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

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, CO₂, 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 CO₂), 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
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: 2
D 1356 Terminology Relating to Sampling and Analysis of Atmospheres
D 3195 Practice for Rotameter Calibration
E 168 Practice for General Techniques of Infrared Quantitative Analysis
E 1252 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 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, \( A = -\log (I_n / I_0) \), 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 (I).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.
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).

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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.
4 The boldface numbers in parentheses refer to the list of references at the end of the standard.
3.2.18 Fourier transform, *n*—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 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, CO₂, or other spectrally interfering compounds before analysis.