Designation: D 6348 – 03

Standard Test Method for Determination of Gaseous Compounds by Extractive Direct Interface Fourier Transform Infrared (FTIR) Spectroscopy[1]

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INTRODUCTION

This extractive FTIR based field test method is used to quantify gas phase concentrations of multiple target analytes from stationary source effluent. Because an FTIR analyzer is potentially capable of analyzing hundreds of compounds, this test method is not analyte or source specific. The analytes, detection levels, and data quality objectives are expected to change for any particular testing situation. It is the responsibility of the tester to define the target analytes, the associated detection limits for those analytes in the particular source effluent, and the required data quality objectives for each specific test program. Provisions are included in this test method that require the tester to determine critical sampling system and instrument operational parameters, and for the conduct of QA/QC procedures. Testers following this test method will generate data that will allow an independent observer to verify the valid collection, identification, and quantification of the subject target analytes.

1. Scope

1.1 This field test method employs an extractive sampling system to direct stationary source effluent to an FTIR spectrometer for the identification and quantification of gaseous compounds. This test method is potentially applicable for the determination of compounds that (*1*) have sufficient vapor pressure to be transported to the FTIR spectrometer and (*2*) absorb a sufficient amount of infrared radiation to be detected.

1.2 This field test method provides near real time analysis of extracted gas samples from stationary sources. Gas streams with high moisture content may require conditioning to minimize the excessive spectral absorption features imposed by water vapor.

1.3 This field test method requires the preparation of a source specific field test plan. The test plan must include the following: (*1*) the identification of the specific target analytes (*2*) the known analytical interferents specific to the test facility source effluent (*3*) the test data quality necessary to meet the specific test requirements and (*4*) the results obtained from the laboratory testing (see Annex A1 for test plan requirements).

1.4 The FTIR instrument range should be sufficient to measure from high ppm(v) to ppb(v) and may be extended to higher or lower concentrations using any or all of the following procedures:

1.4.1 The gas absorption cell path length may be either increased or decreased,

1.4.2 The sample conditioning system may be modified to reduce the water vapor, CO_2, and other interfering compounds to levels that allow for quantification of the target compound(s), and

1.4.3 The analytical algorithm may be modified such that interfering absorbance bands are minimized or stronger/weaker absorbance bands are employed for the target analytes.

1.5 The practical minimum detectable concentration is instrument, compound, and interference specific (see Annex A2 for procedures to estimate the achievable minimum detectable concentrations (MDCs)). The actual sensitivity of the FTIR measurement system for the individual target analytes depends upon the following:

1.5.1 The specific infrared absorptivity (signal) and wavelength analysis region for each target analyte,

1.5.2 The amount of instrument noise (see Annex A6), and

1.5.3 The concentration of interfering compounds in the sample gas (in particular, percent moisture and CO_2), and the amount of spectral overlap imparted by these compounds in the wavelength region(s) used for the quantification of the target analytes.

1.5.4 Any sampling system interferences such as adsorption or outgassing.

1.6 Practices E 168 and E 1252 are suggested for additional reading.

1.7 *This standard does not purport to address all of the safety concerns associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and*

[1] This test method is under the jurisdiction of Committee D22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

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health practices and to determine the applicability of regulatory limitations prior to use. Additional safety precautions are described in Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres[2]

D 3195 Practice for Rotameter Calibration[2]

E 168 Practice for General Techniques of Infrared Quantitative Analysis[3]

E 1252 Practice for General Techniques for Obtaining Infrared Spectra for Qualitative Analysis[3]

2.2 *EPA Methods (40 CFR Part 60 Appendix A)*[4]

Method 1 - Sample and Velocity Traverses for Stationary Sources

Method 2 Series - Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube)

Method 3 Series - Gas Analysis for Carbon Dioxide, Oxygen, Excess Air, and Dry Molecular Weight

Method 4 Series - Determination of Moisture Content in Stack Gases

3. Terminology

3.1 See Terminology D 1356 for definition of terms related to sampling and analysis of atmospheres.

3.2 *Definitions of Terms Specific to This Standard*—This section contains the terms and definitions used in this test method and those that are relevant to extractive FTIR based sampling and analysis of stationary source effluent. When possible, definitions of terms have been drawn from authoritative texts or manuscripts in the fields of air pollution monitoring, spectroscopy, optics, and analytical chemistry.

3.2.1 *absorbance*, *n*—the negative logarithm of the transmission, $A = -\log (I/I_0)$, where I is the transmitted intensity of the light and I_0 is the incident intensity.

3.2.2 *absorptivity*, *adj*—the amount of infrared radiation that is absorbed by each molecule.

3.2.3 *analyte spiking*, *n*—the process of quantitatively co-adding calibration standards with source effluent to determine the effectiveness of the FTIR measurement system to quantify the target analytes.

3.2.4 *analytical algorithm*, *n*—the method used to quantify the concentration of the target analytes and interferences in each FTIR Spectrum. The analytical algorithm should account for the analytical interferences by conducting the analysis in a portion of the infrared spectrum that is the most unique for that particular compound.

3.2.5 *analytical interference*, *n*—the physical effects of superimposing two or more light waves. Analytical interferences occur when two or more compounds have overlapping absorbance bands in their infrared spectra.

3.2.6 *apodization*, *v*—a mathematical transformation carried out on data received from an interferometer to reduce the side lobes of the measured peaks. This procedure alters the instrument's response function. There are various types of transformation; the most common forms are boxcar, triangular, Happ-Genzel, and Beer-Norton functions.

3.2.7 *background spectrum*, *n*—the spectrum taken in the absence of absorbing species or sample gas, typically conducted using dry nitrogen or zero air in the gas cell.

3.2.8 *bandwidth*, *adj*—the width of a spectral feature as recorded by a spectroscopic instrument. This width is listed as the full width at the half maximum of the feature or as the half width at the half maximum of the spectral feature. This is also referred to as the line width **(1)**.[5]

3.2.9 *beam splitter*, *n*—a device located in the interferometer that splits the incoming infrared radiation into two separate beams that travel two separate paths before recombination.

3.2.10 *Beer's law*, *n*—the principal by which FTIR spectra are quantified. 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: (*1*) perfectly monochromatic radiation (*2*) no scattering (*3*) a beam that is strictly collimated (*4*) negligible pressure-broadening effects **(2, 3)**. For an excellent discussion of the derivation of Beer's law, see **(4)**.

3.2.11 *calibration transfer standard*, *n*—a certified calibration standard that is used to verify the instrument stability on a daily basis when conducting sampling.

3.2.12 *classical least squares*, *n*—a common method of analyzing multicomponent infrared spectra by scaled absorbance subtraction.

3.2.13 *condenser system,(dryer)*, *n*—a moisture removal system that condenses water vapor from the source effluent to provide a dry sample to the FTIR gas cell. Part of the sample conditioning system.

3.2.14 *cooler*, *n*—a device into which a quantum detector is placed for maintaining it at a low temperature in an IR system. At a low temperature, the detector provides the high sensitivity that is required for the IR system. The two primary types of coolers are a liquid nitrogen Dewar and a closed-cycle Stirling cycle refrigerator.

3.2.15 *electromagnetic spectrum*, *n*—the total set of all possible frequencies of electromagnetic radiation. Different sources may emit over different frequency regions. All electromagnetic waves travel at the same speed in free space **(5)**.

3.2.16 *extractive FTIR*, *n*—a means of employing FTIR to quantify concentrations of gaseous components in stationary source effluent. It consists of directing gas samples to the FTIR cell without collection on sample media.

3.2.17 *fingerprint region*, *n*—the region of the absorption spectrum of a molecule that essentially allows its unequivocal identification. For example, the organic fingerprint region covers the wave number range from 650 to 1300 cm^{-1}**(6)**.

