concern for this procedure is that the analysis itself follows the classical least squares described mathematically by Haaland and Easterling (13).

8.9.5 Procedure. The individual steps in this section are dependent on the specific software available to the operator. Since the individual packages are not described here, the specific steps required for any one package are not either.

8.10 Post-Analysis Review of the Data

8.10.1 Purpose. The purpose of this section is to provide the operator with a way to check the data for possible problems. This procedure primarily makes use of plotted data in the form of the concentration of one gas plotted against the other and of time sequence plots. There is one statistical determination that can be used to determine if correlations exist between pairs of data. The primary tool used here is for the operator to look for trends in the data where none should exist. The specific tests of the data are described below.

8.10.2 Assumptions. The only assumption is that all of the spectra have been analyzed by use of the least-squares analysis software.

8.10.3 Additional Sections Referenced. No other sections are referenced.

8.10.4 Methodology. The operator should make several plots of the concentration data. The first should be a set of plots of target gas concentration versus time. These plots should be examined for any expected trends in time. For example, ozone in rural areas generally follows a diurnal pattern with a minimum at about 0600 hours and a maximum at about 1500 hours. The concentration values should not go negative to any great extent; although around zero concentration the values may go slightly negative, the average value over time should be zero. Suppression of negative values should never be done in the analysis because then a zero average can never be achieved. If values go negative with time in a regular fashion, then something is amiss with the data. The most likely case is that there is a small remaining absorbance due to the target gas in the water vapor reference spectrum. If the concentration values are much higher than the anticipated values, there may also be a problem with the water vapor reference spectrum. In this case there may have been too much of the target gas absorbance subtracted from the water vapor reference. If that is so, the water vapor reference should be fixed and then the data reanalyzed.

Plots should be made of the target gas concentration versus the water vapor. If the variability of the target gas and the water vapor are correlated and this is not expected, the water vapor reference spectrum must, in most cases, be corrected.

The next step is to plot the concentration values of those gases whose concentrations are expected to be correlated. This includes any gases that are derived from the same source. If the variability of these gases is not correlated, the data must be carefully examined for the cause. There are no good guidelines to judge what is causing that problem, but a nonlinear response of the instrument for one of the gases is a possibility. If that is suspected, the operator must carefully examine the QA data for possible clues.

Another check of the instrument can be made by analyzing the spectra for N_2O. Nitrous oxide is present naturally in the atmosphere with a concentration very close to 300 ppb. The variability in this concentration should be less than ±10%. If this is not the case then all the data must be suspect. Another gas that is always present in the atmosphere is methane. The variability of methane can be fairly large, particularly in the proximity of landfills. That means it is somewhat more difficult to use as a quality check of the data but it can still be used. The value of the atmospheric concentration of methane should never fall to less than about 1.7 ppm.

If the FT-IR instrument is a bistatic one and there is any possibility that the instrument was admitting energy from the sky when the black body radiation measurement was made, there might be a problem with the observed detection limits. If that occurs, it is possible that the analysis is flawed because of emission spectra in the black body radiation.

Another check for the quality of the data can be obtained by examining the errors calculated by the least-squares analysis routine. If there is an abrupt change in the relative error and no obvious reason such as an abrupt change in the water vapor concentration, it may be that a new interfering species, not accounted for in the analysis, has been measured.

Once these checks have been made on the data, the operator must follow the data quality checks that have been written for the specific program that is being studied.

    8.10.5 Procedure.

      8.10.5.1 Plot the data as a function of time and check for unexpected trends.

      8.10.5.2 Plot the target gas data concentration as a function of water and determine if the variability is correlated.

      8.10.5.3 Determine whether N_2O and CH_4 have been correctly measured.

      8.10.5.4 Determine whether correlation of the data exists where correlation is expected.

      8.10.5.5 Review all the QA/QC data taken in compliance with the specific data quality objectives.

9. Quality Assurance

9.1 Summary

The section provides guidance to the operator in determining how well the FT-IR sensor is operating. While this section is labeled "quality assurance", it is by no means adequate to serve as a quality assurance project plan or program plan. Project and program plans are meant to address the specific data quality objectives of a monitoring program, and the final use of the FT-IR data and cannot be adequately covered in this document. Some of the procedures are limited in scope because a satisfactory procedure has not been developed at this time.

9.2 The Determination of Method Noise or Method Noise Equivalent Absorption

    9.2.1 Purpose. The purpose of this section is to allow the operator to determine the method noise. This determination should form part of the routine quality assurance checks made of the instrument. It should be made at least once a day for extended programs and every time the instrument is moved or otherwise changed. This procedure is used to judge whether the instrument is operating properly but not as a gauge of the quality of the data.

    9.2.2 Assumptions

9.2.2.1 This procedure assumes that spectra have been acquired with the same operating parameters (number of co-added scans, resolution, etc.) as the field spectra. The one exception is that the spectra used to determine the method noise should be taken so that no time elapses between them.

9.2.2.2 It is also assumed that software exists that will allow this determination to be made automatically by computer.

9.2.3 Additional Sections Referenced. No other sections are referenced.

9.2.4 Methodology. Instrumental noise is generally considered to be the random fluctuations in the recorded signal. That is not exactly true for the FT-IR system when the data are acquired along a long, open path. Evidently, the time required to allow small but measurable changes in the gaseous atmospheric constituents is short compared to the normal acquisition time of the spectra. Because of that, when two spectra are used to create an absorbance spectrum there is a variability in the result that is not electronic noise alone. This is defined here as the method noise. It is important because it cannot easily be done away with and will contribute to the error of the measurement.

The determination of method noise uses the statistical quantity called the RMS deviation. The mathematical routine normally used for this calculation performs a linear least-squares fit (linear regression) using the data points over a specified wave number region and calculates the RMS deviation from that line. The RMS deviation is defined as the square root of the sum of the differences squared divided by the quantity N-2. The number N is the total number of data points. The differences are calculated by taking the difference between the actual data point and the line; they are then squared and added.

The actual range of wave numbers that can be used changes with resolution, but the number of data points does not. The number of data points used should be 80 points. Thus for a 1-cm^{-1} resolution, the range of wave numbers is 40, because the instrument acquires a data point every half resolution unit. Since this measurement is considered to be the determination of an instrument parameter, the wave number region or regions should be chosen to minimize the effect of water vapor. The water vapor concentrations along the path are known to change rapidly, and that will perhaps cause most of the variability in the signal.

The two single beam spectra that are used to measure the noise should be taken without any time lapse between them. These two spectra are then used to create an absorbance spectrum. Which of the two that is used as the so-called background is irrelevant. Three wave number regions are then used for this determination. For this procedure, the regions are based on a 1-cm^{-1} resolution and are 968–1008, 2480–2520, and 4380–4420 cm^{-1}, respectively. Other regions may be used, but the operator should try to cover the range of wave numbers that are being measured. The 80 data points used in the measurement should also be adhered to. This data should then be recorded and plotted on a quality control chart for comparison purposes.

