EPA TEST METHOD 320

MEASUREMENT OF VAPOR PHASE ORGANIC AND INORGANIC EMISSIONS
BY EXTRACTIVE FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY
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1. Introduction
Persons unfamiliar with basic elements of FTIR spectroscopy should not attempt to use this method.
This method describes sampling and analytical procedures for extractive emission measurements using Fourier transform infrared (FTIR) spectroscopy. Detailed analytical procedures for interpreting infrared spectra are described in the "Protocol for the Use of Extractive Fourier Transform Infrared (FTIR) Spectrometry in Analyses of Gaseous Emissions from Stationary Sources," hereafter referred to as the "Protocol." Definitions not given in this method are given in Appendix A of the Protocol. References to specific sections in the Protocol are made throughout this Method. For additional information refer to references 1, 2, and other EPA reports, which describe the use of FTIR spectrometry in specific field measurement applications and validation tests. The sampling procedure described here is extractive. Flue gas is extracted through a heated gas transport and handling system. For some sources, sample conditioning systems may be applicable. Some examples are given in this method. Note: sample conditioning systems may be used providing the method validation requirements in Sections 9.2 and 13.0 are met.

1.0 Scope and Applicability.
1.1 Analytes. Analytes include hazardous air pollutants for which EPA reference spectra have been developed. Other compounds can also be measured with this method if reference spectra are prepared according to Section 4.6 of the EPA FTIR protocol.
1.2 Applicability. This method applies to the analysis of vapor phase organic or inorganic compounds which absorb energy in the mid-infrared spectral region, about 400 to 4000 cm⁻¹ (25 to 2.5 μm).

This method is for measuring compound-specific concentrations in a multi-component vapor phase sample, which is contained in a closed-path gas cell. Spectra of samples are collected using double beam infrared absorption spectroscopy. A computer program is used to analyze spectra and report compound concentrations.

1.3 Method Range and Sensitivity. Analytical range and sensitivity depend on the frequency-dependent analyte absorptivity, instrument configuration, data collection parameters, and gas stream composition. Instrument factors include: (a) spectral resolution, (b) interferometer signal averaging time, (c) detector sensitivity and response, and (d) absorption path length.
1.3.1 Range. For any optical configuration the analytical range is between the absorbance values of about .01 (infrared transmittance relative to the background = 0.98) and 1.0 (T = 0.1). (For absorbance > 1.0 the relation between absorbance and concentration may not be linear.)

The concentrations associated with this absorbance range depend primarily on the cell path
length and the sample temperature. An analyte absorbance greater than 1.0, can be lowered by decreasing the optical path length. Analyte absorbance increases with a longer path length. Analyte detection also depends on the presence of other species exhibiting absorbance in the same analytical region. Additionally, the estimated lower absorbance limit \( A = 0.01 \) depends on the RMSD noise in the analytical region.

The concentration range of this method is determined by the choice of optical configuration:

- The absorbance for a given concentration can be decreased by decreasing the path length or by diluting the sample. There is no practical upper limit to the measurement range.
- The analyte absorbance for a given concentration may be increased by increasing the cell path length or (to some extent) using a higher resolution. Both modifications also cause a corresponding increased absorbance for all compounds in the sample, and a decrease in the signal throughput. For this reason the practical lower detection range (quantitation limit) usually depends on sample characteristics such as moisture content of the flue gas, the presence of other interferants, and losses in the sampling system.

1.3.2 Sensitivity. The limit of sensitivity for an optical configuration and integration time is determined using Appendix D of the FTIR Protocol: Minimum Analyte Uncertainty, \( (MAU) \). The MAU depends on the RMSD noise in an analytical region, and on the absorptivity of the analyte in the same region.

1.4 Data Quality. Data quality is determined by executing FTIR Protocol pre-test procedures in appendices B to H and post-test procedures in appendices I and J.

Measurement objectives are established by the choice of detection limit \( (DL_i) \) and analytical uncertainty \( (AU_i) \) for each analyte.

An instrumental configuration is selected. Assumptions are made about the flue gas composition. These assumptions may be based on previous test data, data from a similar source or information gathered in a pre-test site survey. Spectral interferants are identified using the selected DL and AU, and band areas from reference spectra and interferant spectra. The baseline noise of the system is measured in each analytical region to determine the MAU of the instrument configuration for each analyte and interferant (MIU).

Data quality for the application is determined, in part, by measuring the RMS (root mean square) noise level in each analytical spectral region (Appendix C of the FTIR Protocol). The RMS noise is defined as the RMSD (root mean square deviation) of the absorbance values in an analytical region from the mean absorbance value in the region.

The MAU is the minimum analyte concentration for which the analytical uncertainty limit \( (AU_i) \) can be maintained; if the measured analyte concentration is less than MAU, then data quality are unacceptable.

2.0 Summary of Method.

2.1 Principle. References 4 - 7 provide background material on infrared spectroscopy and quantitative analysis. A summary is given here.

Infrared absorption spectroscopy is performed by directing an infrared beam through a sample to a detector. The frequency-dependent infrared absorbance of the sample is measured by comparing this detector signal (single beam spectrum) to a signal obtained without a sample in the beam path (background).

Most molecules absorb infrared radiation and the absorbance occurs in a characteristic and reproducible pattern. The infrared spectrum measures fundamental molecular properties and a
compound can be identified from its infrared spectrum alone. Within constraints, there is a linear relationship between infrared absorption and compound concentration. If this frequency dependent relationship (absorptivity) is known (measured), it can be used to measure compound concentration in a sample mixture.

Absorptivity is measured by preparing, in the laboratory, standard samples of compounds at known concentrations and measuring the FTIR "reference spectra" of these standard samples. These "reference spectra" are then used in sample analysis: (1) compounds are detected by matching sample absorbance bands with bands in reference spectra, and (2) concentrations are measured by comparing sample band intensities with reference band intensities.

This method is self-validating provided that the results meet the performance requirement of the QA spike in Sections 9.0 and 8.6.2, and results from a previous method validation study support the use of this method in the application.