3.2.18 *Fourier transform*, *v*—a mathematical transform that allows an aperiodic function to be expressed as an integral sum

[2] *Annual Book of ASTM Standards*, Vol 11.03.

[3] *Annual Book of ASTM Standards*, Vol 03.06.

[4] Available from Superintendent of Documents, U. G. Government Printing Office, Washington, DC 20402.

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

over a continuous range of frequencies **(7)**. The interferogram represents the detector response (intensity) versus time, the Fourier transform function produces intensity as a function of frequency.

3.2.19 *frequency position*, *n*—the accepted exact spectral line position for a specific analyte. A wave number or fractional wavenumber is used to determine whether spectral shifts have occurred with time.

3.2.20 *FTIR*, *n*—an abbreviation for *Fourier transform infrared*. A spectroscopic instrument using the infrared portion of the electromagnetic spectrum. The working component of this system is an interferometer. To obtain the absorption spectrum as a function of frequency, a Fourier transform of the output of the interferometer must be performed. For an in-depth description of the FTIR, see **(8)**.

3.2.21 *fundamental CTS*, *n*—a NIST traceable reference spectrum with known temperature and pressure, that has been recorded with an absorption cell that has been measured using either a laser or other suitably accurate physical measurement device.

3.2.22 *infrared spectrum*, *n*—that portion of the electromagnetic spectrum that spans the region from about 10 cm^{-1} to about 12 500 cm^{-1}. It is divided **(6)** into (*1*) the near-infrared region (from 12 500 to 4000 cm^{-1}), (*2*) the mid-infrared region (from 4000 to 650 cm^{-1}), and (*3*) the far-infrared region (from 650 to 10 cm^{-1}).

3.2.23 *instrument function*, *n*—the function superimposed on the actual absorption line shape by the instrument. This is sometimes referred to as the slit function; a term taken from instruments that use slits to obtain resolution.

3.2.24 *instrument specific reference spectra*, *n*—reference spectra collected on the instrument that collects the actual sample spectra. The instrument specific reference spectra are used in the analytical algorithm.

3.2.25 *intensity*, *n*—the radiant power per unit solid angle. When the term *spectral intensity* is used, the units are watts per steradian per nanometre. 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. However, in the general literature, this definition is more often used for the term *irradiance*, or *normal irradiance* **(9, 10)**.

3.2.26 *interferogram*, *n*—the effects of interference that are detected and recorded by an interferometer, the output of the FTIR and the primary data are collected and stored **(8, 10)**.

3.2.27 *interferometer*, *n*—any of several kinds of instruments used to produce interference effects. The Michelson interferometer used in FTIR instruments is the most famous of a class of interferometers that produce interference by the division of amplitude **(11)**.

3.2.28 *irradiance*, *n*—radiant power per unit projected area of a specified surface. This has units of watts per square centimetre. The term *spectral irradiance* is used to describe the irradiance as a function of wavelength. It has units of watts per square centimetre per nanometre **(9)**.

3.2.29 *laser*, *n*—an acronym for the term *light amplification by stimulated emission of radiation*. A source of light that is highly coherent, both spatially and temporally **(1)**.

3.2.30 *light*, *n*—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}**(5)**.

3.2.31 *system mechanical response time*, *n*—the amount of time that is required to obtain a stable instrument response when directing a non-retained calibration standard through the entire sampling system

3.2.32 *minimum detectable concentration*, *n*—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 three 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 % **(9, 12)**. See Annex A2 of this standard for a series of procedures to measure MDC.

3.2.33 *native effluent concentration*, *n*—the underlying effluent concentration of the target analytes.

3.2.34 *noise equivalent absorbance (NEA)*, *n*—the peak-to-peak noise in the spectrum resulting from the acquisition of two successive background spectra.

3.2.35 *path length*, *n*—the distance that the sample gas interacts with the infrared radiation.

3.2.36 *peak-to-peak noise*, *n*—the absolute difference from the highest positive peak to the lowest negative peak in a defined spectral region.

3.2.37 *reference library*—the available reference spectra for use in developing the analytical algorithm.

3.2.38 *reference spectra*, *n*—spectra of the absorbance versus wave number for a pure sample of a set of gases. These spectra are obtained under controlled conditions of pressure and temperature, pathlength, and known concentration. The spectra are used to obtain the unknown concentrations of gases in stationary source effluent samples.

3.2.39 *resolution*, *n*—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 **(11, 13)**. This definition of resolution and the Raleigh criterion are also valid for the FTIR, 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 centimetres) of the two-interferometer mirrors employed. **(8, 14)**

3.2.40 *root mean square (RMS) noise*, *n*—the root mean square difference between the absorbance values that form a segment in a spectrum and the mean absorbance value of that segment.

3.2.41 *sample conditioning system*, *n*—the part of the sampling system that removes water vapor, CO_2, or other spectrally interfering compounds before analysis.

3.2.42 *sample interface*, *n*—the entire sampling system consisting of the sample probe, sample transport line, and all other components necessary to direct effluent to the FTIR gas cell.

3.2.43 *sampling system interference, n*—an interference that prohibits or prevents delivery of the target analytes to the FTIR gas cell. Examples of potential sampling system interferences are unwanted moisture condensation within the sampling system, heavy deposition of particulate matter or aerosols within the sampling system components, or reactive gases.

3.2.44 *sampling system recovery, n*—the amount of calibration standard that is recovered through the sampling system during the analyte spiking procedure.

3.2.45 *sampling system, n*—see **sample interface**.

3.2.46 *signal-to-noise, n*—in general terms, the signal-to-noise is defined as the area of the target analyte peaks divided by the NEA area in the same spectroscopic region.

3.2.47 *source, n*—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.

3.2.48 *spectral intensity, n*—see **Intensity**.

3.2.49 *spectral interference, n*—when the absorbance features from two or more gases cover the same wave number regions, the gases are said to exhibit spectral interference.

3.2.50 *system zero, n*—a system zero is conducted by directing nitrogen or zero air through the entire sampling system to demonstrate whether any target analytes or interferences are present.

3.2.51 *transmittance, n*—percent transmittance is defined as the amount of infrared radiation that is not absorbed by the sample. $\% T = (I/Io) \times 100$.

3.2.52 *truncation, v*—the act of stopping a process before it is complete. In FTIR spectrometers, the finite movement of the interferometer mirror truncates the theoretically infinite scale of the interferogram.

3.2.53 *volumetric flowrate, n*—See 40 CFR part 60 Appendix A, Method 2. The flowrate is necessary when calculating stationary source emissions in terms of mass per unit of time.

3.2.54 *wave number, n*—the number of electromagnetic waves per centimetre. This term has units of reciprocal centimetres (cm^{-1}).

4. Summary of Test Method

4.1 *Sampling*—Stationary source effluent is extracted from the stack or duct at a constant rate, filtered and conditioned (if required), and transported to the FTIR gas cell for analysis. For sampling hot/wet sample effluent, all sample extraction and measurement system components shall be maintained at temperatures that prevent sample condensation. If sample conditioning is used, then the condenser system (or other device) should minimize the contact between the condensed water vapor and the effluent.

4.2 *Analysis*—Stationary source effluent is directed to the Fourier transform infrared (FTIR) spectrometer gas cell. Individual compounds in the effluent absorb characteristic infrared radiation that is proportional to their concentration. The FTIR system identifies and quantifies multiple compounds simultaneously.

NOTE 1—An FTIR interferometer modulates the polychromatic infrared source so that individual wavelengths in the infrared beam can be differentiated. This is accomplished using a beam splitter which divides the infrared radiation emanating from the source, and forces the two beams to traverse two separate paths (one of which remains constant while the other changes length with time using a moving mirror or other device). The two beams are recombined at the beam splitter to produce a variable phase difference between the two infrared beams. It is the responsibility of the tester to develop or employ the appropriate analytical algorithms (see Annex A7).