9.2.5 Procedure

9.2.5.1 Record two spectra with the same operational parameters that will be used for the acquisition of the field spectra. Do not allow any time to elapse between these spectra.

9.2.5.2 Create an absorbance spectrum by using either of the two spectra taken in Section 9.2.5.1 as a background.

9.2.5.3 Analyze this absorbance spectrum for the RMS deviation in the three wave number regions 968–1008 cm^{-1}, 2480–2520 cm^{-1}, and 4380–4420 cm^{-1}.

9.2.5.4 Record this data in a notebook and plot it on a quality control chart.

9.3 The Measurement of the Return Beam Intensity

9.3.1 Purpose. This section provides guidance to the measurement of the return beam intensity in the case of the monostatic system or the intensity of the IR source at the FT-IR in the case of the bistatic system. This procedure needs to be done only once as long as the detector or the infrared source does not change.

9.3.2 Assumptions. In order that these measurements be realistic, the stray light component or the black body radiation should be subtracted from the spectra. This means those measurement results should be available to the operator or should be made in conjunction with this measurement.

9.3.3 Additional Sections Referenced. Refer to Section 9.4, Measurement of Stray Light, and Section 9.5, The Measurement of Black Body Radiation, if applicable.

9.3.4 Methodology. The return beam intensity determines the operational signal-to-noise ratio of the FT-IR system. This intensity is a variable and depends on the path length chosen, the water vapor in the atmosphere, and other atmospheric conditions. The primary atmospheric conditions that make the return beam intensity change are fog, rain, snow, and sleet. Of these, fog has by far the largest effect. Another cause for a change in the return beam intensity is pollen in the atmosphere. This happens in the spring in areas where there are a large number of pine trees. Finally, for the monostatic geometry, which uses a retroreflector, condensation on the mirror can make dramatic changes in the return beam intensity. There are also instrumental causes of changes in the return beam intensity but they are beyond the scope of this document.

For these reasons, it is prudent to include in a quality assurance program the measurement of the return beam intensity. If the return energy has been degraded by an unacceptable amount, the operator must change the length of the path. Whether the return is acceptable or not is dependent on the data quality objectives from the quality assurance program plan.

This procedure is separated into two parts. The first is a procedure for measuring the return beam intensity as a function of path length. The second is the measurement of return beam intensity as a function of time.

There are two reasons to measure the return beam intensity as a function of path length. The first is to determine when the energy becomes intense enough to saturate the detector. The second is to determine when the infrared energy becomes too small to measure. These measurements then determine experimentally the minimum and maximum usable path length. There are a number of reasons why the return beam intensity should be monitored as a function of time. The primary one is that the return beam intensity will change according to varying weather conditions. The operator must become familiar with the magnitude and the rapidity of these changes.

9.3.5 Procedure

9.3.5.1 Return Beam Intensity as a Function of Path Length.

9.3.5.1.1 Place the light source or the retroreflector at a short distance, say 25 meters, from the detector.

9.3.5.1.2 Align the system to maximize the return signal.

9.3.5.1.3 Record a spectrum and convert this spectrum to a single beam spectrum.

9.3.5.1.4 Record the intensity levels in the 987-cm^{-1} region and in the 2,500-cm^{-1} and the 4,400 cm^{-1} regions. The reason the wave numbers are not given specifically is that the operator should select a maximum in the baseline return intensity in these regions.

9.3.5.1.5 Examine the detector cutoff region at about 650 cm^{-1}. If a dip occurs in this region or the baseline is elevated above zero, then the detector is already saturated.

9.3.5.1.6 If there is no indication of saturation, move the light source or the retroreflector so that the distance separating it and the detector is smaller. Repeat Sections 9.3.5.1.1 through 9.3.5.1.5.

9.3.5.1.7 Continue this process by cutting the distance in half until the single beam spectrum exhibits saturation as described above in the 650-cm^{-1} region. Record this distance. This distance represents the minimum path length that can be used with this particular instrument without altering the instrument.

9.3.5.1.8 Next, move the light source or retroreflector to a distance of 100 m.

9.3.5.1.9 Realign the instrument to maximize the signal.

9.3.5.1.10 Record a spectrum and convert it to a single beam spectrum.

9.3.5.1.11 Record the intensity levels at the same wave numbers as used above.

9.3.5.1.12 Repeat Sections 9.3.5.1.8 through 9.3.5.1.11 by increasing the path length in 50-m increments until the intensity levels no longer change. For the monostatic geometry mode, this will occur when all the energy being recorded comes from the stray light in the instrument. For the bistatic mode, the return signal will diminish to zero in the 4000-cm^{-1} region and then will evolve into the black body radiation spectrum.

9.3.5.1.13 Plot a graph of the return intensity versus path length.

9.3.5.2 Measurement of the Return Beam Intensity as a Function of Time. At least once every day of operation the return beam intensity should be recorded at the wave number regions given above. More frequent measurements should be made when the atmospheric or other conditions listed in Section 9.3.4 occur. The atmospheric conditions should also be recorded. Water vapor plays an important role in the recorded beam intensity so that the partial pressure of water should also be calculated and recorded. A continuous plot of these data should be made showing the intensity as a function of time. The graph should include notations for the various atmospheric conditions listed above.

9.4 The Measurement of Stray Light

9.4.1 Purpose. The monostatic FT-IR systems are prone to having stray light in the instrument. To obtain the best possible accuracy, this stray light component must be subtracted from the field spectra before the analysis is performed. This section describes how to measure the stray light component and is applicable to only the monostatic geometries that modulate the beam with the interferometer before the infrared energy is transmitted along the path and that use a second beam splitter to direct the beam. There are other sources for stray light that arise from overfilled optical components. These are a problem for the manufacturer and are not addressed in this document.

9.4.2 Assumptions. The primary assumption for this procedure is that the FT-IR system being used is of the monostatic geometry. The system has been operating sufficiently long to be past any warm-up periods and it is using the same resolution as when it is acquiring the normal field spectra.

9.4.3 Additional Sections Referenced. No other sections are referenced.

9.4.4 Methodology. The easiest way to measure the stray light with a monostatic system that modulates the beam before the energy is transmitted along the path is to simply slew the system away from the retroreflector. Once this is done, the operator should acquire a spectrum using a large number of co-added scans. If the time required to acquire this spectrum cannot be at least 4 times the length of time to acquire the field spectra, he should then use the longest time possible. The issue here is one of electronic noise, and the electronic noise should diminish as the square root of the time needed to acquire the spectrum. Changes in the atmospheric constituents play no role in this measurement.

This spectrum should be saved as a single beam spectrum with an appropriate name, and it must be subtracted from the single beam field spectra before they are converted to absorbance spectra.

A second way to measure the stray light is to cover the receiving telescope with some opaque, non-reflecting material. Any material that is reflecting acts as a mirror and will give erroneous readings. Any material that is

not opaque will allow some of the beam returning from the retroreflector to be transmitted to the detector. This method is not recommended.