2.2 Sampling and Analysis. In extractive sampling a probe assembly and pump are used to extract flue gas from the source duct and transport the sample to the FTIR gas cell. Typically, the sampling apparatus is similar to that used for single-component CEM measurements. The digitized infrared spectrum of the sample in the FTIR gas cell is measured and stored on a computer. Absorbance band intensities in the spectrum are related to sample concentrations by what is commonly referred to as Beer's Law.

\[ A_i = a_i b c_i \]

where

- \( A_i \) = absorbance at a given frequency of the \( i^{th} \) sample component.
- \( a_i \) = absorption coefficient (absorptivity) of the \( i^{th} \) sample component.
- \( b \) = path length of the cell.
- \( c_i \) = concentration of the \( i^{th} \) sample component.

Analyte spiking is used for quality assurance (QA). In this procedure (Section 8.6.2) an analyte is spiked into the gas stream at the back end of the sample probe. Analyte concentrations in the spiked samples are compared to analyte concentrations in unspiked samples. Since the concentration of the spike is known, this procedure can be used to determine if the sampling system is removing the spiked analyte(s) from the sample stream.

2.3 Reference Spectra Availability. Reference spectra of over 100 HAPs are available in the EPA FTIR spectral library on the EMTIC (Emission Measurement Technical Information Center) computer bulletin board service and at internet address http://info.arnold.af.mil/epa/welcome.htm. Reference spectra for HAPs, or other analytes, may also be prepared according to section 4.6 of the FTIR Protocol.

2.4 Operator Requirements. The FTIR analyst should be trained in setting up the instrumentation, verifying the instrument is functioning properly, and performing routine maintenance. The analyst must evaluate the initial sample spectra to determine if the sample matrix is consistent with pre-test assumptions and if the instrument configuration is suitable. The analyst must be able to modify the instrument configuration, if necessary. The spectral analysis should be supervised by someone familiar with EPA FTIR Protocol procedures.

A technician trained in CEM test methods is qualified to install and operate the sampling
system. This includes installing the probe and heated line assembly, operating the analyte spike system, and performing moisture and flow measurements.

3.0 Definitions.

See Appendix A of the FTIR Protocol for definitions relating to infrared spectroscopy. Additional definitions are given below.

3.1 Analyte. A compound that the method is required to measure. The term "target analyte" is also used. This method is multi-component and a number of analytes can be targeted for a test.

3.2 Reference Spectrum. Infrared spectrum of an analyte prepared under controlled, documented, and reproducible laboratory conditions according to procedures in Section 4.6 of the FTIR Protocol. A library of reference spectra is used to measure analytes in gas samples.

3.3 Standard Spectrum. A spectrum that has been prepared from a reference spectrum through a (documented) mathematical operation. A common example is de-resolving of reference spectra to lower-resolution standard spectra (Protocol, Appendix K). Standard spectra, prepared by approved, and documented, procedures can be used as reference spectra for analysis.

3.4 Concentration. In this method concentration is expressed as a molar concentration, in ppm-meters, or in (ppm-meters)/K, where K is the absolute temperature (Kelvin). The latter units allow the direct comparison of concentrations from systems using different optical configurations or sampling temperatures.

3.5 Interferant. A compound in the sample matrix whose infrared spectrum overlaps with part of an analyte spectrum. The most accurate analyte measurements are achieved when reference spectra of interferants are used in the quantitative analysis with the analyte reference spectra. The presence of an interferant can increase the analytical uncertainty in the measured analyte concentration.

3.6 Gas Cell. A gas containment cell that can be evacuated. It is equipped with the optical components to pass the infrared beam through the sample to the detector. Important cell features include: path length (or range if variable), temperature range, materials of construction, and total gas volume.

3.7 Sampling System. Equipment used to extract sample from the test location and transport the sample gas to the FTIR analyzer. This includes sample conditioning systems.

3.8 Sample Analysis. The process of interpreting the infrared spectra to obtain sample analyte concentrations. This process is usually automated using a software routine employing a classical least squares (cls), partial least squares (pls), or K- or P- matrix method.

3.9 One hundred percent line. A double beam transmittance spectrum obtained by combining two background single beam spectra. Ideally, this line is equal to 100 percent transmittance (or zero absorbance) at every frequency in the spectrum. Practically, a zero absorbance line is used to measure the baseline noise in the spectrum.

3.10 Background Deviation. A deviation from 100 percent transmittance in any region of the 100 percent line. Deviations greater than ±5 percent in an analytical region are unacceptable (absorbance of 0.021 to -0.022). Such deviations indicate a change in the instrument throughput relative to the background single beam.

3.11 Batch Sampling. A procedure where spectra of discreet, static samples are collected. The gas cell is filled with sample and the cell is isolated. The spectrum is collected. Finally, the cell is evacuated to prepare for the next sample.

3.12 Continuous Sampling. A procedure where spectra are collected while sample gas is flowing through the cell at a measured rate.
3.13 Sampling resolution. The spectral resolution used to collect sample spectra.
3.14 Truncation. Limiting the number of interferogram data points by deleting points farthest from the center burst (zero path difference, ZPD).
3.15 Zero filling. The addition of points to the interferogram. The position of each added point is interpolated from neighboring real data points. Zero filling adds no information to the interferogram, but affects line shapes in the absorbance spectrum (and possibly analytical results).
3.16 Reference CTS. Calibration Transfer Standard spectra that were collected with reference spectra.
3.17 CTS Standard. CTS spectrum produced by applying a de-resolution procedure to a reference CTS.
3.18 Test CTS. CTS spectra collected at the sampling resolution using the same optical configuration as for sample spectra. Test spectra help verify the resolution, temperature and path length of the FTIR system.
3.19 RMSD. Root Mean Square Difference, defined in EPA FTIR Protocol, Appendix A.
3.20 Sensitivity. The noise-limited compound-dependent detection limit for the FTIR system configuration. This is estimated by the MAU. It depends on the RMSD in an analytical region of a zero absorbance line.
3.21 Quantitation Limit. The lower limit of detection for the FTIR system configuration in the sample spectra. This is estimated by mathematically subtracting scaled reference spectra of analytes and interferences from sample spectra, then measuring the RMSD in an analytical region of the subtracted spectrum.