NOTE 2—The modulated infrared radiation produced by the interferometer is focused through the gas absorption cell containing the sample to be analyzed. A single interferometer scan is defined as the detector response over the time required to perform a single interferometer motion (that is, allowing the moving mirror or other device to traverse its minimum to maximum path length). Co-addition of numerous sequential interferometer scans produces an averaged interferogram with higher signal-to-noise than a single scan alone.

NOTE 3—A Fourier transform of these data convert them from an interferogram to a single beam infrared spectrum. Transmittance or absorbance double beam spectra are produced by ratioing the single beam spectrum to the background absorbance spectrum. Target analytes are identified and quantified by (*1*) visual inspection of the infrared spectra (*2*) comparing sample spectra to infrared reference spectra and (*3*) computer identification and quantification of infrared spectral patterns using classical least squares or other comparable techniques.

4.3 *Quality Assurance*—Calibration standard gases, and nitrogen or zero air (system blanks) must be analyzed directly by the FTIR instrumentation and through the entire sampling system at the beginning and at the end of each test day to ensure measurement system integrity. Specific QA/QC procedures are detailed in Annex A1-Annex A8.

5. Significance and Use

5.1 The FTIR measurements provide for multicomponent on-site analysis of source effluent.

5.2 This test method provides the volume concentration of detected analytes. Converting the volume concentration to a mass emission rate using a particular compound's molecular weight, and the effluent volumetric flow rate, temperature and pressure is useful for determining the impact of that compound to the atmosphere.

5.3 Known concentrations of target analytes are spiked into the effluent to evaluate the sampling and analytical system's effectiveness for transport and quantification of the target analytes, and to ensure that the data collected are meaningful.

5.4 The FTIR measurement data are used to evaluate process conditions, emissions control devices, and for determining compliance with emission standards or other applicable permits.

5.5 Data quality objectives for each specific testing program must be specified and outlined in a test plan (Annex A1). Supporting data are available from ASTM Headquarters Request RR: D22–1027.

6. Interferences

6.1 *Analytical (Spectral) Interferences*—Analytical interferences occur when the target analyte infrared absorbance features overlap with those of other components present in the sample gas matrix.

NOTE 4—These interferences can make detection of the target analytes difficult or impossible depending upon the strength (concentration relative to the target analyte(s)) of the interfering absorption features. High

concentrations of interferents (such as water vapor and CO_2) can absorb so strongly in the target analyte(s) analysis region that quantification of the target analytes may be prohibited. In many cases, interferences may be overcome using the appropriate analytical algorithms.

6.2 *Sampling System Interferences*—Sampling system interferences occur when target analytes are not transported fully to the instrumentation when compounds damage the measurement system components, or when the sampling system outgases the target analytes or interfering compounds.

NOTE 5—Condensed water, reactive particulate matter, adsorptive sites within the sampling system components, and reactive gases are examples of such potential sampling system interferences. Specific provisions and performance criteria are included in this test method to detect the presence of sampling system interferences.

7. Apparatus

7.1 *Analytical Instrumentation*:

7.1.1 *Fourier Transform Infrared (FTIR) Spectrometer*, with gas absorption cell (having either an adjustable or fixed path length), interferometer response time, and signal-to-noise ratio that are sufficient to perform the analysis called for in the data quality objectives. The FTIR gas cell must have provisions to monitor the pressure and temperature of the contained sample gas.

7.1.2 *Computer/Data Acquisition System*, with compatible FTIR software for control of the FTIR system, acquisition of the infrared data, and analysis of the resulting spectra. This system must have also adequate hard disk storage to archive all necessary data, and back-up media storage.

7.2 *Sampling System*:

7.2.1 *Sampling Probe*, glass, stainless steel or other appropriate material of sufficient length and physical integrity to sustain heating, prevent adsorption of analytes, and to reach the gas sampling point.

7.2.2 *Calibration Assembly*, to introduce calibration standards into the sampling system at the probe outlet, upstream of the primary particulate filter.

NOTE 6—If condensation could occur, then provisions must be made to deliver the calibration standards at the same temperature as that of the effluent samples.

7.2.3 *Particulate Filters*, (recommended) rated at 0.3 µm, placed immediately after the heated probe and after the sample condenser system.

7.2.4 *Pump*, leak-free, with heated head, capable of maintaining an adequate sample flow rate (typically 15 L/min).

7.2.5 *Sampling Line*, heated to prevent sample condensation, made of stainless steel, TFE-fluorocarbon, or other material that minimizes adsorption of analytes, and of minimal length to reach the sampling point(s) of concern.

7.2.6 *Sample Conditioning System*, (if used) a refrigeration unit, permeation dryer, or other device capable of reducing the moisture of the sample gas to a level acceptable for analysis.

NOTE 7—Additional sample conditioning components such as a CO_2 scrubber may be also required to quantify certain analytes at low concentration levels.

7.2.7 *Sample Flow Rotameters*, capable of withstanding sample gas and measurement conditions, calibrated according to Practice D 3195, or equivalent.

7.3 *Auxiliary Equipment*:

7.3.1 *Calibration Gas Manifold*, capable of delivering nitrogen or calibration gases through the sampling system or directly to the instrumentation. The calibration gas manifold should have provisions to (*1*) provide for accurate dilution of the calibration gases as necessary (*2*) to monitor calibration gas pressure and (*3*) introduce analyte spikes into the sample stream (before the particulate filter) at a precise and known flowrate.

7.3.2 *Mass Flow Meters or Controllers*, (optional) with a stated accuracy and calibrated range (for example ±2 % of scale from 0 to 500 mL/min or 0 to 5 L/min) appropriate for the concentrations of calibration or spike gases, or both. Calibrate using Practice D 3195 or equivalent.

7.3.3 *Digital Bubble Meter (or equivalent)*, NIST-traceable with an accuracy of ±2 % of reading, with an adequate range to calibrate the mass flow meters, controllers and rotameters at the specific flow rates (within ±10 %) required to perform the method.

7.3.4 *Tubing*, TFC 316 stainless steel or other inert material, of suitable diameter and length.

7.3.5 *Gas Regulators*, appropriate for individual gas cylinders, constructed of materials that minimize adsorption of analytes.

8. Reagents and Materials

8.1 *Calibration Standards*, compressed gases, permeation tubes and so forth, certified for the CTS measurements (2 % accuracy), instrument calibrations and for conducting analyte spiking (2 % to 10 %).

8.2 *High Purity (HP) Nitrogen or Zero Air*, for collection of FTIR background, for purging sample lines and sampling system components, for diluting sample and calibration gas, and for conducting blank measurements.

8.3 *Liquid Nitrogen (if required)*, for cooling quantum detectors.

9. Hazards

9.1 *Target Analytes*—Many of the compounds that will be analyzed using this test method are toxic and carcinogenic. Therefore, avoid exposure to these chemicals. Because some of the calibration standards are contained in compressed gas cylinders, exercise appropriate safety precautions to avoid accidents in their transport and use.

9.2 *Sampling Location*—This test method may involve sampling at locations having a high positive or negative pressure, high temperatures, elevated heights, or high concentrations of hazardous or toxic pollutants.

9.3 *Mobile or Remote Laboratory*—To avoid exposure to hazardous pollutants and to protect personnel in the laboratory, perform a leak check of the sampling system and inspect the sample exhaust equipment before sampling the calibration standards or effluent. Properly vent the exhaust gases.

10. Reference Spectra

10.1 Prepare or acquire reference spectra for all of the target analytes and interfering compounds that are expected in the source effluent. (Follow the procedures detailed in Annex A3 for preparation and acquisition of reference spectra.)

