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DL and AU values along with calculated areas and MAU values using the protocol procedures.

TABLE 2—EXAMPLE PRE-TEST PROTOCOL CALCULATIONS

Protocol value	Form	Phenol	Methanol	Protocol appendix
Reference concentration ^a (ppm-meters)/K	3.016	3.017	5.064	
Reference Band Area	8.2544	16.6417	4.9416	B
DL (ppm-meters)/K	0.1117	0.1117	0.1117	B
AU	0.2	0.2	0.2	B
CL	0.02234	0.02234	0.02234	B
FL	2679.83	1131.47	1019.95	B
FU	2840.93	1231.32	1041.56	B
FC	2760.38	1181.395	1030.755	B
AAI (ppm-meters)/K	0.18440	0.01201	0.00132	B
RMSD	2.28E-03	1.21E-03	1.07E-03	C
MAU (ppm-meters)/K	4.45E-02	7.26E-03	4.68E-03	D
MAU (ppm at 22)	0.0797	0.0130	0.0084	D

^a Concentration units are: ppm concentration of the reference sample (ASC), times the path length of the FTIR cell used when the reference spectrum was measured (meters), divided by the absolute temperature of the reference sample in Kelvin (K), or (ppm-meters)/K.

2.0 Summary of Method**2.1 Principle**

2.1.1 Molecules are composed of chemically bonded atoms, which are in constant motion. The atomic motions result in bond deformations (bond stretching and bond-angle bending). The number of fundamental (or independent) vibrational motions depends on the number of atoms (N) in the molecule. At typical testing temperatures, most molecules are in the ground-state vibrational state for most of their fundamental vibrational motions. A molecule can undergo a transition from its ground state (for a particular vibration) to the first excited state by absorbing a quantum of light at a frequency characteristic of the molecule and the molecular motion. Molecules also undergo rotational transitions by absorbing energies in the far-infrared or microwave spectral regions. Rotational transition absorbencies are superimposed on the vibrational absorbencies to give a characteristic shape to each rotational-vibrational absorbance "band."

2.1.2 Most molecules exhibit more than one absorbance band in several frequency regions to produce an infrared spectrum (a characteristic pattern of bands or a "fingerprint") that is unique to each molecule. The infrared spectrum of a molecule depends on its structure (bond lengths, bond angles, bond strengths, and atomic masses). Even small differences in structure can produce significantly different spectra.

2.1.3 Spectral band intensities vary with the concentration of the absorbing compound. Within constraints, the relationship between absorbance and sample concentration is linear. Sample spectra are compared to reference spectra to determine the species and their concentrations.

2.2 Sampling and Analysis

2.2.1 Flue gas is continuously extracted from the source, and the gas or a portion of the gas is conveyed to the FTIR gas cell, where a spectrum of the flue gas is recorded. Absorbance band intensities are related to sample concentrations by Beer's Law.

$$A_v = \sum a_i b c_i \quad (6)$$

Where:

A_v = absorbance of the i^{th} component at the given frequency, v .

a = absorption coefficient of the i^{th} component at the frequency, v .

b = path length of the cell.

c = concentration of the i^{th} compound in the sample at frequency v .

2.2.2 After identifying a compound from the infrared spectrum, its concentration is determined by comparing band intensities in the sample spectrum to band intensities in "reference spectra" of the formaldehyde, phenol, methanol, COS and CO. These reference spectra are available in a permanent soft copy from the EPA spectral library on the EMTIC bulletin board. The source may also prepare reference spectra according to Section 4.5 of the FTIR Protocol.

NOTE: Reference spectra not prepared according to the FTIR Protocol are not acceptable for use in this test method. Documentation detailing the FTIR Protocol steps used in preparing any non-EPA reference spectra shall be included in each test report submitted by the source.

2.3 Operator Requirements. The analyst must have some knowledge of source sampling and of infrared spectral patterns to operate the sampling system and to choose a

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suitable instrument configuration. The analyst should also understand FTIR instrument operation well enough to choose an instrument configuration consistent with the data quality objectives.

3.0 Definitions

See Appendix A of the *FTIR Protocol*

4.0 Interferences

4.1 Analytical (or Spectral) Interferences. Water vapor. High concentrations of ammonia (hundreds of ppm) may interfere with the analysis of low concentrations of methanol (1 to 5 ppm). For CO, carbon dioxide and water may be interferants. In cases where COS levels are low relative to CO levels, CO and water may be interferants.

4.2 Sampling System Interferences. Water, if it condenses, and ammonia, which reacts with formaldehyde.

5.0 Safety

5.1 Formaldehyde is a suspected carcinogen; therefore, exposure to this compound must be limited. Proper monitoring and safety precautions must be practiced in any atmosphere with potentially high concentrations of CO.

5.2 This method may involve sampling at locations having high positive or negative pressures, high temperatures, elevated heights, high concentrations of hazardous or toxic pollutants, or other diverse sampling conditions. It is the responsibility of the

tester(s) to ensure proper safety and health practices, and to determine the applicability of regulatory limitations before performing this test method.

6.0 Equipment and Supplies

The equipment and supplies are based on the schematic of a sampling train shown in Figure 1. Either the evacuated or purged sampling technique may be used with this sampling train. Alternatives may be used, provided that the data quality objectives of this method are met.

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 reach gas sampling point.

6.2 Particulate Filters. A glass wool plug (optional) inserted at the probe tip (for large particulate removal) and a filter rated at 1-micron (e.g., Balston™) for fine particulate removal, placed immediately after the heated probe.