Since the noise in subtracted sample spectra may be much greater than in a zero absorbance spectrum, the quantitation limit is generally much higher than the sensitivity. Removing spectral interferences from the sample or improving the spectral subtraction can lower the quantitation limit toward (but not below) the sensitivity.
3.22 Independent Sample. A unique volume of sample gas; there is no mixing of gas between two consecutive independent samples. In continuous sampling two independent samples are separated by at least 5 cell volumes. The interval between independent measurements depends on the cell volume and the sample flow rate (through the cell).
3.23 Measurement. A single spectrum of flue gas contained in the FTIR cell.
3.24 Run. A run consists of a series of measurements. At a minimum a run includes 8 independent measurements spaced over 1 hour.
3.25 Validation. Validation of FTIR measurements is described in Section 13.0. Validation is used to verify the test procedures for measuring specific analytes at a source. Validation provides proof that the method works under certain test conditions.
3.26 Validation Run. A validation Run consists of at least 24 measurements of independent samples. Half of the samples are spiked and half are not spiked. Length of the run is determined by the interval between independent samples.
3.27 Screening. Screening is used when there is little or no available information about a source. The purpose of screening is to determine what analytes are emitted and obtain information about important sample characteristics such as moisture, temperature, and interferences.

Screening results are semi-quantitative (estimated concentrations) or quantitative (identification only). Various optical and sampling configurations may be used. Sample
conditioning systems may be evaluated for their effectiveness in removing interferences. It is unnecessary to perform a complete run under any set of sampling conditions.

Spiking is not necessary. But spiking can be a useful screening tool for evaluating the sampling system, especially if a reactive or soluble analyte is used for the spike.

3.28 Emissions Test. An FTIR emissions test is performed according specific sampling and analytical procedures. These procedures, for the target analytes and the source, are based on previous screening and validation results.

Emission results are quantitative. A QA spike (Sections 8.6.2 and 9.2) is performed under each set of sampling conditions using a representative analyte. Flow, gas temperature and diluent data are recorded concurrently with the FTIR measurements to provide mass emission rates for detected compounds.

3.29 Surrogate. A surrogate is a compound that is used in a QA spike procedure (Section 8.6.2) to represent other compounds. The chemical and physical properties of a surrogate shall be similar to the compounds it is chosen to represent. Under given sampling conditions, usually a single sampling factor is of primary concern for measuring the target analytes: for example, the surrogate spike results can be representative for analytes that are more reactive, more soluble, have a lower absorptivity, or have a lower vapor pressure than the surrogate itself.

4.0 Interferences.

Interferences are divided into two classifications: analytical and sampling.

4.1 Analytical Interferences. An analytical interference is a spectral feature that complicates (in extreme cases may prevent) the analysis of an analyte.

Analytical interferences are classified as background or spectral interference.

4.1.1 Background Interference. This results from a change in throughput relative to the single beam background. It is corrected by collecting a new background and proceeding with the test. In severe instances the cause must be identified and corrected.

Potential causes include: (1) deposits on reflective surfaces or transmitting windows, (2) changes in detector sensitivity, (3) a change in the infrared source output, or (4) failure in the instrument electronics.

In routine sampling throughput may degrade over several hours. Periodically a new background must be collected, but no other corrective action will be required.

4.1.2 Spectral. This results from the presence of interfering compound(s) (interferant) in the sample. Interferant spectral features overlap analyte spectral features. Any compound with an infrared spectrum, including analytes, can potentially be an interferant. The Protocol measures absorbance band overlap in each analytical region to determine if potential interferants should be classified as known interferants (FTIR Protocol, Section 4.9 and Appendix B).

Water vapor and CO$_2$ are common spectral interferants. Both of these compounds have strong infrared spectra and are present in many sample matrices at high concentrations relative to analytes. The extent of interference depends on the (1) interferant concentration, (2) analyte concentration, and (3) the degree of band overlap.

Choosing an alternate analytical region can minimize or avoid the spectral interference. For example, CO$_2$ interferes with the analysis of the 670 cm$^{-1}$ benzene band. However, benzene can also be measured near 3000 cm$^{-1}$ (with less sensitivity).

4.2 Sampling System Interferences. These prevent analytes from reaching the instrument. The analyte spike procedure is designed to measure sampling system interference, if any.

4.2.1 Temperature. A temperature that is too low causes condensation of analytes or water
vapor. The materials of the sampling system and the FTIR gas cell usually set the upper limit of temperature.

4.2.2 Reactive Species. Anything that reacts with analytes. Some analytes, like formaldehyde, polymerize at lower temperatures.

4.2.3 Materials. Poor choice of material for probe, or sampling line may remove some analytes. For example, HF reacts with glass components.

4.2.4 Moisture. In addition to being a spectral interferant, Condensed moisture removes soluble compounds.

5.0 Safety. The hazards of performing this method are those associated with any stack sampling method and the same precautions should be followed.

Many HAPs are suspected carcinogens or present other serious health risks. Exposure to these compounds should be avoided in all circumstances. For instructions on the safe handling of any particular compound, refer to its material safety data sheet.

When using analyte standards, always insure that gases are properly vented and that the gas handling system is leak free. (Always perform a leak check with the system under maximum vacuum and, again, with the system at greater than ambient pressure.) Refer to Section 8.2 for leak check procedures.

This method does not address all of the potential safety risks associated with its use. Anyone performing this method must follow safety and health practices consistent with applicable legal requirements and with prudent practice for each application.

6.0 Equipment and Supplies. The equipment and supplies are based on the schematic of a sampling system shown in Figure 1. Either the batch or continuous sampling procedures may be used with this sampling system. Alternative sampling configurations may also be used, provided that the data quality objectives are met as determined in the post-analysis evaluation. Other equipment or supplies may be necessary, depending on the design of the sampling system or the specific target analytes.

6.1 Sampling Probe. Glass, stainless steel, or other appropriate material of sufficient length and physical integrity to sustain heating, prevent adsorption of analytes, and to transport analytes to the infrared gas cell.

Special materials or configurations may be required in some applications. For instance, high stack sample temperatures may require special steel or cooling the probe. For very high moisture sources it may be desirable to use a dilution probe.

6.2 Particulate Filters. A glass wool plug (optional) inserted at the probe tip (for large particulate removal) and a filter (required) rated for 99 percent removal efficiency at 1-micron (e.g., Balston) connected at the outlet of the heated probe.

6.3 Sampling Line/Heating System. Heated (sufficient to prevent condensation) stainless steel, Teflon, or other material inert to the analytes.