This measurement must be done at the beginning of operation and every time the instrument is altered in any way. For those programs that are short-term field programs, the measurement should be made at the beginning of each field program.

   9.4.5 Procedure.
      9.4.5.1 Set up the instrument in exactly the same way as it will be used to acquire field spectra.
      9.4.5.2 Slew the transmitting telescope off the retroreflector so that there is no beam return signal.
      9.4.5.3 Acquire a spectrum.

9.5 The Measurement of Black Body Radiation

   9.5.1 Purpose. FT-IR systems generally have a field of view larger than the solid angle that the light source or the retroreflector subtends at the far end of the path. The bistatic systems (or those that do not transmit the beam through the interferometer before it transmitted along the path), therefore, admit radiation to the detector from the surrounding background. These systems also respond to any radiation coming from the instrument itself (the instrument is also a radiator of energy). This radiation is commonly referred to as the black body radiation and it must be subtracted from the single beam spectra before the analysis is performed. This procedure describes how to measure that radiation.
   9.5.2 Assumptions. The instrument must be set up in the same manner and with the same background that will be in its field of view during the acquisition of the field spectra.
   9.5.3 Additional Sections Referenced. No other sections are referenced.
   9.5.4 Methodology. The FT-IR systems available today use some form of a heated element as a source of infrared energy. These elements generally have a temperature in the vicinity of 1500°K. The terrestrial surroundings in which the FT-IR operates generally have a temperature around 300°K. All things above absolute zero radiate energy according to their temperature and have a very well known energy distribution in wave number. The distribution of energy peaks at a wave number that is temperature dependent with the cooler body having a peak at lower wave numbers. Also, the energy distribution of a cooler body is lower in intensity at all wave numbers than the distribution of a hotter body. The question arises of what the ratio of intensities is of these two sources. This ratio at the peak of the 300 degree source is about 5. That is, the surroundings can represent about 20% of the energy of the source. Therefore, it must be subtracted from the spectra before the analysis is performed.

The simplest way to acquire a black body spectrum is to set up the instrument in exactly the same way it will be run to take the field spectra. A spectrum should then be acquired with the light source turned off. This spectrum should be saved with an appropriate name.

This spectrum does not appear to change dramatically when the instrument is pointed at terrestrial targets such as buildings or trees. Nor does it change dramatically with slight changes in the ambient temperature (±10°K). A 10% change in temperature will shift the peak by 10%, and that may become important. Remember, however, that a 10% change in temperature is about 30°C. The black body spectrum does, however, change dramatically if the sky is included in the instrument's field of view. In this case an emission spectrum appears from the atmosphere, and this is very difficult to handle. The black body spectrum can also change dramatically if hot

sources other than the primary light source are allowed into the field of view of the instrument. The operator is advised to take precautions so that these conditions are avoided.

In order to minimize the noise introduced by the subtraction process, the number of scans used to acquire the spectrum should be large. An acquisition time of more than 15 min is probably excessive. It is prudent to run such a spectrum at least once every day during the study. These spectra should be investigated for changes, particularly when there are large swings in temperature. This is possible during the early fall, when the temperature can range from cold at night to quite warm in the daytime.

9.5.5 Procedure
9.5.5.1 Set up the FT-IR along the same path that will be used to acquire the field spectra.
9.5.5.2 Acquire a spectrum over a long acquisition time with the infrared source off.
9.5.5.3 Store the spectrum with an appropriate name.

9.6 The Determination of the Detection Limit

9.6.1 Purpose. The purpose of this routine is to provide the operator with a mechanism for determining the detection limits for the various gases. The definition of the detection limit is given here as the minimum concentration of the target gas that can be detected in the presence of all the usually encountered spectral interferences.

9.6.2 Assumptions. The instrument is operating with the same parameter settings as those used for collecting the field spectra. That is, the path length, resolution, number of co-added scans, and the apodization function are the same in both cases. If the instrument has an ancillary gas cell, this must be empty.

9.6.3 Additional Sections Referenced. No other sections are referenced.

9.6.4 Methodology. The detection limit of the FT-IR systems is a dynamic quantity that will change as the atmospheric conditions change. The variability of the target gas, water vapor, and all of the other interfering species concentrations contributes to the variability of this measurement. Some researchers have suggested that the I_0 spectrum used to create the absorption spectrum when measuring the detection limits be the same as that used for the field spectra. However, that cannot be done if a synthetic background is used since the field spectra are expected to contain some quantity of the target gas. If any other arbitrary background is used the measurement will certainly reflect the variability of the target gas, at least. To overcome most of the effects of this problem, the operator should use spectra whose acquisition times are no longer than about five minutes. If the field spectra are acquired at shorter times then the shorter time should be used. If the field spectra are acquired at longer times because the anticipated variability of the target gas is small, then it is appropriate to use the longer times.

The detection limit as determined in this procedure is the result of a calculation using a set of 15 individual absorption spectra. The 16 individual single beam spectra used for this determination are acquired in 5-min intervals and no time is allowed to elapse between them. The absorption spectra are then created by using the first and the second single beam spectra, the second and the third, and the third and the fourth, and so on until the 15 absorption spectra are obtained. These absorption spectra are analyzed in exactly the same way that all field spectra are to be analyzed and over the same wave number region. The analysis should result in a set of numbers that are very close to zero because most of the effects of the gas variability have been removed. The numerical results should be both positive and negative and for a very large set of data should average to zero. Three times the standard deviation of this calculated set of concentrations is defined to be the detection limit.

There is reason to believe that this procedure gives the most optimistic (lowest) value for the detection limit because it removes most of the effects of the interfering species. However, the other suggested procedures seem to introduce as much uncertainty, and this procedure may actually be used for further diagnostics of the post-analysis review of the data (see Section 8.10).

9.6.5 Procedure.

9.6.5.1 Acquire a set of 16 single beam spectra in exactly the same manner that will be used for the field spectra.

9.6.5.2 Use the first spectrum as a background to create an absorbance spectrum from the second spectrum.

9.6.5.3 Use the second spectrum as the background and create an absorbance spectrum from the third spectrum.

9.6.5.4 Continue this process until all 15 absorbance spectra have been created.

9.6.5.5 Analyze each of the spectra for the target gas concentration.

9.6.5.6 Calculate the standard deviation of the set of concentration values.

9.6.5.7 Multiply the result of Section 9.6.5.6 by 3 to obtain the detection limit.

9.7 The Determination of Precision

9.7.1 Purpose. Precision is a measure of the FT-IR system's ability to make repeatable measurements when challenged with the same sample. This section provides guidance to the operator on how to make that determination for some gases.

9.7.2 Assumptions. The FT-IR system has the capability for installing a gas cell in the beam so that the entire beam passes through it. This is something that the manufacturer has to build into the design of the system and is not under the control of the operator. While the measurements are being made, the instrument is operating in the same way that it is used to collect the field spectra.