6.3 Sampling Line/Heating System. Heated (maintained at 250 ±25 degrees F) stainless steel, Teflon™, or other inert material that does not adsorb the analytes, to transport the sample to analytical system.

6.4 Stainless Steel Tubing. Type 316, e.g., $\frac{3}{8}$ in. diameter, and appropriate length for heated connections.

6.5 Gas Regulators. Appropriate for individual gas cylinders.

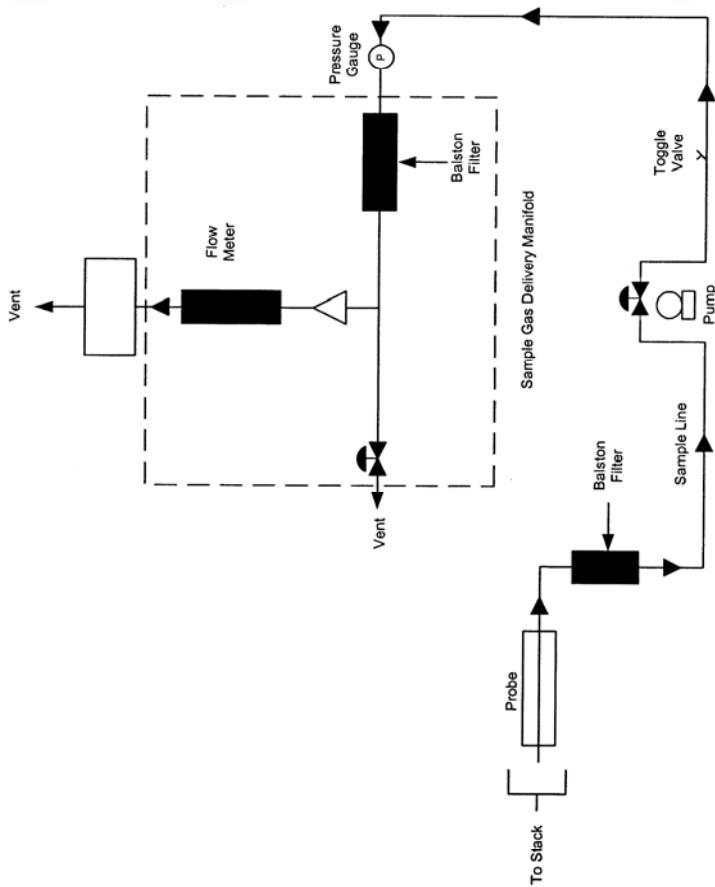


Figure 1. The extractive FTIR sampling system.

6.6 Teflon™ Tubing. Diameter (e.g., $\frac{3}{16}$ in.) and length suitable to connect cylinder regulators.

6.7 Sample Pump. A leak-free pump (e.g., KNF™), with by-pass valve, capable of pulling sample through entire sampling system at a rate of about 10 to 20 L/min. If placed before the analytical system, heat the pump and use a pump fabricated from materials non-reactive to the target pollutants. If the pump is located after the instrument, systematically record the sample pressure in the gas cell.

6.8 Gas Sample Manifold. A heated manifold that diverts part of the sample stream to the analyzer, and the rest to the by-pass discharge vent or other analytical instrumentation.

6.9 Rotameter. A calibrated 0 to 20 L/min range rotameter.

6.10 FTIR Analytical System. Spectrometer and detector, capable of measuring formaldehyde, phenol, methanol, COS and CO to the predetermined minimum detectable level. The system shall include a personal computer with compatible software that provides real-time updates of the spectral profile during sample collection and spectral collection.

6.11 FTIR Cell Pump. Required for the evacuated sampling technique, capable of evacuating the FTIR cell volume within 2 minutes. The FTIR cell pump should allow the operator to obtain at least 8 sample spectra in 1 hour.

6.12 Absolute Pressure Gauge. Heatable and capable of measuring pressure from 0 to 1000 mmHg to within ± 2.5 mmHg (e.g., Baratron™).

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

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7.0 Reagents and Standards

7.1 Ethylene (Calibration Transfer Standard). Obtain NIST traceable (or Protocol) cylinder gas.

7.2 Nitrogen. Ultra high purity (UHP) grade.

7.3 Reference Spectra. Obtain reference spectra for the target pollutants at concentrations that bracket (in ppm-meter/K) the emission source levels. Also, obtain reference spectra for SF₆ and ethylene. Suitable concentrations are 0.0112 to 0.112 (ppm-meter)/K for SF₆ and 5.61 (ppm-meter)/K or less for ethylene. The reference spectra shall meet the criteria for acceptance outlined in Section 2.2.2. The optical density (ppm-meters/K) of the reference spectrum must match the optical density of the sample spectrum within (less than) 25 percent.

8.0 Sample Collection, Preservation, and Storage

Sampling should be performed in the following sequence: Collect background, collect CTS spectrum, collect samples, collect post-test CTS spectrum, verify that two copies of all data were stored on separate computer media.

8.1 Pretest Preparations and Evaluations. Using the procedure in Section 4.0 of the *FTIR Protocol*, determine the optimum sampling system configuration for sampling the target pollutants. Table 2 gives some example values for AU, DL, and MAU. Based on a study (Reference 1), an FTIR system using 1 cm⁻¹ resolution, 22 meter path length, and a broad band MCT detector was suitable for meeting the requirements in Table 2. Other factors that must be determined are:

a. Test requirements: AU_i, CMAX_i, DL_i, OFU_i, and t_{AN} for each.

b. Interferants: See Table 1.

c. Sampling system: L_{S'}, P_{min}, P_{S'}, T_{S'}, t_{SS}, V_{SS}: fractional error, MIL.

d. Analytical regions: 1 through N_m, FL_m, FC_m, and FU_m, plus interferants, FFU_m, FFL_m, wavenumber range FNU to FNL. See Tables 1 and 2.