6.4 Gas Distribution Manifold. A heated manifold allowing the operator to control flows of gas standards and samples directly to the FTIR system or through sample conditioning systems. Usually includes heated flow meter, heated valve for selecting and sending sample to the analyzer, and a by-pass vent. This is typically constructed of stainless steel tubing and fittings, and high-temperature valves.

6.5 Stainless Steel Tubing. Type 316, appropriate diameter (e.g., 3/8 in.) and length for heated connections. Higher grade stainless may be desirable in some applications.

6.6 Calibration/Analyte Spike Assembly. A three way valve assembly (or equivalent) to introduce
analyte or surrogate spikes into the sampling system at the outlet of the probe upstream of the out-of-stack particulate filter and the FTIR analytical system.

6.7 Mass Flow Meters. These are used for measuring analyte spike flow. The MFM should be calibrated in the range of 0 to 5 L/min and be accurate to ± 2 percent (or better) of the flow meter span.

6.8 Gas Regulators. Appropriate for individual gas standards.

6.9 Teflon Tubing. Diameter (e.g., 3/8 in.) and length suitable to connect cylinder regulators to gas standard manifold.

6.10 Sample Pump. A leak-free pump (e.g., KNF), with by-pass valve, capable of producing a sample flow rate of at least 10 LPM through 100 ft of sample line. If the pump is positioned upstream of the distribution manifold and FTIR system, use a heated pump that is constructed from materials non-reactive to the analytes. If the pump is located downstream of the FTIR system, the gas cell sample pressure will be lower than ambient pressure and it must be recorded at regular intervals.

6.11 Gas Sample Manifold. Secondary manifold to control sample flow at the inlet to the FTIR manifold. This is optional, but includes a by-pass vent and heated rotameter.

6.12 Rotameter. A 0 to 20 LPM rotameter. This meter need not be calibrated.

6.13 FTIR Analytical System. Spectrometer and detector, capable of measuring the analytes to the chosen detection limit. The system shall include a personal computer with compatible software allowing automated collection of spectra.

6.14 FTIR Cell Pump. Required for the batch sampling technique, capable of evacuating the FTIR cell volume within 2 minutes. The pumping speed should allow the operator to obtain 8 sample spectra in 1 hour.

6.15 Absolute Pressure Gauge. Capable of measuring pressure from 0 to 1000 mmHg to within ± 2.5 mmHg (e.g., Baratron®).

6.16 Temperature Gauge. Capable of measuring the cell temperature to within ± 2°C.

6.17 Sample Conditioning. One option is a condenser system, which is used for moisture removal. This can be helpful in the measurement of some analytes. Other sample conditioning procedures may be devised for the removal of moisture or other interfering species. The analyte spike procedure of Section 9.2, the QA spike procedure of Section 8.6.2, and the validation procedure of Section 13 demonstrate whether the sample conditioning affects analyte concentrations. Alternatively, measurements can be made with two parallel FTIR systems; one measuring conditioned sample, the other measuring unconditioned sample.

Another option is diluting the sample. The dilution factor measurement must be documented and accounted for in the reported concentrations. An alternative to dilution is to lower the sensitivity of the FTIR system by decreasing the cell path length, or to use a short-path cell in conjunction with a long path cell to measure more than one concentration range.

7.0 Reagents and Standards.

7.1 Analyte(s) and Tracer Gas. Obtain a certified gas cylinder mixture of all the analyte(s) at concentrations (± 2 percent) near (in ppm-meter/K) the emission source levels. If practical, the analyte standard cylinder should also contain the tracer gas at a concentration which gives a measurable absorbance at a dilution factor of at least 10:1. Two ppm SF₆ is sufficient for a path length of 22 meters at 250°F.

7.2 Calibration Transfer Standard(s). Select the calibration transfer standards (CTS) according to section 4.5 of the FTIR Protocol. Obtain a NIST traceable gravimetric standard of the CTS (± 2
7.3 Reference Spectra. Obtain reference spectra for each analyte, interferant, surrogate, CTS, and tracer. If EPA reference spectra are not available, use reference spectra prepared according to procedures in Section 4.6 of the EPA FTIR Protocol.

8.0 Sampling and Analysis Procedure.

Three types of testing can be performed: (1) screening, (2) emissions test, and (3) validation. Each is defined in Section 3. Determine the purpose(s) of the FTIR test.

Test requirements include: (a) $A_{UL}$, $D_{UL}$, $O_{UL}$, $C_{MAX}$, and $t_{AN}$ for each, (b) potential interferants, (c) sampling system factors, e.g., $P_{min}$, $V_{SS}$, $L_{S}$, $P_{s}$, $T_{S}$, $t_{SS}$, MIL, fractional error, and (d) analytical regions, e.g., $m = 1$ to $M$, $F_{LM}$, $F_{CM}$, and $F_{UM}$, plus interferants, $F_{FU}$, $F_{FL}$, wavenumber range $F_{NU}$ to $F_{NL}$.

If necessary, sample and acquire an initial spectrum. From analysis of this preliminary spectrum determine a suitable operational path length.

Set up the sampling train as shown in Figure 1 or use an appropriate alternative configuration.

The following sections provide guidance on pre-test calculations in the EPA protocol, sampling and analytical procedures, and post-test protocol calculations.

8.1 Pretest Preparations and Evaluations. Using the procedure in section 4.0 of the FTIR Protocol, determine the optimum sampling system configuration for measuring the target analytes. Use available information to make reasonable assumptions about moisture content and other interferences.

8.1.1 Analytes. Select the required detection limit ($D_{UL}$) and the maximum permissible analytical uncertainty ($A_{UL}$) for each analyte (labeled from 1 to $i$). Estimate, if possible, the maximum expected concentration for each analyte, $C_{MAX}$. The expected measurement range is fixed by $D_{UL}$ and $C_{MAX}$ for each analyte ($i$).

8.1.2 Potential Interferants. List the potential interferants. This usually includes water vapor and $CO_{2}$, but may also include some analytes and other compounds.

8.1.3 Optical Configuration. Choose an optical configuration that can measure all of the analytes within the absorbance range of .01 to 1.0 (this may require more than one path length). Use Protocol sections 4.3 to 4.8 for guidance in choosing a configuration and measuring CTS.