11. Procedure

11.1 Complete the procedures identified in Annex A1-Annex A3.

11.2 *Pretest Preparations and Evaluations*:

11.2.1 *Pre-Test*—Determine the sampling system performance in the laboratory in accordance with procedures detailed in Annex A4, Annex A5, and Annex A6 before conducting any field-testing. The procedures in these annexes need only be conducted once before any testing using this measurement system. Thereafter, these procedures are to be conducted during the testing. Results from these annexes should be kept with the measurement system so that system performance can be determined relative to past performance.

11.2.2 Measure and record the following:

11.2.2.1 The system pathlength using the CTS (Annex A4),

11.2.2.2 The sampling system mechanical response time using the CTS (Annex A4),

NOTE 8—The analytical algorithm results from the system pathlength check and from the sampling system mechanical response time check should agree to within 5 %.

11.2.2.3 The sampling system response time for the target analytes or similar compound (Annex A4),

11.2.2.4 The time required to achieve a system zero after exposure to the analytes (Annex A4),

11.2.2.5 The sampling system recovery for the analytes or similar compounds using the analyte spiking technique (Annex A5),

11.2.2.6 The noise equivalent absorbance (Annex A6), and

11.2.2.7 The selected water vapor frequency position and instrument resolution (Annex A6). Water vapor and instrument resolution band positions can be selected by the tester, but must remain constant so that instrument stability may be demonstrated.

11.3 *Field Sampling and Analysis*:

Conduct the calculations as detailed in Annex A2 for the particular test matrix.

11.3.1 *Flow Rate and Moisture Determination*—If effluent volumetric flow rates are required, perform EPA Methods 1 through 3. Determine the source effluent moisture content to within 2 % using the FTIR analytical algorithm, Method 4, wet-bulb dry-bulb measurements, saturation calculations, or other applicable means.

NOTE 9—If the moisture content of the flue gas is greater than appropriate for the instrument, condition the gas sample before introduction into the FTIR analyzer.

11.3.2 *Sample Interface Preparation*—Assemble the sampling system.

11.3.2.1 Allow the sample interface system components to reach stable operating temperatures and flow rates.

11.3.2.2 Conduct a sample interface leak check. This procedure is not mandatory if a system mechanical response time check is conducted in the field (see Annex A4.5).

NOTE 10—Conduct the leak check under the same pressure or partial vacuum conditions identical to the conditions anticipated during a test. Operate the sampling system at a constant flow rate during the entire test.

11.3.3 *FTIR Background*—Flow nitrogen or zero air through the FTIR gas cell directly.

11.3.3.1 Acquire a background spectrum (*Io*) according to manufacturers's instructions. Use the same gas cell conditions (that is, temperature, pressure, and pathlength) as used for sample analysis. Use the same number (or greater) of interferometer scans as that used during sample analysis.

11.3.4 *Pre-Test Calibration Transfer Standard (CTS)*—Flow the calibration transfer standard gas through the FTIR gas cell, Analyze the CTS gas and verify the results are within 5 % of the certified value.

11.3.5 *System Recovery*—Perform the analyte spiking procedure for the selected analytes according to procedures detailed in Annex A5.

11.3.5.1 Analyze and verify that the analyte recoveries are within the stated test data quality objectives for accuracy before proceeding.

11.3.5.2 Record the measurement results and percent recovery for each of the spiked analytes.

11.3.6 *System Zero Analysis*—Flow nitrogen or zero air through the entire sampling system.

11.3.6.1 Analyze the gas sample and record the time required for the measured concentrations of residual calibration gases to fall to 5 % of their original value or to a value that is acceptable to initiate sampling.

11.3.7 *Acquire FTIR Spectra*—Extract effluent sample gas for a period equal to or greater than the system response time before acquiring the first FTIR sample spectrum.

NOTE 11—Extract the effluent continuously between successive sample analysis to ensure constant equilibration within the sample interface system.

11.3.7.1 Obtain the requisite number of co-added interferometer scans and save data to a unique file name.

11.3.8 *Sample Analysis*—Analyze the sample spectra according to procedures outlined in Annex A7.

11.3.8.1 Identify and quantify the concentrations of the target analytes according to Section 12.

11.3.9 *Test Run*—Typical test run durations are 60 min unless otherwise specified in the test plan.

11.3.9.1 For test run durations longer than 60 min, continue to acquire and analyze additional samples.

11.4 *Post-test CTS*—At the end of each test, (or at the end of each day) flow the calibration transfer standard gas through the FTIR gas cell.

11.4.1 Analyze the CTS gas and verify that the pathlength results agree to within 5 % of the certified value of the CTS. Record the measurement results.

NOTE 12—If the results do not agree to within 5 % of the expected value, then the results from the run may be suspect. Identify and include the source of error in the test report.

11.5 *Data Storage*—Identify all samples with a unique file name.

11.5.1 Save the most fundamental data practical (interferograms or single beam spectra) for a period that is determined by the test program (that is, for one to five years).

11.5.2 Ensure that appropriate sample information (for example, sample pressure, temperature, and cell path length and so forth) is included in the header record of the data file, or otherwise saved, so that it may be correlated with the data. Storage of data files to backup media is recommended.

12. Calculations – Data Quantification

12.1 Prepare a computer analysis program or set of programs (for example, classical least squares, partial least squares, inverse least squares, and so forth) that contain all target analytes and interferences, appropriate for the anticipated effluent conditions. Follow procedures detailed in Annex A7.

NOTE 13—The analytical algorithm program(s) shall perform the analyses for all test plan specified analytes and interferents based upon the selected analytical infrared absorbance regions and the reference spectra to be used for quantification.

12.2 Calculate the MDC following the procedures identified in Annex A2.

12.3 Report the specific target analyte and interferent concentrations based upon the specific reference absorption path length, temperature, and pressure.

12.4 Report the error estimated for the measurement values based upon residual absorbance or other appropriate statistical means (follow procedures detailed in Annex A2).

13. Post Test QA/QC

13.1 Conduct the procedures detailed in Annex A8.

14. Reporting

14.1 Report the concentration results for the target analytes provided by the FTIR analysis.

14.1.1 Include also the minimum detectable concentration and the associated error of the measurement for each analyte.

14.1.2 The temperature, pressure, and pathlength of the FTIR gas sample cell, and

14.1.3 The source of the reference spectra used to prepare the analytical algorithm.

14.2 Include in the test report the results of all CTS analyses, the results of all analyte spiking runs and the results of all test method QA/QC activities conducted. Use the table format in Fig. A4.1 or similar.

14.3 Include records of the manufacturer's certificates of analysis for calibration transfer standards and all other calibration and analyte-spiking standards used during the test.

15. Precision and Bias

15.1 *Data Quality Objectives*—A statement of the overall test data quality objectives must be included in each test plan (see Annex A1).

15.1.1 In general, an accuracy of ±20 % and a precision of ±10 % for each measurement value should be possible when procedures detailed in this standard are followed. In practice, an accuracy of 10 % and precision of 5 % are routinely achieved.

16. Keywords

16.1 Fourier transform infrared spectroscopy; stack gas analysis; stationary source

ANNEXES

(Mandatory Information)

A1. TEST PLAN REQUIREMENTS

A1.1 The purpose of the test plan is to define the test objectives in terms of required data quality objectives. The data quality requirements are determined by the end use of the data. For example, qualitative data are sufficient in many cases where determining the presence or absence of compounds is desired. Other test scenarios, however, require quantitative results with a known degree of accuracy.

A1.2 The following are required for inclusion in all FTIR test plans: (*1*) a statement of the test data quality objectives (*2*) the number of test runs that will be conducted and their duration (*3*) the averaging period(s) for each sample spectrum collected during each test run, (*4*) the results provided by Annex A4 (Fig. A4.1 provides an example format), and (*5*) the results provided by Annex A2.