8.1.1 If necessary, sample and acquire an initial spectrum. Then determine the proper operational pathlength of the instrument to obtain non-saturated absorbances of the target analytes.

8.1.2 Set up the sampling train as shown in Figure 1.

8.2 Sampling System Leak-check. 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 note the leakage rate. The leakage rate shall be ≤200 mL/min.

8.3 Analytical System Leak-check.

8.3.1 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 ΔP_v after 2 minutes.

8.3.2 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 ΔP_p after 2 minutes.

8.3.3 Measure the barometric pressure, P_b in mmHg.

8.3.4 Determine the percent leak volume %V_L for the signal integration time t_{SS} and for ΔP_{max}, i.e., the larger of ΔP_v or ΔP_p, as follows:

$$\%V_L = 50t_{SS} \frac{\Delta P_{max}}{P_{SS}} \quad (2)$$

Where:

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

8.3.5 Leak volumes in excess of 4 percent of the sample system volume V_{SS} are unacceptable.

8.4 Background Spectrum. Evacuate the gas cell to ≤ mmHg, and fill with dry nitrogen gas to ambient pressure. 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 the spectra of the background interferogram and processed single-beam background spectrum on two separate computer media (one is used as the back-up). If continuous sampling will be used during sample collection, collect the background spectrum with nitrogen gas flowing through the cell at the same pressure and temperature as will be used during sampling.

8.5 Pre-Test Calibration Transfer Standard. Evacuate the gas cell to ≤5 mmHg absolute pressure, and fill the FTIR cell to atmospheric pressure with the CTS gas. Or, purge the cell with 10 cell volumes of CTS gas. Record the spectrum. If continuous sampling will be used during sample collection, collect the CTS spectrum with CTS gas flowing through the cell at the same pressure and temperature as will be used during sampling.

8.6 Samples

8.6.1 Evacuated Samples. Evacuate the absorbance cell to ≤5 mmHg absolute pressure. Fill the cell with flue gas to ambient pressure and record the spectrum. Before taking the next sample, evacuate the cell until no further evidence of absorption exists. Repeat this procedure to collect at least 8 separate spectra (samples) in 1 hour.

8.6.2 Purge Sampling. Purge the FTIR cell with 10 cell volumes of flue gas and at least for about 10 minutes. Discontinue the gas cell purge, isolate the cell, and record the sample spectrum and the pressure. Before

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taking the next sample, purge the cell with 10 cell volumes of flue gas.

8.6.3 Continuous Sampling. Spectra can be collected continuously while the FTIR cell is being purged. The sample integration time, t_{ss} , the sample flow rate through the FTIR gas cell, and the total run time must be chosen so that the collected data consist of at least 10 spectra with each spectrum being of a separate cell volume of flue gas. More spectra can be collected over the run time and the total run time (and number of spectra) can be extended as well.

8.7 Sampling QA, Data Storage and Reporting

8.7.1 Sample integration times should be sufficient to achieve the required signal-to-noise ratios. Obtain an absorbance spectrum by filling the cell with nitrogen. Measure the RMSD in each analytical region in this absorbance spectrum. Verify that the number of scans is sufficient to achieve the target MAU (Table 2).

8.7.2 Identify all sample spectra with unique file names.

8.7.3 Store on two separate computer media a copy of sample interferograms and processed spectra. The data shall be available to the Administrator on request for the length of time specified in the applicable regulation.

8.7.4 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, integration time), and the spectral file name. Keep a hard copy of these data sheets.

8.8 Signal Transmittance. While sampling, monitor the signal transmittance through the instrumental system. If signal transmittance (relative to the background) drops below 95 percent in any spectral region where the sample does not absorb infrared energy, obtain a new background spectrum.

8.9 Post-run CTS. After each sampling run, record another CTS spectrum.

8.10 Post-test QA

8.10.1 Inspect the sample spectra immediately after the run to verify that the gas matrix composition was close to the expected (assumed) gas matrix.

8.10.2 Verify that the sampling and instrumental parameters were appropriate for the conditions encountered. For example, if the moisture is much greater than anticipated, it will be necessary to use a shorter path length or dilute the sample.

8.10.3 Compare the pre and post-run CTS spectra. They shall agree to within -5 percent. See FTIR Protocol, Appendix E.

9.0 Quality Control

Follow the quality assurance procedures in the method, including the analysis of pre and post-run calibration transfer standards (Sec-

tions 8.5 and 8.9) and the post-test quality assurance procedures in Section 8.10.

10.0 Calibration and Standardization

10.1 Signal-to-Noise Ratio (S/N). The S/N shall be sufficient to meet the MAU in each analytical region.

10.2 Absorbance Pathlength. Verify the absorbance path length by comparing CTS spectra to reference spectra of the calibration gas(es). See FTIR Protocol, Appendix E.

10.3 Instrument Resolution. Measure the line width of appropriate CTS bands(s) and compare to reference CTS spectra to verify instrumental resolution.

10.4 Apodization Function. Choose appropriate apodization function. Determine any appropriate mathematical transformations that are required to correct instrumental errors by measuring the CTS. Any mathematical transformations must be documented and reproducible.

10.5 FTIR Cell Volume. Evacuate the cell to ≤ 5 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:

$$V_{ss} = \frac{V_m \frac{P_m}{T_m}}{\left[\frac{P_f - P_i}{T_f - T_i} \right]} \quad (8)$$

As an alternative to the wet test meter/calibrated dry gas meter procedure, measure the inside dimensions of the cell cylinder and calculate its volume.