8.1.4 Fractional Reproducibility Uncertainty (FRU). The FRU is determined for each analyte by comparing CTS spectra taken before and after the reference spectra were measured. The EPA paraxylene reference spectra were collected on 10/31/91 and 11/01/91 with corresponding CTS spectra "cts1031a," and "cts1101b." The CTS spectra are used to estimate the reproducibility (FRU) in the system that was used to collect the references. The FRU must be < $A_{UL}$.

The protocol Appendix E is used to calculate the FRU from CTS spectra. Figure 2 plots results for 0.25 cm$^{-1}$ CTS spectra in EPA reference library: $S_{1}$ (cts1101b- cts1031a), and $S_{2}$ [(cts1101b + cts1031a)/2]. The RMSD (SRMS) is calculated in the subtracted baseline, $S_{y}$, in the corresponding CTS region from 850 to 1065 cm$^{-1}$. The area (BAV) is calculated in the same region of the averaged CTS spectrum, $S_{y}$.

8.1.5 Known Interferents. Use Appendix B of the EPA FTIR Protocol.

8.1.6 Calculate the Minimum Analyte Uncertainty, MAU (Section 1.3.2 discusses MAU and protocol Appendix D gives the MAU procedure). The MAU for each analyte, $i$, and each analytical region, $m$, depends on the RMS noise.

8.1.7 Analytical Program. See FTIR Protocol, Section 4.10. Prepare computer program based on
the chosen analytical technique. Use as input reference spectra of all target analytes and expected interferents. Reference spectra of additional compounds should also be included in the program if their presence (even transient) in the samples is considered possible.

The program output should be in ppm (or ppb) and should be corrected for differences between the reference path length, \( L_R \), temperature, \( T_R \), and pressure, \( P_R \), and the conditions used for collecting the sample spectra. If sampling is performed at ambient pressure, then any pressure correction is usually small relative to corrections for path length and temperature, and may be neglected.

8.2 Leak-check.

8.2.1 Sampling System. A typical FTIR extractive sampling train is shown in Figure 1. Leak-check from the probe tip to pump outlet as follows: Connect a 0– to 250-mL/min rate meter (rotameter or bubble meter) to the outlet of the pump. Close off the inlet to the probe, and record the leak rate. The leak rate shall be \( \leq 200 \text{ mL/min} \).

8.2.2 Analytical System Leak-check. Leak check the FTIR cell under vacuum and under pressure (greater than ambient). Leak check connecting tubing and inlet manifold under pressure.

8.2.2.1 For the evacuated sample technique, close the valve to the FTIR cell, and evacuate the absorption cell to the minimum absolute pressure \( P_{min} \). Close the valve to the pump, and determine the change in pressure \( \Delta P_v \) after 2 minutes.

8.2.2.2 For both the evacuated sample and purging techniques, pressurize the system to about 100 mmHg above atmospheric pressure. Isolate the pump and determine the change in pressure \( \Delta P_p \) after 2 minutes.

8.2.2.3 Measure the barometric pressure, \( P_b \) in mmHg.

8.2.2.4 Determine the percent leak volume \( \% V_L \) for the signal integration time \( t_{SS} \) and for \( \Delta P_{max} \), i.e., the larger of \( \Delta P_v \) or \( \Delta P_p \), as follows:

\[
\% V_L = 50 \frac{t_{SS} \Delta P_{max}}{P_{SS}}
\]

where 50 = 100% divided by the leak-check time of 2 minutes.

8.2.2.5 Leak volumes in excess of 4 percent of the FTIR system volume \( V_{SS} \) are unacceptable.

8.3 Detector Linearity. Once an optical configuration is chosen, use one of the following procedures to verify that the detector response is linear.

If detector response is not linear, decrease aperture, or attenuate the infrared beam. After a change in the instrument configuration perform a linearity check until it is demonstrated that the detector response is linear.

8.3.1 Vary the power incident on the detector by modifying the aperture setting. Measure the background and CTS at three instrument aperture settings: (1) at the aperture setting to be used in the testing, (2) at one half this aperture and (3) at twice the proposed testing aperture. Compare the three CTS spectra. CTS band areas should agree to within the uncertainty of the cylinder standard and the RMSD noise in the system.

If test aperture is the maximum aperture, collect CTS spectrum at maximum aperture, then close the aperture to reduce the IR throughput by half. Collect a second background and CTS at the smaller aperture setting and compare the spectra as above.

8.3.2 Use neutral density filters to attenuate the infrared beam. Set up the FTIR system as it will be used in the test measurements. Collect a CTS spectrum. Use a neutral density filter to
attenuate the infrared beam (either immediately after the source or the interferometer) to approximately 1/2 its original intensity. Collect a second CTS spectrum. Use another filter to attenuate the infrared beam to approximately 1/4 its original intensity. Collect a third background and CTS spectrum. Compare the CTS spectra as above.

8.3.3 Observe the single beam instrument response in a frequency region where the detector response is known to be zero. Verify that the detector response is "flat" and equal to zero in these regions.

8.4 Data Storage Requirements. All field test spectra shall be stored on a computer disk and a second backup copy must stored on a separate disk. The stored information includes sample interferograms, processed absorbance spectra, background interferograms, CTS sample interferograms and CTS absorbance spectra. Additionally, documentation of all sample conditions, instrument settings, and test records must be recorded on hard copy or on computer medium. Table 1 gives a sample presentation of documentation.

8.5 Background Spectrum. Evacuate the gas cell to • 5 mmHg, and fill with dry nitrogen gas to ambient pressure (or purge the cell with 10 volumes of dry nitrogen). Verify that no significant amounts of absorbing species (for example water vapor and CO₂) are present. Collect a background spectrum, using a signal averaging period equal to or greater than the averaging period for the sample spectra. Assign a unique file name to the background spectrum. Store two copies of the background interferogram and processed single-beam spectrum on separate computer disks (one copy is the back-up).

8.5.1 Interference Spectra. If possible, collect spectra of known and suspected major interferences using the same optical system that will be used in the field measurements. This can be done on-site or earlier. A number of gases, e.g. CO₂, SO₂, CO, NH₃, are readily available from cylinder gas suppliers.