9.7.3 Additional Sections Referenced. No other sections are referenced.

9.7.4 Methodology. The precision with which a measurement is made with the FT-IR instruments is, at the present time, very difficult to measure. The best method that has been suggested is one that uses a cell of some sort that is filled with a high concentration of gas and is then placed in the beam. However, this process is quite error-prone and it has not been shown to work well with a mixture of gases. A second difficulty is that it cannot be used for all the gases that can be potentially measured with the FT-IR. The primary reason is that the concentration of the gas in the cell has to be high in order to produce a measurable absorption. Many gases have a vapor pressure that is too low to achieve these concentrations. No procedure has been established for making these measurements of polar compounds. Additionally, not all the commercially available instruments have at the present time been designed to accept a cell in an appropriate position of the optical path.

However, for those instruments and for those gases that can be measured, the procedure is as follows. A cell whose length is short compared to the path length is filled with a high concentration of gas. The cell is placed in the infrared beam so that all of the energy passes through the cell. Then a set of spectra is acquired and these are converted to absorption spectra. These absorption spectra are analyzed for the target gas. The relative standard deviation of this set of measurements is given as the precision.

This procedure is also quite similar to the procedure for the measurement of accuracy. The measurement of precision, however, does not require an exact knowledge of the concentration of the gas, but rather the gas concentration must remain constant. Thus the gas concentrations used can be made up in the field at a lower cost to the monitoring program.

Determining the precision of the FT-IR monitoring system is complicated by the fact that the measurements are made over an open path in the atmosphere. It cannot be assumed that the concentration of the various atmospheric gases will be constant in time, and this fact will impact the precision measurements. This procedure calls for the precision measurements to be made by using the same path length that is generally used for acquiring field spectra. Therefore, the precision will vary in time and will be dependent on the variability of not only the target gas but also the variability of the interfering species. The precision measurement described is therefore a method precision and includes all of the parameters that must be considered in the field spectra analysis.

The cell can be filled in a number of ways, but the preferred way is to use a gas of the appropriate concentration from a prepared cylinder that has been purchased for this purpose. The proper mixture can be calculated as follows:

- The absorption coefficient of the gas can be calculated from the reference spectrum by using $\alpha = A/cl$, where A is the absorbance at the peak of the reference spectrum and cl is the concentration–path length product, which is supplied with the reference spectrum for the reference gas.

- Next, the desired absorbance when the cell is filled is selected. This can be set at 0.05.

- Then c is calculated from $c = A/\alpha l$, where $A = 0.05$, α is the absorption coefficient calculated above, and l is the length of the cell in meters if the reference gas has a concentration–path length product in parts per million per meter.

- The concentration calculated above has units of parts per million if the concentration–path length product for the reference gas has units of parts per million per meter. This is the concentration to use when purchasing a cylinder of gas. The fill gas of the cylinder must not absorb in the infrared, and the gas preferred for this is nitrogen.

Before the target gas is introduced into the cell, the cell should be flushed with nitrogen until at least five volumes of the cell have passed through it. At the present time the preferred method for introducing the target gas is with a flowing system. The gas should remain flowing during the measurement.

9.7.5 Procedure.

9.7.5.1 Calculate the appropriate concentration for the target gas and obtain a cylinder of that concentration.

9.7.5.2 Set up the instrument as it will be used to acquire the field spectra.

9.7.5.3 Place the cell in the instrument and flush it with dry nitrogen so that at least five volumes of the cell have passed through it.

9.7.5.4 Flow the target gas through the cell, and after three volumes of the cell have passed through, acquire a set of 15 spectra.

9.7.5.5 Analyze these spectra for the target gas.

9.7.5.6 Express the relative standard deviation of this set of concentrations as the precision.

9.8 The Determination of Accuracy

9.8.1 Purpose. Accuracy is a measure of the ability of the FT-IR to measure a known concentration of gas. This procedure may allow the operator to determine the accuracy of the FT-IR measurements for some gases. This measurement is very difficult to make and no exact procedure has been accepted.

9.8.2 Assumptions. The FT-IR must have the capability for installing a gas cell that is short compared to the path length in the instrument so that the entire infrared beam passes through it. This must be included in the manufacturer's design of the instrument, and whether or not the cell can be placed in the beam is not under the control of the operator. The measurements for accuracy should be made with the instrument operating in the same way as it is when acquiring normal field spectra.

9.8.3 Additional Sections Referenced. No other sections are referenced.

9.8.4 Methodology. The general procedure to be used for the determination of accuracy is essentially identical to the procedure for the determination of precision. The difference is that for the measurement of accuracy the concentration of the gas in the cell must be known. Obtaining this knowledge poses some special problems, and preparation of the sample gas by the individual operators is not recommended at this time. Rather, whenever possible a cylinder of prepared gas should be purchased; for convenience, this prepared mixture is called the reference gas for the rest of this procedure. However, the vapor pressure of some gases is too low to allow the purchase of appropriate concentrations. Even if a cylinder is purchased, there is some difficulty with knowing what the concentration in the cell is, particularly for the polar compounds.

If a cell is to be used for this measurement then the first step is to calculate the concentration that is required. It is anticipated that the accuracy of the measurement is dependent on the concentration that is being measured. Therefore, the operator must make some judgement of what that concentration is to be. To obtain the concentration in the cell, the operator must multiply the anticipated concentration by the ratio of the path length used for the monitoring program to the cell length. Thus if the path length to be used in the acquisition phase is 100 m and the cell length is 20 cm, then the operator must multiply the anticipated concentration by 500 to get the required concentration of the reference gas in the cell.

Once the proper mixture of gas has been obtained, the operator must introduce it into the cell. At the present time it is recommended that the gas should be flowed through the cell continually during the measurement. Before the measurement is attempted, the gas should be allowed to flow through the cell until at least five volumes of the cell have passed through it.

At the beginning of this measurement the cell should be flushed with dry nitrogen and then a spectrum should be acquired. The reference gas is then flowed through the cell and a second spectrum acquired while the gas is flowing. The cell should then be flushed with dry nitrogen again and a third spectrum recorded.

The average value of the target gas concentration found from the first and third spectra is subtracted from the value determined for the target gas from the second spectrum. This value is then used as the recorded value for the measurement. This procedure is repeated five times in a day, and the average value of these five measurements is used as the accuracy measurement. The percent accuracy is then defined as the average value found above divided by the known concentration of the cylinder gas value times 100. This value should be recorded and plotted on a control chart made for that purpose.

If a flowing system is used, the flow rate must be small so that there is no measurable pressure change in the cell. Flow rates of a few cubic centimeters per minute are acceptable and would require no measurement of the pressure. When the cell is purged to remove the target gas, the volume of purge gas used should be at least 5 times the volume of the cell.

The procedure described here has not been studied in depth, and little written material exists in the literature. Questions such as what the material of the lead lines are to be made of, whether the pressure must be measured in the cell, and whether the lines have to be heated have not been answered at this time. It is also not clear

whether this procedure can be used with a mixture of gas or if only a single species must be used at a time. It seems possible that, in the future, a procedure using the water in the atmosphere can be used for this measurement. Absorbance due to water is in every important part of the spectrum that is used with FT-IR measurements, and it will be in every spectrum. Water can also be measured independently with techniques other than the FT-IR so that a verification step can be performed. However, the use of water has not been explored at all.