11.0 Procedure

Refer to Sections 4.6-4.11, Sections 5, 6, and 7, and the appendices of the FTIR Protocol.

12.0 Data Analysis and Calculations

a. Data analysis is performed using appropriate reference spectra whose concentrations can be verified using CTS spectra. Various analytical programs are available to relate sample absorbance to a concentration standard. Calculated concentrations should be verified by analyzing spectral baselines after mathematically subtracting scaled reference spectra from the sample spectra. A full description of the data analysis and calculations may be found in the FTIR Protocol (Sections 4.0, 5.0, 6.0 and appendices).

b. Correct the calculated concentrations in sample spectra for differences in absorption

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pathlength between the reference and sample spectra by:

$$C_{corr} = \left[\frac{L_r}{L_s} \right] \left[\frac{T_s}{T_r} \right] C_{calc} \quad (9)$$

Where:

C_{corr} = The pathlength corrected concentration.

C_{calc} = The initial calculated concentration (output of the Multicomp program designed for the compound).

L_r = The pathlength associated with the reference spectra.

L_s = The pathlength associated with the sample spectra.

T_s = The absolute temperature (K) of the sample gas.

T_r = The absolute gas temperature (K) at which reference spectra were recorded.

13.0 Reporting and Recordkeeping

All interferograms used in determining source concentration shall be stored for the period of time required in the applicable regulation. The Administrator has the option of requesting the interferograms recorded during the test in electronic form as part of the test report.

14.0 Method Performance

Refer to the FTIR Protocol.

15.0 Pollution Prevention [Reserved]

16.0 Waste Management

Laboratory standards prepared from the formaldehyde and phenol are handled according to the instructions in the materials safety data sheets (MSDS).

17.0 References

- (1) "Field Validation Test Using Fourier Transform Infrared (FTIR) Spectrometry To Measure Formaldehyde, Phenol and Methanol at a Wool Fiberglass Production Facility." Draft. U.S. Environmental Protection Agency Report. Entropy, Inc., EPA Contract No. 68D20163, Work Assignment 1-32, December 1994 (docket item II-A-13).

- (2) "Method 301—Field Validation of Pollutant Measurement Methods from Various Waste Media," 40 CFR part 63, appendix A.

METHOD 319—DETERMINATION OF FILTRATION EFFICIENCY FOR PAINT OVERSPRAY ARRESTORS

1.0 Scope and Application

1.1 This method applies to the determination of the initial, particle size dependent, filtration efficiency for paint arrestors over the particle diameter range from 0.3 to 10 μm . The method applies to single and multiple stage paint arrestors or paint arrestor

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media. The method is applicable to efficiency determinations from 0 to 99 percent. Two test aerosols are used—one liquid phase and one solid phase. Oleic acid, a low-volatility liquid (CAS Number 112-80-1), is used to simulate the behavior of wet paint overspray. The solid-phase aerosol is potassium chloride salt (KCl, CAS Number 7447-40-7) and is used to simulate the behavior of a dry overspray. The method is limited to determination of the initial, clean filtration efficiency of the arrestor. Changes in efficiency (either increase or decrease) due to the accumulation of paint overspray on and within the arrestor are not evaluated.

1.2 Efficiency is defined as 1—Penetration (e.g., 70 percent efficiency is equal to 0.30 penetration). Penetration is based on the ratio of the downstream particle concentration to the upstream concentration. It is often more useful, from a mathematical or statistical point of view, to discuss the upstream and downstream counts in terms of penetration rather than the derived efficiency value. Thus, this document uses both penetration and efficiency as appropriate.

1.3 For a paint arrestor system or subsystem which has been tested by this method, adding additional filtration devices to the system or subsystem shall be assumed to result in an efficiency of at least that of the original system without the requirement for additional testing. (For example, if the final stage of a three-stage paint arrestor system has been tested by itself, then the addition of the other two stages shall be assumed to maintain, as a minimum, the filtration efficiency provided by the final stage alone. Thus, in this example, if the final stage has been shown to meet the filtration requirements of Table 1 of §63.745 of subpart GG, then the final stage in combination with any additional paint arrestor stages also passes the filtration requirements.)

2.0 Summary of Method

2.1 This method applies to the determination of the fractional (i.e., particle-size dependent) aerosol penetration of several types of paint arrestors. Fractional penetration is computed from aerosol concentrations measured upstream and downstream of an arrestor installed in a laboratory test rig. The aerosol concentrations upstream and downstream of the arrestors are measured with an aerosol analyzer that simultaneously counts and sizes the particles in the aerosol stream. The aerosol analyzer covers the particle diameter size range from 0.3 to 10 μm in a minimum of 12 contiguous sizing channels. Each sizing channel covers a narrow range of particle diameters. For example, Channel 1 may cover from 0.3 to 0.4 μm , Channel 2 from 0.4 to 0.5 μm . * * * By taking the ratio of the

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downstream to upstream counts on a channel by channel basis, the penetration is computed for each of the sizing channels.

2.2 The upstream and downstream aerosol measurements are made while injecting the test aerosol into the air stream upstream of the arrestor (ambient aerosol is removed with HEPA filters on the inlet of the test rig). This test aerosol spans the particle size range from 0.3 to 10 μm and provides sufficient upstream concentration in each of the optical particle counter (OPC) sizing channels to allow accurate calculation of penetration, down to penetrations of approximately 0.01 (i.e., 1 percent penetration; 99 percent efficiency). Results are presented as a graph and a data table showing the aerodynamic particle diameter and the corresponding fractional efficiency.