Water vapor spectra can be prepared by the following procedure. Fill a sample tube with distilled water. Evacuate above the sample and remove dissolved gasses by alternately freezing and thawing the water while evacuating. Allow water vapor into the FTIR cell, then dilute to atmospheric pressure with nitrogen or dry air. If quantitative water spectra are required, then follow the reference spectrum procedure for neat samples (protocol, Section 4.6). Often, interference spectra need not be quantitative, but for best results the absorbance must be comparable to the interference absorbance in the sample spectra.

8.6 Pre-Test Calibrations

8.6.1 Calibration Transfer Standard. Evacuate the gas cell to • 5 mmHg absolute pressure, and fill the FTIR cell to atmospheric pressure with the CTS gas. Alternatively, purge the cell with 10 cell volumes of CTS gas. (If purge is used, verify that the CTS concentration in the cell is stable by collecting two spectra 2 minutes apart as the CTS gas continues to flow. If the absorbance in the second spectrum is no greater than in the first, within the uncertainty of the gas standard, then this can be used as the CTS spectrum.) Record the spectrum.

8.6.2 QA Spike. This procedure assumes that the FTIR method has been validated for at least some of the target analytes at the source.

For emissions testing perform a quality assurance spike. Use a certified standard, if possible, of an analyte, which has been validated at the source. One analyte standard can serve as a QA surrogate for other analytes which are less reactive or less soluble than the standard.

Perform the spike procedure of Section 9.2. Record spectra of at least three independent (Section 3.22) spiked samples. Calculate the spiked component of the analyte concentration.
the average spiked concentration is within 0.7 to 1.3 times the expected concentration, then proceed with the testing. If applicable, apply the correction factor from the Method 301 validation test (not the result from the QA spike).

8.7 Sampling.

If analyte concentrations vary rapidly with time, CEM sampling is preferable using the smallest cell volume, fastest sampling rate and fastest spectra collection rate possible.

CEM sampling requires the least operator intervention even without an automated sampling system. For continuous monitoring at one location over long periods, CEM sampling is preferred.

Batch sampling and continuous static sampling are used for screening and performing test runs of finite duration. Either technique is preferred for sampling several locations in a matter of days.

Batch sampling gives reasonably good time resolution and insures that each spectrum measures a discreet (and unique) sample volume.

Continuous static (and CEM) sampling provide a very stable background over long periods. Like batch sampling, continuous static sampling also insures that each spectrum measures a unique sample volume.

It is essential to pass the leak check procedure under vacuum (Section 8.2) to use the batch sampling procedure. It is essential to pass the leak check under positive pressure to use the continuous static or CEM sampling procedures.

Each sampling technique is described below.

8.7.1 Batch Sampling. Evacuate the absorbance cell to • 5 mmHg absolute pressure. Fill the cell with flue gas to ambient pressure, isolate the cell, and record the spectrum. Before taking the next sample, evacuate the cell until no spectral evidence of sample absorption remains. Repeat this procedure to collect 8 spectra of separate samples in 1 hour.

8.7.2 Continuous Static Sampling. Purge the FTIR cell with 10 cell volumes of sample gas. Isolate the cell, collect the spectrum of the static sample and record the pressure. Before measuring the next sample, purge the cell with 10 more cell volumes of sample gas.

8.7.3 Continuous (CEM) Sampling. See Performance Specification 15 for FTIR CEMs (40 CFR, Part 60, Appendix B).

8.8 Sampling QA and Reporting.

8.8.1 Sample integration times should be sufficient to achieve the required signal-to-noise ratio. Obtain an absorbance spectrum by filling the cell with N₂. Measure the RMSD in each analytical region in this absorbance spectrum. Verify that the number of scans used is sufficient to achieve the target MAU.

8.8.2 Assign a unique file name to each spectrum.

8.8.3 Store two copies of sample interferograms and processed spectra on separate computer disks.

8.8.4 For each sample spectrum, document the sampling conditions, the sampling time (while the cell was being filled), the time the spectrum was recorded, the instrumental conditions (path length, temperature, pressure, resolution, signal integration time), and the spectral file name. Keep a hard copy of these data sheets.

8.9 Signal Transmittance. While sampling, monitor the signal transmittance. If signal transmittance (relative to the background) changes by 5 % (absorbance = -.02 .02) in any analytical spectral region, obtain a new background spectrum.

8.10 Post-test CTS. After the sampling run, record another CTS spectrum.
8.11 Post-test QA.
8.11.1 Inspect the sample spectra immediately after the run to verify that the gas matrix composition was close to the expected (assumed) gas matrix.
8.11.2 Verify that the sampling and instrumental parameters were appropriate for the conditions encountered. For example, if the moisture is much greater than anticipated, it may be necessary to use a shorter path length or dilute the sample.
8.11.3 Compare the pre- and post-test CTS spectra. The peak absorbance in pre- and post-test CTS must be ± 5 percent of the mean value. See Appendix E of the FTIR Protocol.

9.0 Quality Control.

Use analyte spiking (Sections 8.6.2, 9.2 and 13.0) to verify the sampling system can transport the analytes from the probe to the FTIR system.

9.1 Spike Materials. Use a certified standard (accurate to ± 2 percent) of the target analyte, if one can be obtained.

If a certified standard cannot be obtained, follow the procedures in Section 4.6.2.2 of the EPA FTIR Protocol.

9.2 Spiking Procedure. Quality Assurance (QA) spiking (Section 8.6.2) is a calibration procedure used before testing. QA spiking involves following the spike procedure below to obtain at least three spiked samples. The analyte concentrations in the spiked samples are compared to the expected spike concentration to verify that the sampling system is working properly. Usually, when QA spiking is used, the method has already been validated at a similar source for the analyte in question. The QA spike demonstrates that the validated sampling conditions are being duplicated. If the QA spike fails then the sampling system shall be repaired before testing proceeds.

The method validation procedure (Section 13.0) involves a more extensive use of the analyte spike procedure below. Spectra of at least 12 independent spiked and 12 independent unspiked samples are recorded. The concentration results are analyzed statistically to determine if there is a systematic bias in the method for measuring a particular analyte. If there is a systematic bias, within the limits allowed by Method 301, then a correction factor is applied to the analytical results. If the systematic bias is greater than the allowed limits, then the method is not valid and cannot be used.