A1.3 The form in Fig. A1.1 (or similar) must be included in each test plan.

A1.4 Additional information that should be included in the test plan are (*1*) a generalized facility specific process description and airflow schematic (*2*) a schematic of the sampling system (*3*) the sampling location pressure, temperature, and approximate volumetric flow rate (*4*) the percent moisture and CO_2 content of the effluent (these can be estimated) (*5*) the height from grade or the approximate distance from the sampling location to the mobile laboratory or analytical system location and (*6*) any health and safety concerns.

Compounds	Infrared Analysis Region	Expected Concentration Range	Measurement System Achievable Minimum Detectable Concentrations (Annex 2)	Required Measurement System Accuracy and Precision for Test Application
Target Analytes				
Interfering Compounds				

FIG. A1.1 Test Specific Target Analytes and Data Quality Objectives

A2. DETERMINATION OF FTIR MEASUREMENT SYSTEM MINIMUM DETECTABLE CONCENTRATIONS (MDC) AND OVERALL CONCENTRATION UNCERTAINTIES

A2.1 Determination of FTIR Measurement System Minimum Detectable Concentration

A2.1.1 The minimum detectable concentration (MDC) for each target analyte in the sample matrix must be determined before and after the test program using the methods described below.

NOTE A2.1—The FTIR extractive measurement system MDC for each target analyte is a function of the three main components: 1) instrument noise, 2) analytical algorithm error, and 3) sampling system influences.

NOTE A2.2—The instrument noise is the most fundamental noise and includes only the FTIR instrument itself. The analytical algorithm error consists of the error imparted on the "true value" of the measurement by the software and use of reference spectra to analyze the data. The sampling system influences are defined by the ability of the sample probe, heated extractive sample line and other associated components to deliver the target analytes to the instrumentation.

A2.2 Pre-Test Estimate of Instrument Noise-Limited Minimum Detectable Concentration. MDC#1

A2.2.1 Measure the Noise Equivalent Absorbance (NEA) in each of the regions used for analysis according to Section A6.1. Determine the RMS value of NEA for analyte m in its analysis region in accordance with:

$$NEA_{rms}^{m} = \sqrt{\frac{1}{n}\sum_{j=1}^{N_m}(NEA_i^m)^2} \quad \text{(A2.1)}$$

where:

N = the number of absorbance points in the *analysis region* for analyte m, and

NEA_i^m = the individual absorbance values of the noise spectrum in the *analysis region* used for analyte m.

A2.2.2 Convert the $NEA_{rms}{}^{m}$ for each of the analytes to a noise limited concentration using:

$$MDC\#1 = \frac{NEA_{rms}^{m}}{REF_{rms}^{m}} * \frac{C_{ref} * L_{ref}}{L_{cell}} \quad \text{(A2.2)}$$

where:

$MDC\#1$ = the noise limited minimum detectable concentration for analyte m (ppm),

$NEA_{rms}{}^{m}$ = the root mean square absorbance value obtained on the reference spectrum for the same analysis region as used in evaluating A2.1,

C_{ref} = is the concentration that was used in generating the reference spectrum for analyte m,

L_{ref} = is the path length that was used in generating the reference spectrum of analyte m, and

L_{cell} = is the path length of the cell which is to be used to perform the measurements.

NOTE A2.3—The instrument noise defines the lower boundary for the measurement system MDC. The actual measurement system MDC will be above this value. See Note A2.2 above.

A2.3 Pre-Test Estimate of Analytical Algorithm Error Minimum Detectable Concentrations. MDC#2 & MDC#3

NOTE A2.4—Depending on the type of data readily available before the test, MDC#2 or MDC#3 can be used in place of MDC#1.

NOTE A2.5—MDC#2 (A2.3.1) requires a set of spectra closely approximating the test matrix but void of the analytes of interest (blank samples with major interferents present). MDC#3 (A2.3.2) requires data similar to the expected measurement stream of the emission source where the major analytes and interferences are present.

NOTE A2.6—Spectra should be actual measured spectra, but can be generated "synthetically" by adding appropriate reference spectra if needed.

NOTE A2.7—If synthetic spectra are used in this application, the reference spectra used to prepare the synthetic spectrum can not be the same as those used in the analytical algorithm. The synthetic spectra must be comprised of distinct linear combinations of independent spectra.

A2.3.1 Determine the analytical algorithm error by using blank samples representative of the actual source to be tested. (MDC#2)

NOTE A2.8—The spectra representing the sample matrix must include all significant interferences at optical depths of at least 90 % of the maximum optical depth anticipated in the actual sample, but should exclude the target analytes. The set of spectra should span the variations anticipated in these interferents in the actual sample.

A2.3.1.1 Quantify the blank samples using the analytical algorithm that will be used to quantify the field test data.

NOTE A2.9—The analytical algorithm should be able to produce both positive and negative analyte concentrations.

A2.3.1.2 Quantify the concentration for each field test target analyte using a minimum of eight independent spectra, and calculate the mean in accordance with the following equation:

$$C_{ave}^{m} = \frac{1}{P}\sum_{p=1}^{P} C_{p}^{m} \tag{A2.3}$$

where:

$C_{ave}{}^{m}$ = average concentration for analyte m representing the Analytical Bias for this compound,
P = number of sample spectra used, and
$C_{p}{}^{m}$ = concentration results produced by the analytical algorithm for target analyte m on spectrum p of the set.

NOTE A2.10—This method produces the average analytical algorithm error. Ideally, this number should be zero because the target analytes are not present in these spectra.

A2.3.1.3 Refine the analytical algorithm until the is as close to zero as possible for each target analyte.

A2.3.1.4 Calculate the pre-test MDC#2 using the following equation:

$$MDC_2\,[ppm] = 3\sqrt{\frac{1}{P}\sum_{p=1}^{P}(C_{ave}^{m} - C_{p}^{m})^2} \tag{A2.4}$$

NOTE A2.11—This number is three times the root mean square deviation ($3 \times \mathrm{RMS}^{D}$) for each target analyte.

A2.3.2 Determine the analytical algorithm error using residual equivalent absorbance, MDC#3.

NOTE A2.12—This MDC estimate is evaluated in an identical manner as the noise limited detection of A2.2, but is based on the residual equivalent absorbance (REA) in the spectra.

NOTE A2.13—The residual equivalent absorbance (REA) is the absorbance left after the analysis routines have accounted for all analytes (absorbances) in the spectrum. Many Classical Least Square (CLS) algorithms return this residual spectrum directly. If not, it can be obtained through manual subtraction of the reference spectra as discussed below.

NOTE A2.14—The spectral residual is also used by most CLS algorithms to produce the reported standard error. In many cases the CLS errors returned for each analyte averaged over the set of test spectra can be used as MDC#3.

A2.3.2.1 Select a set of spectra representative of the source to be tested.

A2.3.2.2 Generate the spectral residual in each analysis region using the gas concentrations produced by the analytical algorithm to be used for data analysis.

A2.3.2.3 If the analytical algorithm does not produce a residual value after analysis, generate residual values by using a scaling factor. Scale each reference spectrum to the value returned by the analytical algorithm and subtract this scaled reference spectrum from the data spectrum. The scaling factor for each reference spectrum will be:

$$\left(\frac{C_d}{C_r}\right)*\left(\frac{L_d}{L_r}\right)*\left(\frac{P_d}{P_r}\right)*\left(\frac{T_r}{T_d}\right) \tag{A2.5}$$

where: subscript d represents a data spectrum value and subscript r represents a reference spectrum value, and

C = the gas concentration in the spectrum,
L = the path length used in generating the spectrum,
P = the gas pressure used in generating the spectrum, and
T = the absolute gas temperature used in generating the spectrum.