3.0 Definitions

Aerodynamic Diameter—diameter of a unit density sphere having the same aerodynamic properties as the particle in question.

Efficiency is defined as equal to 1—Penetration.

Optical Particle Counter (OPC)—an instrument that counts particles by size using light scattering. An OPC gives particle diam-

eters based on size, index of refraction, and shape.

Penetration—the fraction of the aerosol that penetrates the filter at a given particle diameter. Penetration equals the downstream concentration divided by the upstream concentration.

4.0 Interferences

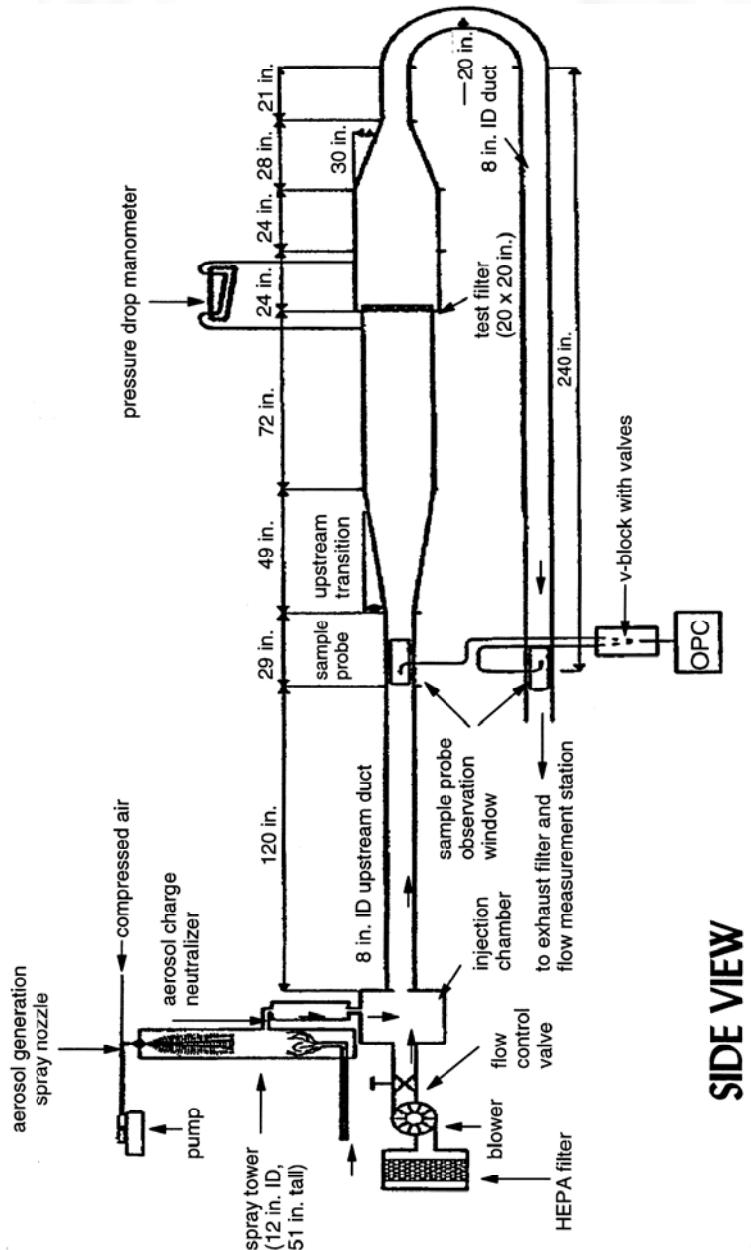
4.1 The influence of the known interferences (particle losses) are negated by correction of the data using blanks.

5.0 Safety

5.1 There are no specific safety precautions for this method above those of good laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

6.0 Equipment and Supplies

6.1 Test Facility. A schematic diagram of a test duct used in the development of the method is shown in Figure 319-1.



6.1.1 The test section, paint spray section, and attached transitions are constructed of stainless and galvanized steel. The upstream and downstream ducting is 20 cm diameter

polyvinyl chloride (PVC). The upstream transition provides a 7° angle of expansion to provide a uniform air flow distribution to the paint arrestors. Aerosol concentration is

Figure 319-1. Schematic illustration of the fractional efficiency test rig.

measured upstream and downstream of the test section to obtain the challenge and penetrating aerosol concentrations, respectively. Because the downstream ducting runs back under the test section, the challenge and penetrating aerosol taps are located physically near each other, thereby facilitating aerosol sampling and reducing sample-line length. The inlet nozzles of the upstream and downstream aerosol probes are designed to yield isokinetic sampling conditions.

6.1.2 The configuration and dimensions of the test duct can deviate from those of Figure 319-1 provided that the following key elements are maintained: the test duct must meet the criteria specified in Table 319-1; the inlet air is HEPA filtered; the blower is on the upstream side of the duct thereby creating a positive pressure in the duct relative

to the surrounding room; the challenge air has a temperature between 50 ° and 100 °F and a relative humidity of less than 65 percent; the angle of the upstream transition (if used) to the paint arrestor must not exceed 7 °; the angle of the downstream transition (if used) from the paint arrestor must not exceed 30 °; the test duct must provide a means for mixing the challenge aerosol with the upstream flow (in lieu of any mixing device, a duct length of 15 duct diameters fulfills this requirement); the test duct must provide a means for mixing any penetrating aerosol with the downstream flow (in lieu of any mixing device, a duct length of 15 duct diameters fulfills this requirement); the test section must provide a secure and leak-free mounting for single and multiple stage arrestors; and the test duct may utilize a 180 ° bend in the downstream duct.