9.8.5 Procedure.

9.8.5.1 Calculate the required concentration of the reference gas and obtain a cylinder with that concentration.

9.8.5.2 Set up the FT-IR with the same operating conditions used to acquire the field spectra.

9.8.5.3 Install the cell in the beam if necessary and flush it with dry nitrogen.

9.8.5.4 Acquire a spectrum.

9.8.5.5 Flow the reference gas through the cell so that at least five volumes of the cell pass through it.

9.8.5.6 Acquire a second spectrum with the reference gas flowing.

9.8.5.7 Flush the cell with dry nitrogen again and acquire a third spectrum.

9.8.5.8 Analyze all three spectra for the target gas by using the same background as used for the field spectra.

9.8.5.9 Find the concentration of the reference gas from the result of analyzing the second spectrum minus the average value of the first and third spectra.

9.8.5.10 Repeat Sections 9.8.5.3 through 9.8.5.9 five times in any one day of operation.

9.8.5.11 Determine the percent accuracy as the average value of the five measurements divided by the known concentration of the reference cell times 100.

9.9 The Measurement of Resolution

9.9.1 Purpose. The purpose of this procedure is to provide the operator with a means for measuring the resolution of the FT-IR instrument.

9.9.2 Assumptions. The spectra used to make this determination have been acquired with the same instrumental parameters as those used for the field spectra. Particularly, the apodization function and the path length must be the same.

9.9.3 Additional Sections Referenced. No other sections are referenced.

9.9.4 Methodology. The resolution of the FT-IR is an important parameter in that it determines the specificity of the measurements. The instrument resolution does not exhibit dramatic changes from day to day and needs to be measured infrequently. However, whenever any change is made to the instrument optics, including the light source, the resolution must be remeasured. The resolution can also change when the path length changes if the instrument does not have an appropriate field stop to clearly define the field of view regardless of the optical path length. If that is the case, the resolution should be measured at whatever path lengths are used. The FT-IR resolution is also dependent on the apodization function that is used when single beam spectra are created from interferograms, and if more than one apodization function is used then the resolution should be measured for each. The operator needs to be aware of the instrument resolution for a number of reasons. The spectra from two instruments cannot be compared if the resolutions are not the same. The use of reference spectra at resolutions different from that of the instrument creates problems with accuracy. Subtracting one spectrum from another with different resolutions is also a problem. The manufacturers of these devices list the nominal resolution, but a listed resolution of, for example, 1 cm^{-1} should not be interpreted as an exact number.

To measure the resolution, an absorption spectrum must be used. An absorption line that is narrow in comparison to the instrument's line function must be used, and the spectral line used must be a single line. If changes in the instrument resolution occur, they should be noticeable in the high-wave-number region first.

Six primary atmospheric constituents are present in every spectrum. They are water vapor, methane, carbon dioxide, nitrous oxide, ozone, and carbon monoxide. Of these, only the absorption features of water vapor and carbon monoxide can be used to measure the instrument resolution. If the path length is great enough and the water vapor concentration is large enough, then the atmospheric constituent deuterated water can also be used.

In addition to these, absorption features from other gases in high concentrations in conjunction with a short cell can be used. The important feature of any line that is selected for resolution measurements is that it be a single line and be narrow compared to the instrument's nominal operating resolution. Thus methane cannot be used because the lines are not single lines. Whatever feature is chosen, it must not be impacted by any interfering species, as this has the same effect as having double lines. The absorption features of ammonia or hydrogen chloride can be used. HCl is actually a good choice because it absorbs in the high-wave-number region. However, it is not generally present in high enough quantities in the atmosphere to be measured in every spectrum.

There are a number of lines that can be used in the water vapor spectrum that can be used for this measurement. They are at the wave numbers 1014.2, 1149.46, 1187.02, and 2911.88. It should be noted that many of the water lines are already saturated as far as the instrument response is concerned at a vapor pressure of 3 torr. So any line used must be checked to make sure it is not saturated. For carbon monoxide there is at least one line at 2168.9 that can be used. These lines should easily be observed in spectra that have been taken with path lengths greater than 100 m (total).

The resolution for the FT-IR is defined as the full width at half maximum (FWHM) for either of the these lines. Thus to determine the instrument's resolution, an absorbance spectrum must be created with a synthetic background. The operator needs to have a large number of data points across the line in order to make this measurement, and it should be remembered that the system takes only two data points per nominal resolution element. The best way to create this absorption spectrum is to record an interferogram and then zero fill by at least a factor of 4 before computing the Fourier transform. If that is not possible, then the absorbance spectrum must be interpolated to increase the number of data points.

The absorbance at the peak must be measured, and any non-zero baseline value must be subtracted from that measurement. The result of this subtraction is the peak height. Then the entire width of the line at one-half the peak absorbance is measured in wave numbers. This is the required measure of the resolution of the instrument.

    9.9.5 Procedure.
       9.9.5.1 Obtain an interferogram with the FT-IR operating at the same path length as will be used for the acquisition of the field spectra.
       9.9.5.2 Zero fill the interferogram by at least a factor of 4.
       9.9.5.3 Perform the Fourier transform on the interferogram.
       9.9.5.4 Create an absorbance spectrum using a synthetic background.
       9.9.5.5 Isolate one of the lines and measure the peak height.
       9.9.5.6 Subtract any non-zero baseline measurement.
       9.9.5.7 Measure the full width of the line at one half the absorbance measured in Section 9.9.5.6. This is the resolution.

9.10 The Determination of Nonlinear Instrument Response

   9.10.1 Purpose. The FT-IR instrument can respond nonlinearly to changes in the light intensity for several reasons. There are two instrumental conditions that must be guarded against, and these are discussed here. The first is that the electrical gain is set too high, and this can cause the analog-to-digital (A/D) converter to be saturated. The second is that the light source itself is too intense, and this causes the detector response to become nonlinear. This procedure is intended to give the operator a means for determining when either of these conditions exist.
   9.10.2 Assumptions. The instrument is operating under the same conditions as it will be to acquire the field spectra.
   9.10.3 Additional Sections Referenced. No other sections are referenced.
   9.10.4 Methodology. A nonlinear response can be caused by excessive source intensity or amplifier gain. All of the FT-IR systems that are used for remote sensing use A/D converters to convert the analog detector signal to a digitized form. Most use either a 16 bit or an 18 bit converter, and that defines the range of voltages that can be monitored. If the source intensity and amplifier gain combination is too high, then the A/D converter can be saturated. This manifests itself as a sudden drop in the signal being recorded when the source or the retroreflector is moved closer to the detector. When this happens, the system gain must be lowered, if that possibility exists, or the path length must be changed.

The second type of nonlinear response is somewhat more difficult to determine. This occurs if too much light falls on the detector. The detector converts the incident light photons to an electrical signal. There is a limit for how many photons can be converted to electrons, and when this limit is exceeded the detector response becomes nonlinear.