A2.3.2.4 Analyze the residual spectra using the methods of A2.2, but replacing the Noise Equivalent Absorbance (NEA) with the Residual Equivalent Absorbance (REA). The equations corresponding to Eq A2.1 and Eq A2.2 are then:

$$REA_{rms}^{m} = \sqrt{\frac{1}{N}\sum_{j=1}^{N_m}(REA_i^m)^2} \tag{A2.6}$$

and

$$MDC\#3 = \frac{REA_{rms}^{m}}{REF_{rms}^{m}} * \frac{C_{ref} * L_{ref}}{L_{cell}} \tag{A2.7}$$

Here all terms are as in Eq A2.1 and Eq A2.2, but with REA being the residual spectrum absorbance and the corresponding minimum detectible concentration for analyte m from the residual spectra. If a number of test spectra are analyzed the average value for each analyte is used.

A2.4 Field Verification of MDC—Measurement System Minimum Detectable Concentration

A2.4.1 If the target analytes were not measured above the system noise, and the measurement system detection limit must be known to satisfy regulatory or other requirements use the analyte spiking procedure contained in Annex A5.

A2.4.2 Spike the target analytes in question at an equivalent in-stack concentration that approximates two to three-times the estimated MDC#2 or MDC#3 value (whichever used).

A2.4.3 Quantify the spiked effluent concentration and determine the measurement system MDC using the REA of the analysis and Eq A2.7.

A2.5 Post Test Estimates of Detection Limit

A2.5.1 Conduct the procedures identified in A2.3.2 on actual field test data.

A3. FTIR REFERENCE SPECTRA

A3.1 If commercially prepared, or other available reference libraries are transferred and used to quantify data, then the FTIR spectral resolution and line position (see Annex Annex A6), gas cell path length, temperature and pressure, and the apodization function must be known for these library spectra. The resolution, line position, and apodization function used for collection of field spectral data must be the same as the reference spectra used to quantify the gas concentration(s). Appropriate corrections for sample temperature, pressure, and path length must be made also when using such references to quantify field spectra.

A3.2 Preparation of instrument specific reference spectra must be conducted using certified calibration standards, NIST traceable standards, or other primary standards having a certified analysis.

A3.3 When preparing instrument specific reference spectra, determine the reference gas cell absorption path length required to produce spectra of the required optical depth.

A3.3.1 Select a calibration transfer standard. Ethylene and Freon 22 have been used successfully; however, use of Freon 22 should be minimized especially when venting to the atmosphere.

NOTE A3.1—The calibration transfer standard (CTS) shall be certified to 2 % analytical accuracy or better, and must be analyzed before acquiring each series of reference spectra to provide a path length marker to the series.

A3.3.2 Record the interferogram or single beam absorbance spectrum of the certified CTS gas mixture while flowing the gas continuously through the gas cell.

A3.3.3 Determine the reference cell absorption path length as follows. Record the temperature, pressure, and concentration of the gas used in A3.3.2, as well as the manufacturer's nominal absorption path length, the nominal spectral resolution, and the CTS signal integration period. Calculate the reference cell absorption path length according to the following equation:

$$Lr = Lf(Tr/Tf)\,(Pf/Pr)\,(Cf/Cr)\,\{Ar/Af\} \quad \text{(A3.1)}$$

where:

Lr = reference cell absorption path length,
Lf = fundamental CTS absorption path length,
Tr = absolute temperature of reference CTS gas,
Tf = absolute temperature of fundamental CTS gas,
Pr = absolute pressure of reference CTS gas,
Pf = absolute pressure of fundamental CTS gas,
Cr = concentration of the reference CTS gas,
Cf = concentration of the fundamental CTS gas, and
$\{Ar/Af\}$ = ratio of the reference CTS absorbance to the fundamental CTS absorbance, determined by classical least squares, integrated absorbance area, spectral subtraction, or peak absorbance techniques.

NOTE A3.2—If integrated absorbance areas or peak absorbance techniques are employed in determining the ratio {Ar/Af}, all spectra used in the determination must be corrected beforehand for baseline offset and slope.

NOTE A3.3—Fundamental CTS spectra should be either 1) NIST-traceable or 2) recorded using a NIST-traceable standard gas and an absorption cell whose path length has been measured using a laser and/or a suitably accurate physical measurement device. An operational definition of "fundamental CTS spectra" is provided in 3.2.

NOTE A3.4—Eq A3.1 holds to 10 % only to within the ranges $0.85 \leq (Tr/Tf) \leq 1.15$ and $0.85 \leq (Pf/Pr) \leq 1.15$ for many compounds. If such gas density corrections are applied outside of this range, verify that the all anticipated data quality objectives for each analyte compound can still be met.

NOTE A3.5—To reduce possible errors associated with absorbance (convolution) non-linearities, it is recommended that the products (Lr Cr) and (Lf Cf) differ by no more than a factor of two.

A3.3.4 Record the reference absorption spectra of the certified standard gases of the desired analyte. Flow the standard gas continuously through the absorption cell during these measurements.

NOTE A3.6—Acquire the requisite number of interferometer scans to achieve the signal-to-noise ratio required to meet all anticipated data quality objectives.

A3.3.5 Document the details of the mathematical process by which the reference spectra are generated from each interferogram, including the apodization function. Record also the gas pressure and temperature, certified standard concentrations, reference absorption path length, nominal spectral resolution, and signal integration period.

A3.4 It is required that spectra be available for multiple concentration levels for each target analyte. The maximum optical depth reported for any analyte in a sample spectrum may not exceed the maximum optical depth represented by the reference spectra for that analyte. The accuracy of the entire reference spectrum set must be demonstrated by application of the analytical algorithm described in Annex A7 (see Section A.7.5).

NOTE A3.7—It is advantageous to develop a large number of reference spectra over a large range of optical depths. This practice tends to reduce analytical errors related to convolution and detector non-linearities.

NOTE A3.8—For accurate low concentration measurements, low concentration level reference spectra must be included in the analytical algorithm.

A4. REQUIRED PRE-TEST PROCEDURES

A4.1 Pre-test procedures shall be conducted at least once before any FTIR emissions testing. The procedures are recommended also before testing at each *new source*. A new source is defined to be one that has a sample matrix (interferents), and target analytes that differ substantially from previously tested sources.

A4.2 Follow the procedures defined in 11.3.2 and 11.3.3 (sample interface equilibration and background I_o acquisition).

A4.3 Conduct a system zero by directing nitrogen or zero air through the entire sampling system including the primary particulate matter filter.

NOTE A4.1—This procedure is necessary to prove the absence of sample transport line or other measurement system component contamination. The presence of large CO_2 or H_2O infrared spectral bands will be indicative of system leakage.

A4.4 Determine the sample cell absorption path length as follows. Direct the sample CTS gas directly through the sample absorption cell and acquire its absorbance spectrum. Record the temperature, pressure, and concentration of the sample CTS gas, as well manufacturer's nominal absorption path length, the nominal spectral resolution, and the signal integration period. Calculate the sample cell path absorption lengthin accordance with the following equation:

$$Ls = Lr(Ts/Tr)\,(Pr/Ps)\,(Cr/Cs)\,\{As/Ar\} \quad \text{(A4.1)}$$

where:

Ls	=	sample cell absorption path length,
Lr	=	reference CTS absorption path length,
Ts	=	absolute temperature of sample CTS gas,
Tr	=	absolute temperature reference CTS gas,
Ps	=	absolute pressure of sample CTS gas,
Pr	=	absolute pressure of reference CTS gas,
Cs	=	concentration of the sample CTS gas,
Cr	=	concentration of the reference CTS gas, and
{As/Ar}	=	ratio of the sample CTS absorbance to the reference CTS absorbance, determined by classical least squares, integrated absorbance area, spectral subtraction, or peak absorbance techniques.