TABLE 319-1—QC CONTROL LIMITS

h	Frequency and description	Control limits
OPC zero count	Each Test. OPC samples HEPA-filtered air.	<50 counts per minute.
OPC sizing accuracy check	Daily. Sample aerosolized PSL spheres	Peak of distribution should be in correct OPC channel.
Minimum counts per channel for challenge aerosol.	Each Test	Minimum total of 500 particle counts per channel.
Maximum particle concentration	Each Test. Needed to ensure OPC is not overloaded.	<10% of manufacturer's claimed upper limit corresponding to a 10% count error.
Standard Deviation of Penetration	Computed for each test based on the CV of the upstream and downstream counts.	<0.10 for 0.3 to 3 µm diameter. <0.30 for >3 µm diameter.
0% Penetration	Monthly	<0.01.
100% Penetration—KCl	Triplicate tests performed immediately before, during, or after triplicate arrestor tests.	0.3 to 1 µm: 0.90 to 1.10. 1 to 3 µm: 0.75 to 1.25. 3 to 10 µm: 0.50 to 1.50.
100% Penetration—Oleic Acid	Triplicate tests performed immediately before, during, or after triplicate arrestor tests.	0.3 to 1 µm: 0.90 to 1.10. 1 to 3 µm: 0.75 to 1.25. 3 to 10 µm: 0.50 to 1.50.

6.2 Aerosol Generator. The aerosol generator is used to produce a stable aerosol covering the particle size range from 0.3 to 10 µm diameter. The generator used in the development of this method consists of an air atomizing nozzle positioned at the top of a 0.30-m (12-in.) diameter, 1.3-m (51-in.) tall, acrylic, transparent, spray tower. This tower allows larger sized particles, which would otherwise foul the test duct and sample lines, to fall out of the aerosol. It also adds drying air to ensure that the KCl droplets dry to solid salt particles. After generation, the aerosol passes through an aerosol neutralizer (Kr^{85} radioactive source) to neutralize any electrostatic charge on the aerosol (electrostatic charge is an unavoidable consequence of most aerosol generation methods). To improve the mixing of the aerosol with the air stream, the aerosol is injected counter to the airflow. Generators of other designs may be used, but they must produce a stable aerosol concentration over

the 0.3 to 10 µm diameter size range; provide a means of ensuring the complete drying of the KCl aerosol; and utilize a charge neutralizer to neutralize any electrostatic charge on the aerosol. The resultant challenge aerosol must meet the minimum count per channel and maximum concentration criteria of Table 319-1.

6.3 Installation of Paint Arrestor. The paint arrestor is to be installed in the test duct in a manner that precludes air bypassing the arrestor. Since arrestor media are often sold unmounted, a mounting frame may be used to provide back support for the media in addition to sealing it into the duct. The mounting frame for 20 in. × 20 in. arrestors will have minimum open internal dimensions of 18 in. square. Mounting frames for 24 in. × 24 in. arrestors will have minimum open internal dimensions of 22 in. square. The open internal dimensions of the mounting frame shall not be less than 75 percent of the approach duct dimensions.

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6.4 Optical Particle Counter. The upstream and downstream aerosol concentrations are measured with a high-resolution optical particle counter (OPC). To ensure comparability of test results, the OPC shall utilize an optical design based on wide-angle light scattering and provided a minimum of 12 contiguous particle sizing channels from 0.3 to 10 μm diameter (based on response to PSL) where, for each channel, the ratio of the diameter corresponding to the upper channel bound to the lower channel bound must not exceed 1.5.

6.5 Aerosol Sampling System. The upstream and downstream sample lines must be made of rigid electrically-grounded metallic tubing having a smooth inside surface, and they must be rigidly secured to prevent movement during testing. The upstream and downstream sample lines are to be nominally identical in geometry. The use of a short length (100 mm maximum) of straight flexible tubing to make the final connection to the OPC is acceptable. The inlet nozzles of the upstream and downstream probes must be sharp-edged and of appropriate entrance diameter to maintain isokinetic sampling within 20 percent of the air velocity.

TABLE 319-2—PROPERTIES OF THE TEST AND CALIBRATION AEROSOLS

	Refractive index	Density, g/cm^3	Shape
Oleic Acid (liquid-phase challenge aerosol)	1.46 nonabsorbing	0.89	Spherical.
KCl (solid-phase challenge aerosol)	1.49	1.98	Cubic or agglomerated cubes.
PSL (calibration aerosol)	1.59 nonabsorbing	1.05	Spherical.

8.0 Sample Collection, Preservation, and Storage

8.1 In this test, all sampling occurs in real-time, thus no samples are collected that require preservation or storage during the test. The paint arrestors are shipped and stored to avoid structural damage or soiling. Each arrestor may be shipped in its original box from the manufacturer or similar cardboard box. Arrestors are stored at the test site in a location that keeps them clean and dry.

Each arrestor is clearly labeled for tracking purposes.

9.0 Quality Control

9.1 Table 319-1 lists the QC control limits.

9.2 The standard deviation (σ) of the penetration (P) for a given test at each of the 15 OPC sizing channels is computed from the coefficient of variation (CV, the standard deviation divided by the mean) of the upstream and downstream measurements as:

$$\sigma_P = P \sqrt{\left(CV_{\text{upstream}}^2 + CV_{\text{downstream}}^2 \right)} \quad (\text{Eq. 319-1})$$

For a properly operating system, the standard deviation of the penetration is <0.10 at particle diameters from 0.3 to 3 μm and less than 0.30 at diameters $>3 \mu\text{m}$.