There may also be a nonlinear response from the fact that HgCdTe detectors exhibit nonlinear behavior in their response to infrared energy. This circumstance is not covered here and should be corrected by the manufacturer.

In everyday operation, the easiest way to detect the second kind of nonlinearity is to examine the portion of the single beam spectrum at wave numbers below the detector cutoff. This is in the 650–680-cm^{-1} region for most HgCdTe detectors. If a dip below zero occurs in that region or if the signal is above zero at wave numbers below that region, the system's response may be nonlinear.

There are two ways to check the system's response. Both involve the use of screens to diminish the light intensity while the response is being viewed. If the screens have meshes that reduce the intensity by known amounts, the response should be diminished by that amount also. If the instrument responds differently, the system is nonlinear.

Wire screens can be purchased in a number of mesh sizes, and the mesh size determines how much light will get blocked. Plastic screens should not be used because they may exhibit selective absorption. Aluminum screening that is used for window screening is satisfactory but may not reduce the intensity enough. It is best to use screens of different mesh when using the procedure described below rather than two layers of screening with the same mesh.

The following procedure needs to be done only if the operator suspects that the system is operating in a nonlinear way.

9.10.5 Procedure.

  9.10.5.1 Set the FT-IR system up as it will be used for acquisition of the field spectra.

  9.10.5.2 Move the source or the retroreflector to twice the original distance.

  9.10.5.3 Examine the signal. If a sudden increase in the signal strength occurs, then the A/D converter is saturated.

  9.10.5.4 With the source on and the retroreflector at the distance used for the field spectra, acquire a single beam field spectrum and examine the intensity in the detector cutoff region. If a dip occurs, the detector may be saturated.

  9.10.5.5 If the dip that is described in Section 9.10.5.4 occurs, insert a wire screen in the beam so that it covers the entire beam and record the signal level.

  9.10.5.6 Insert a second screen in the beam and record the signal again. If the screens are the same, each should diminish the beam in the same ratio. If that does not happen, the system is nonlinear in response and the infrared energy must be decreased by some means such as increasing the path length, closing the iris in the instrument, etc.

9.11 The Determination of Water Vapor Concentration

  9.11.1 Purpose. It is suggested that the water vapor content in the atmosphere be monitored independently of the FT-IR measurements. This is not an individual procedure like the preceding portions of this method in that it does not explain the siting criteria for making water vapor measurements. It is rather a discussion as to why the measurement is important.

  9.11.2 Assumptions. There are no assumptions about the FT-IR system associated with this process.

  9.11.3 Additional Sections Referenced. No other sections are referenced.

  9.11.4 Methodology. Absorption due to water vapor is the predominant feature in the spectra acquired by the FT-IR remote sensor. It also seems to be one of the most difficult compounds to deal with in the analysis. There are measurable changes in the observed water vapor from spectrum to spectrum. Data from a local airport weather service is not satisfactory to understand the changes and their effects on the analysis. Large and abrupt changes in the water vapor content can be expected. When that occurs it is likely that the background spectrum and the water vapor reference spectrum will have to be remade. But the only way to know that these changes have occurred is to measure the water independently.

Some argument can be made that the water vapor concentration can be obtained by simply adding water to the list of analyzed gases. However, it is not simple to make that measurement. Many of the water vapor lines are very strongly absorbing when the vapor pressure is 3 or 4 torr. The atmospheric vapor pressure in most areas is at least 5 times higher than that. That makes line selection for analysis quite problematic.

Since the water vapor can easily be measured in a continuous fashion it seems prudent to make the measurement independently of the FT-IR. One post-analysis check of the data is to look for a correlation between the concentrations of the target gas and water vapor. To accomplish that, the operator must determine what the water vapor concentration is. The following discussion describes a way of doing that.

The water vapor concentration can be obtained by measuring the relative humidity and the ambient temperature. These values, along with the Smithsonian psychrometric tables, are then used to calculate the water vapor concentration. The psychrometric tables can be found in the *Handbook of Chemistry and Physics* (14), which is published yearly.

There are solid-state devices available today that allow reliable measurements of the relative humidity and the ambient temperature. These devices give results to within a few percent of relative humidity and a few tenths of a degree for the temperature. The operator will need a way to record the output from these devices. This can be accomplished with a data logger that allows for multichannel, multiday recording.

The sensors can be placed anywhere along the path but must be shielded from the sun. A complete description of how to configure the placement of these devices is well outside the scope of this document. For a complete discussion of these measurements, the operator should consult the following document: *Quality Assurance Handbook for Air Pollution Measurements*, *Volume IV—Meteorological Measurements* (15). Once the water vapor concentration is known, it should be plotted as a function of time and then compared with the target gas concentration as discussed in the procedure for post-analysis data checking (see Section 8.10). The operator should pay particular attention to the periods where abrupt changes in the water vapor occur.

10. References

1. Russwurm, G. M., and Childers, J.W., *FT-IR Open-Path Monitoring Guidance Document*, U. S. Environmental Protection Agency, Research Triangle Park, NC, EPA/600/R-96/040, April 1996.

2. Pfeiffer, H. G., and Liebhafsky, H. A., "The Origins of Beer's Law," *J. Chem. Educ.*, Vol. 28:123-125, 1951.

3. Lothian, G. F., "Beer's Law and Its Use in Analysis," *Analyst*, Vol. 88:678, 1963.

4. Champeney, D. C., *Fourier Transforms and Their Physical Applications*, Academic Press, London, 1973.

5. Nicolet Analytical Instruments, *FT-IR Theory,* Nicolet Analytical Instruments, Madison, WI, 1986.
6. Griffiths, P. R., and deHaseth, J. A., *Fourier Transform Infrared Spectrometry*, John Wiley and Sons, New York, 1986.

7. Halliday, D., and Resnick, R. *Fundamentals of Physics*, Wiley and Sons, New York, 1974.

8. Stone, J. M., *Radiation and Optics*, McGraw-Hill, New York, 1963.

9. Tolansky, S., *An Introduction to Interferometry,* John Wiley and Sons, New York, 1962.

10. Calvert, J. G., "Glossary of Atmospheric Chemistry Terms (Recommendations 1990)," *Pure Appl. Chem.*, Vol. 62(11):2167-2219, 1990.

11. Long, G. L., and Winefordner, J. D., "Limit of Detection: A Closer Look at the IUPAC Definition," *Anal. Chem.*, Vol. 55(7):712A-724A, 1983.

12. Rennilson, J. J., "Retroreflection Measurements: A Review," *Appl. Opt.*, Vol. 19:1234, 1980.

13. Haaland, D. M., and Easterling, R. G., "Application of New Least-Squares Methods for the Quantitative Infrared Analysis of Multicomponent Samples," *Appl. Spectrosc.*, 36(6):665-673, 1982.

14. *Handbook of Chemistry and Physics*, CRC Press, Cleveland, OH.