9.2.1 Introduce the spike/tracer gas at a constant flow rate of
- 10 percent of the total sample flow. (Note: Use the rotameter at the end of the sampling train to estimate the required spike/tracer gas flow rate.) Use a flow device, e.g., mass flow meter (± 2%), to monitor the spike flow rate. Record the spike flow rate every 10 minutes.

9.2.2 Determine the response time (RT) of the system; continuously collect spectra of the spiked effluent until the spectrum of the spiked component is constant for 5 minutes. The RT is the interval from the first measurement until the spike becomes constant. Wait for 2 × RT, then collect spectra of two independent spiked samples gas. Duplicate analyses of the spiked concentration shall be within 5 percent of the mean of the two measurements.

9.2.3 Calculate the dilution ratio using the tracer gas as follows:

\[ DF = \frac{SF_{6(\text{direct})}}{SF_{6(\text{spike})}} \]
\[ CS = \frac{SF_{6(\text{spike})}}{SF_{6(\text{direct})}} \]

\[ CS = \frac{DF}{DF} \]
where

\[
\begin{align*}
\text{DF} & = \text{Dilution factor of the spike gas; this value shall be } \cdot 10. \\
\text{SF}_{6\text{dir}} & = \text{SF}_6 \text{ (or tracer gas) concentration measured directly in undiluted spike gas.} \\
\text{SF}_{6\text{spk}} & = \text{Diluted SF}_6 \text{ (or tracer gas) concentration measured in a spiked sample.} \\
\text{Spike}_{\text{dir}} & = \text{Concentration of the analyte in the spike standard measured by filling the FTIR cell directly.} \\
\text{CS} & = \text{Expected concentration of the spiked samples.}
\end{align*}
\]

10.0 Calibration and Standardization.
10.1 Signal-to-Noise Ratio (S/N). The RMSD in the noise must be less than one tenth of the minimum analyte peak absorbance in each analytical region. For example if the minimum peak absorbance is 0.01 at the required DL, then RMSD measured over the entire analytical region must be \( \cdot 0.001 \).
10.2 Absorbance Path length. Verify the absorbance path length by comparing reference CTS spectra to test CTS spectra. See Appendix E of the FTIR Protocol.
10.3 Instrument Resolution. Measure the line width of appropriate test CTS band(s) to verify instrument resolution. Alternatively, compare CTS spectra to a reference CTS spectrum, if available, measured at the nominal resolution.
10.4 Apodization Function. In transforming the sample interferograms to absorbance spectra use the same apodization function that was used in transforming the reference spectra.
10.5 FTIR Cell Volume. Evacuate the cell to \( \cdot 5 \text{ mmHg} \). Measure the initial absolute temperature \((T_i)\) and absolute pressure \((P_i)\). Connect a wet test meter (or a calibrated dry gas meter), and slowly draw room air into the cell. Measure the meter volume \((V_m)\), meter absolute temperature \((T_m)\), and meter absolute pressure \((P_m)\), and the cell final absolute temperature \((T_f)\) and absolute pressure \((P_f)\). Calculate the FTIR cell volume \(V_{SS}\), including that of the connecting tubing, as follows:

\[
V_{SS} = V_m \frac{P_m}{T_m} \left[ \frac{P_f}{T_f} - \frac{P_i}{T_i} \right]
\]

11.0 Data Analysis and Calculations.

Analyte concentrations shall be measured using reference spectra from the EPA FTIR spectral library. When EPA library spectra are not available, the procedures in Section 4.6 of the Protocol shall be followed to prepare reference spectra of all the target analytes.
11.1 Spectral De-resolution Reference spectra can be converted to lower resolution standard spectra (Section 3.3) by truncating the original reference sample and background interferograms. Appendix K of the EPA FTIR Protocol gives specific deresolution procedures.

Deresolved spectra shall be transformed using the same apodization function and level of zero filling as the sample spectra. Additionally, pre-test FTIR protocol calculations (e.g., FRU, MAU, FCU) shall be performed using the de-resolved standard spectra.
11.2 Data Analysis Various analytical programs are available for relating sample absorbance to a concentration standard. Calculated concentrations shall be verified by analyzing residual
baselines after mathematically subtracting scaled reference spectra from the sample spectra. A full description of the data analysis and calculations is contained in the FTIR Protocol (sections 4.0, 5.0, 6.0 and appendices).

Correct calculated concentrations in sample spectra for differences in absorption path length and temperature between the reference and sample spectra by

\[ C_{corr} = \left( \frac{L_r}{L_s} \right) \left( \frac{T_s}{T_r} \right) C_{calc} \]

where:

- \( C_{corr} \) = Concentration, corrected for path length.
- \( C_{calc} \) = Concentration, initial calculation (output of the analytical program designed for the compound).
- \( L_r \) = Reference spectra path length.
- \( L_s \) = Sample spectra path length.
- \( T_s \) = Absolute temperature of the sample gas, K.
- \( T_r \) = Absolute gas temperature of reference spectra, K.

12.0 Method Performance.

12.1 Spectral Quality. Refer to the FTIR Protocol appendices for analytical requirements, evaluation of data quality, and analysis of uncertainty.

12.2 Sampling QA/QC. The analyte spike procedure of Section 9, the QA spike of Section 8.6.2, and the validation procedure of Section 13 are used to evaluate the performance of the sampling system and to quantify sampling system effects, if any, on the measured concentrations.

This method is self-validating provided that the results meet the performance requirement of the QA spike in Sections 9.0 and 8.6.2 and results from a previous method validation study support the use of this method in the application.

Several factors can contribute to uncertainty in the measurement of spiked samples. The following list suggests some factors which can be controlled to provide better accuracy in the spiking procedure.

- Flow meter. An accurate mass flow meter is accurate to ± 1 % of its span. If a flow of 1 LPM is monitored with such a MFM, which is calibrated in the range of 0-5 LPM, then the flow measurement has an uncertainty of 5 %. This may be improved by re-calibrating the meter at the specific flow rate to be used.

- Calibration gas. Usually the calibration standard is certified to within ± 2 %. With reactive analytes, such as HCl, the certified accuracy in a commercially available standard may be no better than ± 5 %.