9.3 Data Quality Objectives (DQO).

9.3.1 Fractional Penetration. From the triplicate tests of each paint arrestor model, the standard deviation for the penetration measurements at each particle size (i.e., for each sizing channel of the OPC) is computed as:

$$s = \left[\sum (P_i - \bar{P})^2 / (n - 1) \right]^{1/2} \quad (\text{Eq. 319-2})$$

where P_i represents an individual penetration measurement, and \bar{P} the average of the 3 ($n = 3$) individual measurements.

9.3.2 Bias of the fractional penetration values is determined from triplicate no-filter and HEPA filter tests. These tests determine the measurement bias at 100 percent penetration and 0 percent penetration, respectively.

9.3.3 PSL-Equivalent Light Scattering Diameter. The precision and bias of the OPC sizing determination are based on sampling a known diameter of PSL and noting whether the particle counts peak in the correct channel of the OPC. This is a pass/fail measurement with no calculations involved.

9.3.4 Airflow. The precision of the measurement must be within 5 percent of the set point.

10.0 Calibration and Standardization

10.1 Optical Particle Counter. The OPC must have an up-to-date factory calibration. Check the OPC zero at the beginning and end of each test by sampling HEPA-filtered air. Verify the sizing accuracy on a daily basis (for days when tests are performed) with 1-size PSL spheres.

10.2 Airflow Measurement. Airflow measurement devices must have an accuracy of 5 percent or better. Manometers used in conjunction with the orifice plate must be inspected prior to use for proper level, zero, and mechanical integrity. Tubing connections to the manometer must be free from kinks and have secure connections.

10.3 Pressure Drop. Measure pressure drop across the paint arrestor with an inclined manometer readable to within 0.01 in. H₂O. Prior to use, the level and zero of the manometer, and all tubing connections, must be inspected and adjusted as needed.

11.0 Procedure

11.1 Filtration Efficiency. For both the oleic acid and KCl challenges, this procedure is performed in triplicate using a new arrestor for each test.

11.1.1 General Information and Test Duct Preparation

11.1.1.1 Use the "Test Run Sheet" form (Figure 319-2) to record the test information.

RUN SHEET

Part 1. General Information

Date and Time: _____

Test Operator: _____

Test #: _____

Paint Arrestor: _____

Brand/Model _____

Arrestor Assigned ID # _____

Condition of arrestor (i.e., is there any damage? Must be new condition to proceed): _____

Manometer zero and level confirmed? _____

Part 2. Clean Efficiency Test

Date and Time: _____

Optical Particle Counter: _____

20 min. warm up _____

Zero count (<50 counts/min) _____

Daily PSL check _____

PSL Diam: _____ μm

File name for OPC data: _____

Test Conditions: _____

Air Flow: _____

Temp & RH: Temp _____ °F RH _____ %

Atm. Pressure: _____ in. Hg

(From mercury barometer)

Aerosol Generator: (record all operating parameters)

Test Aerosol: _____

(Oleic acid or KCl) _____

Arrestor: _____

Pressure drop: at start _____ in. H₂O

at end _____ in. H₂O

Condition of arrestor at end of test (note any physical deterioration): _____

FIGURE 319-2. TEST RUN SHEET

Other report formats which contain the same information are acceptable.

11.1.1.2 Record the date, time, test operator, Test #, paint arrestor brand/model and its assigned ID number. For tests with no arrestor, record none.

11.1.1.3 Ensure that the arrestor is undamaged and is in "new" condition.

11.1.1.4 Mount the arrestor in the appropriate frame. Inspect for any airflow leak paths.

11.1.1.5 Install frame-mounted arrestor in the test duct. Examine the installed arrestor to verify that it is sealed in the duct. For tests with no arrestor, install the empty frame.

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11.1.1.6 Visually confirm the manometer zero and level. Adjust as needed.

11.1.2 Clean Efficiency Test.

11.1.2.1 Record the date and time upon beginning this section.

11.1.2.2 Optical Particle Counter.

11.1.2.2.1 General: Operate the OPC per the manufacturer's instructions allowing a minimum of 20 minutes warm up before making any measurements.

11.1.2.2.2 Overload: The OPC will yield inaccurate data if the aerosol concentration it is attempting to measure exceeds its operating limit. To ensure reliable measurements, the maximum aerosol concentration will not exceed 10 percent of the manufacturer's claimed upper concentration limit corresponding to a 10 percent count error. If this value is exceeded, reduce the aerosol concentration until the acceptable conditions are met.

11.1.2.2.3 Zero Count: Connect a HEPA capsule to the inlet of the OPC and obtain printouts for three samples (each a minimum of 1-minute each). Record maximum cumulative zero count. If the count rate exceeds 50 counts per minute, the OPC requires servicing before continuing.

11.1.2.2.4 PSL Check of OPC Calibration: Confirm the calibration of the OPC by sampling a known size PSL aerosol. Aerosolize the PSL using an appropriate nebulizer. Record whether the peak count is observed in the proper channel. If the peak is not seen in the appropriate channel, have the OPC recalibrated.

11.1.2.3 Test Conditions:

11.1.2.3.1 Airflow: The test airflow corresponds to a nominal face velocity of 120 FPM through the arrestor. For arrestors having nominal 20 in. x 20 in. face dimensions, this measurement corresponds to an airflow of 333 cfm. For arrestors having nominal face dimensions of 24 in. x 24 in., this measurement corresponds to an airflow of 480 cfm.