15. *Quality Assurance Handbook for Air Pollution Measures, Volume IV—Meteorological Measurements*, U. S. Environmental Protection Agency, EPA-600/R-94-038b, Research Triangle Park, NC, May 1994.
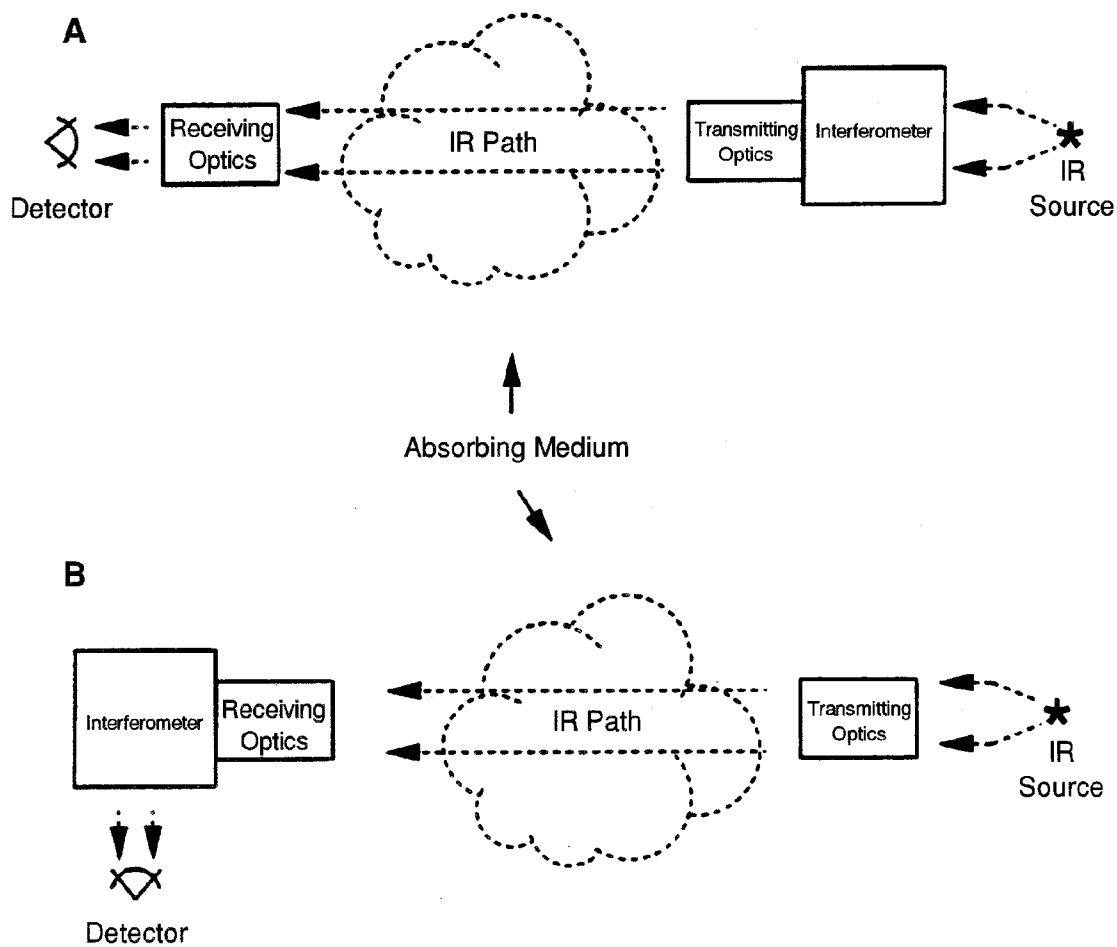
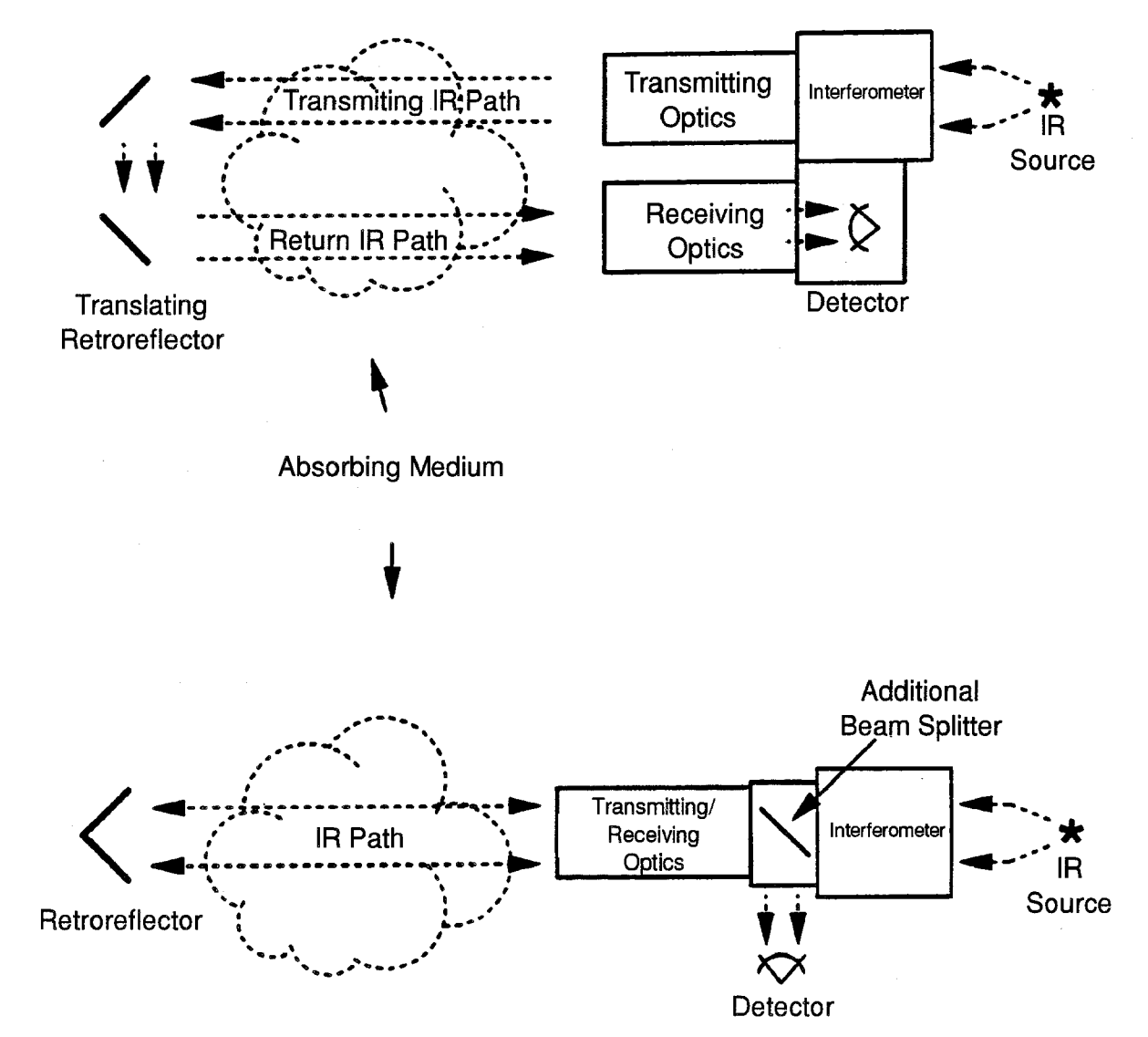Figure 1. The bistatic configuration of an FT-IR system.