NOTE A4.2—If integrated absorbance areas or peak absorbance measures are employed in determining the ratio {As /Ar}, all spectra used in the determination should be corrected beforehand for baseline offset and slope.

NOTE A4.3—The optical depth of the reference CTS spectrum should be derived from a fundamental CTS spectrum. Fundamental CTS spectra should be either 1) NIST-traceable or 2) recorded using a NIST-traceable standard gas and an absorption cell whose path length has been measured using a laser and/or a suitably accurate physical measurement device. An operational definition of "fundamental CTS spectra" is provided in 3.2.

NOTE A4.4—Eq A4.1 holds to 10 % only to within the ranges $0.85 \leq (Ts/Tr) \leq 1.15$ and $0.85 \leq (Pr/Ps) \leq 1.15$ for many compounds. If such gas density corrections are applied outside of this range, verify that the all anticipated data quality objectives for each analyte compound can still be met.

NOTE A4.5—To reduce possible errors associated with convolution non-linearities, it is recommended that the products (Ls Cs) and (Lr Cr) differ by no more than a factor of two.

NOTE A4.6—Acquire the requisite number of interferometer scans to achieve the signal-to-noise ratio required to meet all anticipated data quality objectives.

A4.5 Conduct a system mechanical response time test by directing the CTS gas through the entire sampling system including the primary particulate matter filter.

NOTE A4.7—The mechanical response time is the time required for the gas to equilibrate fully within the sampling system. It is a function of the length of sample transport line, the gas cell volume, and the flow-rate through the FTIR sample cell.

A4.5.1 Record the system mechanical response time (the time required to achieve 95 % of the full scale reading) and the identity of the gas used.

A4.6 Conduct a system equilibration response time test by directing the most reactive or adsorptive target analyte(s) through the entire sampling system including the primary particulate matter filter.

NOTE A4.8—This tests the time required to condition the line fully, and is expressed usually as the time required to achieve 95 % of the expected full-scale reading.

A4.6.1 Record the system equilibration response time and the identity and concentration of the gas used.

A4.7 Conduct a system recovery check using the analyte spiking technique (follow procedures listed in Annex A5).

A4.7.1 Record the identity and percent recovery of the spike gas.

NOTE A4.9—The most reactive target analyte(s) is specific for each particular testing situation. Use all of the target analytes may be cost prohibitive and may not be possible or necessary. It is the responsibility of the tester to determine what spike compounds are required or a particular testing situation.

A4.8 Conduct a second system zero by directing nitrogen or zero air through the entire sampling system including the primary particulate matter filter.

A4.8.1 Record data continuously until the sample spectra are absent of the spiked analytes (until 95 % of downscale reading is met).

NOTE A4.10—This procedure will determine the time required to achieve zero after exposing the system to the analyte(s).

A4.8.2 Record the time for the system zero after exposure to the analytes.

A4.9 Include Fig. A4.1, or similar in the test plan.

Parameter Measured	Gas	Concentration	Path Length	Equilibration Time	Dilution Factor	% Recovery
Path Length A4.4						
Mechanical Response Time A4.5						
System Response Time A4.6						
Analyte Spike Recovery A7.						
System Zero A4.8						

FIG. A4.1 Measurement System Capabilities

A5. ANALYTE SPIKING TECHNIQUE

A5.1 This procedure is conducted to determine the effectiveness of the sampling and analytical system for transporting and quantifying the target analytes.

A5.2 This procedure is conducted when the test data quality objectives require data acquisition of well-known accuracy.

A5.3 Collect effluent and obtain sample spectra to determine the native concentration of target analytes.

A5.4 Direct the analyte spike calibration gas into the FTIR gas cell only, and quantify the results using the analytical algorithm.

A5.5 Direct the analyte spiking standard into the sampling system with the sample conditioning apparatus in place (if used) and co-mix with the effluent (upstream of the particulate filter) at a known flowrate using calibrated mass flow meters, controllers, or rotameters.

NOTE A5.1—If a high concentration of acid gas or other compounds are present that react with the spike gas to form a solid particulate, such as addition of HCl into a stream containing high relative concentration of NH_3, it may be necessary to, use alternate filtration media (that is, TFE-fluorocarbon coated), maintain the sampling system close to the effluent temperature if possible, or monitor the reactive gas concentration level until spiking may be conducted. Many times analyte spiking criteria can not be achieved due to reactive gases at varying concentration levels. In these cases, an alternate spike gas should be used to demonstrate the effectiveness of the measurement system. This is needed when field verification of the measurement MDC is required as in A2.4.

NOTE A5.2—Calibration gas is co-mixed with ambient air (or humidified ambient air) during the pre-test laboratory study, and with actual source effluent during emissions testing.

A5.5.1 The flow ratio of calibration gas to ambient air or source effluent shall be no greater than 1:10 (one part calibration gas to ten parts total flow) for the determination of sample recovery. Flow ratios of less than 1:10 may be used also.

NOTE A5.3—Use of a tracer gas compound such as sulfur hexafluoride (SF_6) blended with the calibration standards at a known concentration allows for accurate quantification of the exact dilution factor (which negates the need to calibrate accurately the mass flow meters, controllers, and rotameters). It is important to use and to calibrate accurately the mass flow meters, mass flow controllers, and rotameters used during the procedure if a tracer compound is not present in the spike gas.

A5.5.2 The concentration of the resultant spiked gas should approximate the effluent concentration (or be within 50 %). For example, if the native concentration of the target analyte is 5 ppm, then approximately 5 ppm should be spiked into the effluent. The resultant concentration of the target analyte in the spiked effluent should then approximate 10 ppm. This is often difficult to accomplish due to (*1*) the uncertainty of the effluent concentration (many times unknown before the testing commences) (*2*) the available concentrations of certified calibration standards brought to the field (*3*) the calibration range of the mass flow controllers (*4*) the requirement that the spike flow to total flow ratio must not exceed 1:10.

A5.5.2.1 Therefore, for the 50 % criteria to be met, the level spiked into the effluent may be from 2.5 ppm to 7.5 ppm based upon a 5 ppm effluent concentration.

A5.5.2.2 If the concentration of the target analyte(s) is below the measurement system MDC, and the MDC must be verified in the field, spiking must be conducted at the lowest possible concentration level.

A5.5.2.3 Spike at a level that is approximately 2-3 times the MDC value provided in A2.4 for field verification of the actual system MDC.

A5.5.3 Allow the analyte spike to equilibrate fully before acquisition of the sample.

A5.5.4 Quantify the concentration of the target analytes using the analytical algorithm.

A5.6 Calculate the dilution factor of the calibration gas using either of the following two methods. The spike dilution factor is used to calculate the expected analyte concentrations in spiked flue gas.

$$DF = \{ SF_{6\ \text{spike results}} / SF_{6\ \text{direct results}} \} \quad \text{(A5.1)}$$

where:

DF = the dilution factor of the spike gas, should approximate 0.1 or less,

$_{\text{direct}}$ = the SF_6 concentration measured directly in undiluted spike gas, and

$_{\text{spike}}$ = the diluted SF_6 concentration measured in a spiked sample.

or alternately;

$$\text{DF} = \text{measured calibration gas flow / total system flow} \quad \text{(A5.2)}$$

Example: 0.1 lpm spike gas/(0.9 lpm stack gas + 0.1 lpm spike gas) = 0.1

A5.7 Determine the bias between the observed spike value and the expected response (that is, the equivalent concentration of the spiked material plus the analyte concentration adjusted for spike dilution) according to the following equation.

$$B = Sa - Udil - Cs \quad \text{(A5.3)}$$

where:

B = bias at spike level,

Sa = total concentration of the analytes in the spiked samples, and

$Udil$ = mean concentration of the native analyte(s) determined from analysis of the unspiked samples, and

CS = (certified concentration of calibration standards) × DF

NOTE A5.4—If the measured analyte concentration is equal to zero in the unspiked samples, then $Udil = 0$ in Eq 3. However, if a spiked analyte is present in the flue gas at a measurable concentration, then the bias, B, must be calculated accounting for the dilution of the native analyte component by the spike gas. Thus, for use in Eq 3, the unspiked concentration is converted to its diluted value in the spiked sample by the following equation.

$$Udil = Ua \times (1 - DF) \quad \text{(A5.4)}$$

where:

Ua = concentration of the analytes in the unspiked samples,

$Udil$ = concentration of analytes in spiked sample effluent accounting for dilution, and

DF = dilution factor from Eq 2.