- Temperature. Temperature measurements of the cell should be quite accurate. If practical, it is preferable to measure sample temperature directly, by inserting a thermocouple into the cell chamber instead of monitoring the cell outer wall temperature.

- Pressure. Depends on the accuracy of the barometer. But fluctuations in pressure throughout a day may be as much as 2.5 % with weather variations.

13.0 Method Validation Procedure.

This validation procedure, which is based on EPA Method 301 (40 CFR Part 63, Appendix A), may be used to validate this method for the analytes in a gas matrix. Validating at one source may also apply to another type of source, if it can be shown that the flue gas characteristics are similar at both sources.
Section 5.3 of Method 301, the Analyte Spike procedure, is used with the modifications below. The statistical analysis of the results follows Section 6.3 of EPA Method 301. Section 3 of this method defines terms that are not defined in Method 301.

- The analyte spike is performed dynamically. This means the spike flow is continuous and constant as spiked samples are measured.
- The spike gas is introduced at the back of the sample probe.
- Spiked effluent is carried through all sampling components downstream of the probe.
- A single FTIR system (or more) may be used to collect and analyze spectra (not quadruplicate integrated sampling trains).
- All of the validation measurements are performed sequentially in a single “run” (Section 3.26).
- The measurements analyzed statistically are each independent (Section 3.22).
- A validation data set can consist of more than 12 spiked and 12 unspiked measurements.

13.1 Batch Sampling. Either procedure may be used. Section 13.1.1 may be used for stable processes. If process emissions are highly variable, the procedure in Section 13.1.2 is suggested. 13.1.1 With a single FTIR instrument and sampling system begin by collecting spectra of two unspiked samples. Introduce the spike flow into the sampling system and allow 10 cell volumes to purge the sampling system and FTIR cell. Collect spectra of two spiked samples. Turn off the spike and allow 10 cell volumes of unspiked sample to purge the FTIR cell. Repeat this procedure until the 24 (or more) samples are collected.

In batch sampling, collect spectra of 24 distinct samples. (Each distinct sample consists of filling the cell to ambient pressure after the cell has been evacuated.)

13.1.2 Alternatively, a separate probe assembly, line, and sample pump can be used for spiked sample. Verify and document that sampling conditions are the same in both the spiked and the unspiked sampling systems. This can be done by wrapping both sample lines in the same heated bundle. Keep the same flow rate in both sample lines.

Measure samples in sequence in pairs. After two spiked samples are measured, evacuate the FTIR cell, and turn the manifold valve so that spiked sample flows to the FTIR cell. Allow the connecting line from the manifold to the FTIR cell to purge thoroughly (the time depends on the line length and flow rate). Collect a pair of spiked samples. Repeat the procedure until at least 24 measurements are completed.

13.2 Simultaneous Measurements With Two FTIR Systems. If unspiked effluent concentrations of the target analyte(s) vary significantly with time, it may be desirable to perform synchronized measurements of spiked and unspiked sample.

Use two FTIR systems, each with its own cell and sampling system to perform simultaneous spiked and unspiked measurements. The optical configurations should be similar, if possible. The sampling configurations shall be the same. One sampling system and FTIR analyzer measures spiked effluent. The other sampling system and FTIR analyzer measures unspiked flue gas.

Both systems shall use the same sampling procedure (i.e., batch or continuous).

13.2.1 If batch sampling is used, synchronize the cell evacuation, cell filling, and collection of spectra. Fill both cells at the same rate (in cell volumes per unit time).

13.2.2 In continuous sampling, adjust the sample flow through each gas cell so that the same number of cell volumes pass through each cell in a given time (i.e. \( T_{C_1} = T_{C_2} \) in reference 8). For specific FTIR CEM procedures See reference 8.

13.3 Statistical Treatment. The statistical procedure of EPA Method 301, Section 6.3 is used to
evaluate the bias and precision. 

For FTIR testing a validation "run" is defined as spectra of 24 independent samples, 12 of which are spiked with the analyte(s) and 12 of which are not spiked. 

13.3.1 Bias. Determine the bias (defined by EPA Method 301, Section 6.3.2) as follows:

\[
B = S_m - M_m - CS
\]

where

- \( B \) = Bias at spike level.
- \( S_m \) = Mean concentration of the analyte spiked samples.
- \( M_m \) = Mean concentration of the unspiked samples.
- \( CS \) = Expected concentration of the spiked samples (equation 4).

13.3.2 Correction Factor. Use Section 6.3.2.2 of EPA Method 301 to evaluate the statistical significance of the bias. If it is determined that the bias is significant, then use Section 6.3.3 of Method 301 to calculate a correction factor (CF). Analytical results of the test method are multiplied by the correction factor, if \( 0.7 \times CF \times 1.3 \). If it is determined that the bias is significant and \( CF > \pm 30 \% \), then the test method is considered to "not valid."

If measurements do not pass validation, evaluate the sampling system, instrument configuration, and analytical system to determine if improper set-up or a malfunction was the cause. If so, repair the system and repeat the validation.

14.0 Pollution Prevention.

The extracted sample gas is vented outside the enclosure containing the FTIR system and gas manifold after the analysis. In typical method applications the vented sample volume is a small fraction of the source volumetric flow and its composition is identical to that emitted from the source.

When analyte spiking is used, spiked pollutants are vented with the extracted sample gas. Approximately \( 1.6 \times 10^{-4} \) to \( 3.2 \times 10^{-4} \) lbs of a single HAP may be vented to the atmosphere in a typical validation run of 3 hours. (This assumes a molar mass of 50 to 100 g, spike rate of 1.0 LPM, and a standard concentration of 100 ppm). Minimize emissions by keeping the spike flow off when not in use.

15.0 Waste Management.

Small volumes of laboratory gas standards can be vented through a laboratory hood. Neat samples must be packed and disposed according to applicable regulations. Surplus materials may be returned to supplier for disposal.

16.0 References


Table 1. EXAMPLE PRESENTATION OF SAMPLING DOCUMENTATION.

<table>
<thead>
<tr>
<th>Sample Time</th>
<th>Spectrum File Name</th>
<th>Background File Name</th>
<th>Sample conditioning</th>
<th>Process condition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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</table>

Figure 1. Example of an extractive sampling system.

Figure 2. Plot of FRU results for p-xylene.