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

This standard is issued under the fixed designation D6348; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

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. Concentration results are provided. 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.

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

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1.5.4 Any sampling system interferences such as adsorption or outgassing.

1.6 Practices E168 and E1252 are suggested for additional reading.

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

1.8 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Additional safety precautions are described in Section 9.

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D3195 Practice for Rotameter Calibration

E168 Practices for General Techniques of Infrared Quantitative Analysis

E1252 Practice for General Techniques for Obtaining Infrared Spectra for Qualitative Analysis

2.2 *EPA Methods (40 CFR Part 60 Appendix A):*[3]

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 *Definitions*—See Terminology D1356 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**).[4]

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.

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

[3] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, http://www.access.gpo.gov.

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

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 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 *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.

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

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

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

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

3.2.36 *primary particulate matter filter, n*—filter of 0.3 microns or less to remove particulate matter and thus protect the sample interface. The analyte spike must be delivered upstream (that is, on the "dirty side") of the primary particulate matter filter (if used).

3.2.37 *reactive compounds, n*—compound(s) available in compressed gas form with a certified concentration within ±10 % accuracy. The compound is used as an overall surrogate for the test program target analytes for the purpose of conducting analyte spikes and for QA purposes. The test program manager, client, or regulator agency is responsible for determining the reactive compounds to be used for this purpose.

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

3.2.39 *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.

3.2.40 *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)**

3.2.41 *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.

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

3.2.43 *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.

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

3.2.45 *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.

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

3.2.47 *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.

3.2.48 *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.

3.2.49 *spectral intensity, n*—see *intensity*.

3.2.50 *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.

3.2.51 *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.

3.2.52 *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.

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

3.2.54 *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.

3.2.55 *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.

3.2.56 *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).[5]

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 D3195, 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

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D22-1027. Contact ASTM Customer Service at service@astm.org.

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 D3195 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 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