Example:

Ua = 10 ppm,

DF = 0.1,

$Udil$ = 10 ppm (1-0.1), and

$Udil$ = 9 ppm.

A5.8 Calculate the percent recovery of the spiked analytes using the following equation.

$$\%R = \{\text{concentration observed}\}/\text{concentration expected}\} \times 100 \quad \text{(A5.5)}$$

where:

concentration observed = concentration of the individual analytes in the spiked sample calculated by the analytical algorithm, and

concentration expected = $Cs + Udil$.

Acceptable recoveries are defined by the test data quality objectives for accuracy. In general, spike recoveries within 30 % should be achievable when procedures detailed in the test method are followed.

A6. DETERMINATION OF SYSTEM PERFORMANCE PARAMETERS—NOISE EQUIVALENT ABSORBANCE (NEA), LINE POSITION, RESOLUTION, AND DETECTOR LINEARITY

A6.1 NEA

A6.1.1 Determine the absolute FTIR system NEA by flowing nitrogen or zero air through the gas sample cell. Collect a background spectrum and a sample spectrum in succession while continuously flowing nitrogen or zero air.

NOTE A6.1—Use the same averaging time for sample collection as that to be used during actual sample collection.

A6.1.2 Measure and record the peak to peak, and RMS noise in the resultant spectrum in the wavelength region(s) to be used for the target compound analysis.

A6.2 Line Position

A6.2.1 Determine the system line position by flowing ambient air through the gas sample cell and acquiring a spectrum. Determine and record the wavelength that corresponds to the maximum peak absorbance (line position) of water vapor in the region 1918 cm^{-1}, or from 3045 to 3050 cm^{-1} (or other suitable spectral region that remains consistent).

A6.2.2 Expand the isolated water vapor lines to fill the screen display, and superimpose a reference spectrum of water vapor that is used in the analytical algorithm. Visually inspect the two spectra to determine whether a shift in the line position has occurred. If the water vapor lines in the ambient air spectrum are shifted by more than 15 % of the instrumental resolution relative to the water vapor reference spectrum, corrective action may be necessary.

A6.3 Resolution

A6.3.1 Verify and record the system resolution by flowing ambient air through the gas sample cell, and allowing the pressure of the cell to stabilize at subatmospheric pressure (approximately 100 torr). Collect an absorbance spectrum and

measure the resolution at the ½ width and ½ maximum height of the water vapor lines in the region 1918 cm^{-1}, or from 3045 to 3050 cm^{-1} or other suitable region that remains constant.

A6.4 Detector Linearity

A6.4.1 Verify the detector function by measuring the CTS standard, or other representative standard at variable intensity. Use the expected test aperture setting, and one half and two times this setting to conduct the measurements. Compare the band areas of the three spectra.

A7. PREPARATION OF ANALYTICAL QUANTIFICATION ALGORITHM

A7.1 This procedures assumes that the FTIR operational software contains a classical least squares (or alternative) analytical algorithm designated for analysis of FTIR spectra. Manual quantification by subtraction and scaling techniques are not discussed (follow procedures detailed in Annex A8 for manual subtraction suggestions).

A7.2 Acquire reference spectra as described in Annex A3.

A7.3 Prepare the analytical algorithm for the specific target analytes as per manufacturers instructions.

A7.3.1 Include in the analytical algorithm reference spectra for all target analytes at concentrations approximating those in the anticipated sample matrix.

A7.3.2 Include in the analytical algorithm reference spectra for all known interferences at concentrations approximating those in the anticipated sample matrix.

NOTE A7.1—It is required that: A) more than one concentration level for each target analyte and interferent be included in the analytical algorithm, or B) the algorithm is linearized over the range of use, or C) the algorithm has been demonstrated to be linear. This is especially true for non-linear infrared absorbing compounds such as carbon monoxide, formaldehyde, or hydrochloric acid.

A7.4 Specify the analysis regions in the analytical algorithm to be used to quantify each target analyte.

NOTE A7.2—Select analysis regions having absorbance values of less than 1 (regions that are not opaque in the infrared), and that are void of the interfering compounds. In many cases this may prove difficult. It may be necessary to chose several small analysis regions where the target analyte absorbance is greater than the interfering compounds. It is helpful to include portions of the baseline in the analysis regions.

A7.5 Verify that the analytical algorithm functions properly by quantifying individual reference spectra that comprise the analytical algorithm. Determine the error of the analytical algorithm for the target analytes to ensure that the data quality objectives of the test.

A7.6 Determine the analytical accuracy of the algorithm by (*1*) the analyte spiking technique described in Annex A5 (*2*) comparison to measurements provided by other analytical techniques (*3*) analysis of *audit spectra* (*4*) tests of the algorithm using known mixtures (*5*) conducting an EPA Method 301 *validation* test

NOTE A7.3—If the FTIR analytical algorithm has been *validated* using EPA Method 301, then the previously determined accuracy and precision may be inferred to a new source provided that (*1*) the maximum optical depth for each analyte and interferent does not differ by more than 5 % of the optical depth encountered during the previous validation (a shorter pathlength or sample dilution may be used to meet this condition) (*2*) additional analytical interferences are not present which introduce absorbance bands greater than the expected absorbance of the minimum detectable analyte concentration in each analytical region and (*3*) the analysis temperature and pressure do not vary by more than 5 % from the conditions used during the previous validation.

NOTE A7.4—Transference of a validated algorithm to a new instrument requires that (*1*) the measured RMS noise is less than or equal to the RMS noise of the previous instrument and (*2*) the new instrument resolution meets or exceeds the resolution used during previous testing, and (*3*) the sampling system does not interfere with the measurement. The new instrument resolution must be within 115 % of the previous instrument in order to transfer the analytical algorithm.

A8. POST-TEST QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES

A8.1 Post-test QA/QC is aimed at spot checking the large data sets that can result from FTIR systems and confirming that the concentrations returned by the automated analytical algorithms are valid, within the stated test data quality objectives, and not influenced by interference. This is done through manual quantitation of select spectra.

A8.2 Select representative spectra for analysis from each test run.

NOTE A8.1—Select spectra that span the total run time, and that cover extremes of the measurement conditions (if these existed during testing).

A8.3 Conduct the procedures for determining line position, resolution, and noise levels in the spectra using procedures detailed in Annex A6.

A8.3.1 Verify that the line positions have not shifted by more than 15 % of the resolution, and the resolution has not changed by more than 15 % of that determined before testing.

A8.4 Select one spectrum that represents the run average and one spectrum that represents the run outlier target analyte concentrations.

A8.4.1 Obtain the difference spectrum of these two spectra.

A8.4.2 Manually compare the observed spectral features for the target analytes with those contained in the reference spectra and quantify the gas concentration(s) of the target analytes by;

comparison of integrated band areas, peak-to-peak comparisons or scaling techniques.

A8.4.3 Calculate the analyte concentration in the difference spectrum using the analytical algorithm and compare the manually calculated concentration of the difference spectrum to that calculated by the analytical algorithm.

A8.4.4 If the values are not within 20 % for A8.4.3 take corrective action by modifying the analytical algorithm appropriately, or using alternate reference spectra.

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