Transmiting IR Path

Transmitting Optics

Interferometer

IR Source

Return IR Path

Receiving Optics

Detector

Translating Retroreflector

Absorbing Medium

Additional Beam Splitter

IR Path

Transmitting/ Receiving Optics

Interferometer

IR Source

Retroreflector

Detector

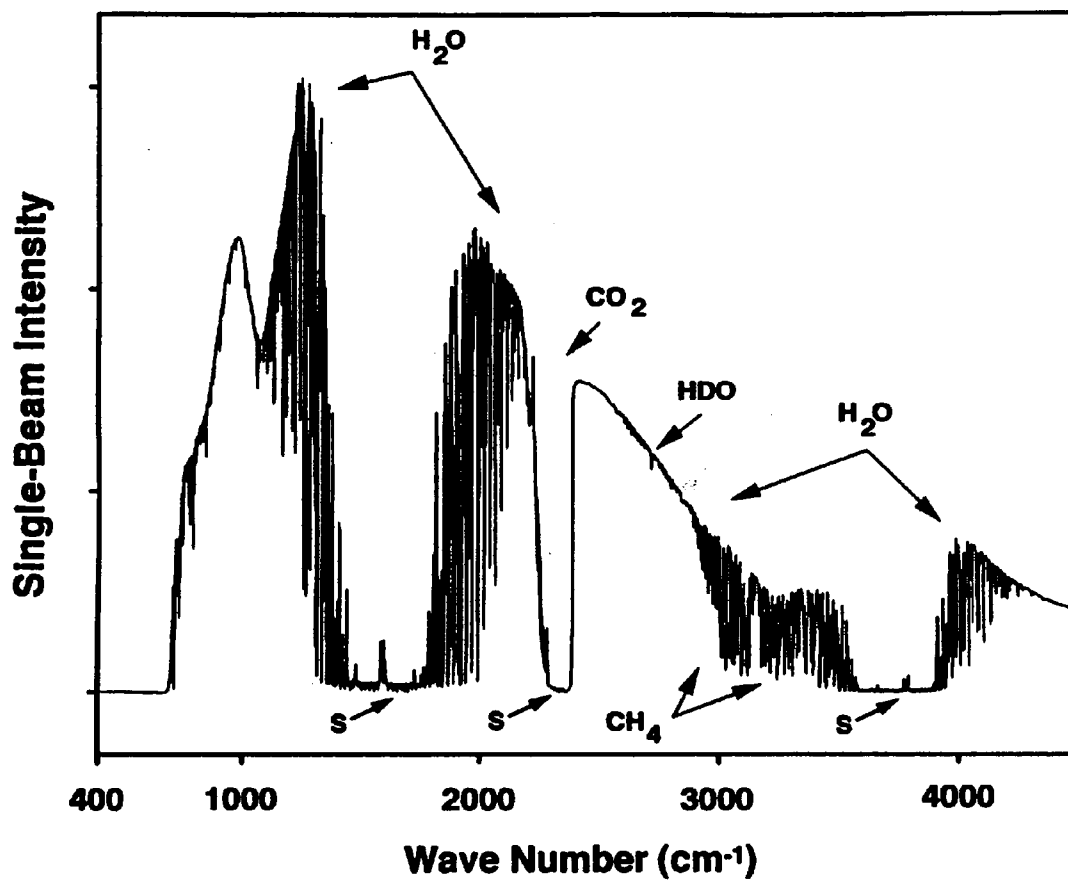Figure 2. The monostatic configuration of an FT-IR system.

Figure 3. Single-beam spectrum acquired by using a monostatic system and a 414-m path.
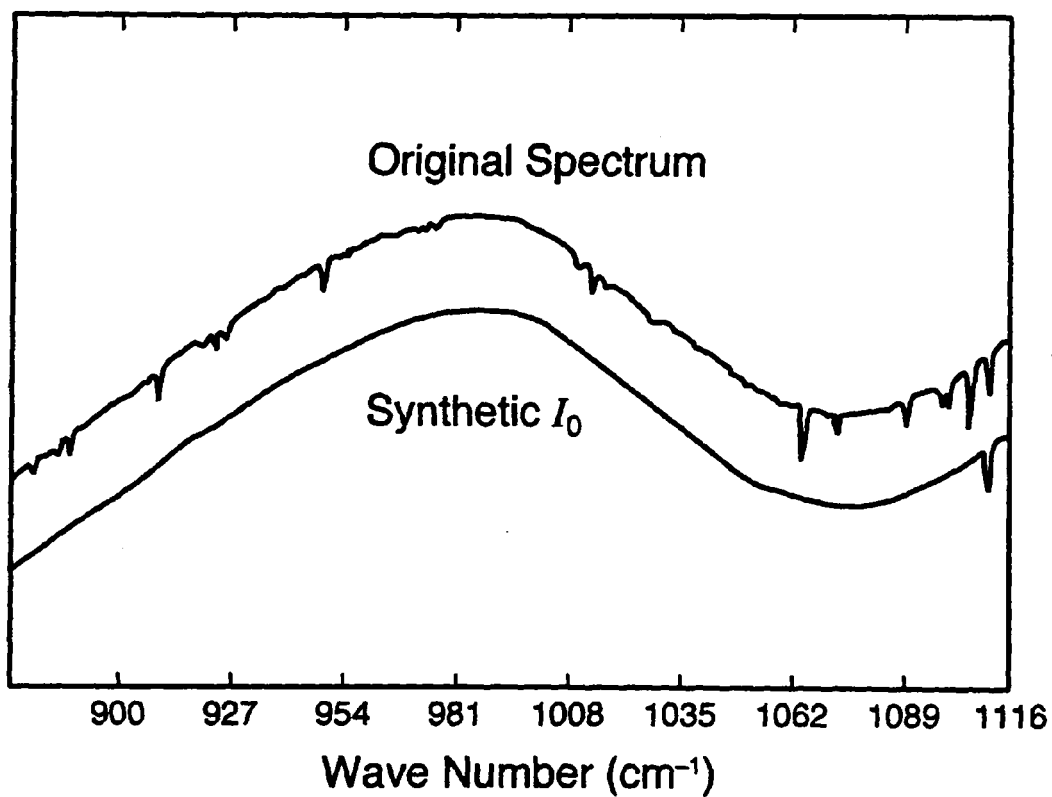*[Note: S indicates stray light.]*

Figure 4. Synthetic I_o spectrum for an FT-IR absorbance.
[Note: The peak at 1110 cm^{-1} has intentionally been left in as a fiducial point.]