11.1.2.3.2 Temperature and Relative Humidity: The temperature and relative humidity of the challenge air stream will be measured to within an accuracy of $\pm 2^{\circ}\text{F}$ and ± 10 percent RH. To protect the probe from fouling, it may be removed during periods of aerosol generation.

11.1.2.3.3 Barometric Pressure: Use a mercury barometer. Record the atmospheric pressure.

11.1.2.4 Upstream and Downstream Background Counts.

11.1.2.4.1 With the arrestor installed in the test duct and the airflow set at the proper value, turn on the data acquisition computer and bring up the data acquisition program.

11.1.2.4.2 Set the OPC settings for the appropriate test sample duration with output for both printer and computer data collection.

11.1.2.4.3 Obtain one set of upstream-downstream background measurements.

11.1.2.4.4 After obtaining the upstream-downstream measurements, stop data acquisition.

11.1.2.5 Efficiency Measurements:

11.1.2.5.1 Record the arrestor pressure drop.
11.1.2.5.2 Turn on the Aerosol Generator. Begin aerosol generation and record the operating parameters.

11.1.2.5.3 Monitor the particle counts. Allow a minimum of 5 minutes for the generator to stabilize.

11.1.2.5.4 Confirm that the total particle count does not exceed the predetermined upper limit. Adjust generator as needed.

11.1.2.5.5 Confirm that a minimum of 50 particle counts are measured in the upstream sample in each of the OPC channels per sample. (A minimum of 50 counts per channel per sample will yield the required minimum 500 counts per channel total for the 10 upstream samples as specified in Table 319-1.) Adjust generator or sample time as needed.

11.1.2.5.6 If you are unable to obtain a stable concentration within the concentration limit and with the 50 count minimum per channel, adjust the aerosol generator.

11.1.2.5.7 When the counts are stable, perform repeated upstream-downstream sampling until 10 upstream-downstream measurements are obtained.

11.1.2.5.8 After collection of the 10 upstream-downstream samples, stop data acquisition and allow 2 more minutes for final purging of generator.

11.1.2.5.9 Obtain one additional set of upstream-downstream background samples.

11.1.2.5.10 After obtaining the upstream-downstream background samples, stop data acquisition.

11.1.2.5.11 Record the arrestor pressure drop.

11.1.2.5.12 Turn off blower.

11.1.2.5.13 Remove the paint arrestor assembly from the test duct. Note any signs of physical deterioration.

11.1.2.5.14 Remove the arrestor from the frame and place the arrestor in an appropriate storage bag.

11.2 Control Test: 100 Percent Penetration Test. A 100 percent penetration test must be performed immediately before each individual paint arrestor test using the same challenge aerosol substance (i.e., oleic acid or KCl) as to be used in the arrestor test. These tests are performed with no arrestor installed in the test housing. This test is a relatively stringent test of the adequacy of the overall duct, sampling, measurement, and aerosol generation system. The test is performed as a normal penetration test except the paint arrestor is not used. A perfect system would yield a measured penetration of 1 at all particle sizes. Deviations from 1 can occur due to particle losses in the duct.

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differences in the degree of aerosol uniformity (i.e., mixing) at the upstream and downstream probes, and differences in particle transport efficiency in the upstream and downstream sampling lines.

11.3 Control Test: 0 Percent Penetration. One 0 percent penetration test must be performed at least monthly during testing. The test is performed by using a HEPA filter rather than a paint arrestor. This test assesses the adequacy of the instrument response time and sample line lag.

12.0 Data Analysis and Calculations

12.1 Analysis. The analytical procedures for the fractional penetration and flow velocity measurements are described in Section 11. Note that the primary measurements, those of the upstream and downstream aerosol concentrations, are performed with the OPC which acquires the sample and analyzes it in real time. Because all the test data are collected in real time, there are no analytical procedures performed subsequent to the actual test, only data analysis.

12.2 Calculations.

12.2.1 Penetration.

Nomenclature

U = Upstream particle count

D = Downstream particle count

U_b = Upstream background count

D_b = Downstream background count

P_{100} = 100 percent penetration value determined immediately prior to the arrestor test computed for each channel as:

$$P_{100} = \frac{(\bar{D} - \bar{D}_b)}{(\bar{U} - \bar{U}_b)}$$

P = Penetration of the arrestor corrected for

P_{100}

ρ = sample standard deviation

CV = coefficient of variation = ρ/mean

E = Efficiency.

Overbar denotes arithmetic mean of quantity,

Analysis of each test involves the following quantities:

- P_{100} value for each sizing channel from the 100 percent penetration control test,
- 2 upstream background values,
- 2 downstream background values,
- 10 upstream values with aerosol generator on, and
- 10 downstream values with aerosol generator on.

Using the values associated with each sizing channel, the penetration associated with each particle-sizing channel is calculated as:

$$P = \frac{(\bar{D} - \bar{D}_b)}{(\bar{U} - \bar{U}_b)} / P_{100} \quad (\text{Eq. 319-3})$$

$$E = 1 - P \quad (\text{Eq. 319-4})$$

Most often, the background levels are small compared to the values when the aerosol generator is on.

12.3 The relationship between the physical diameter (D_{Physical}) as measured by the OPC to the aerodynamic diameter (D_{Aero}) is given by:

$$D_{\text{Aero}} = D_{\text{Physical}} \sqrt{\frac{\rho_{\text{Particle}}}{\rho_0} \frac{CCF_{\text{Physical}}}{CCF_{\text{Aero}}}} \quad (\text{Eq. 319-5})$$

Where:

ρ_0 = unit density of 1 g/cm³.

ρ_{Particle} = the density of the particle, 0.89 g/cm³ for oleic acid.

CCF_{Physical} = the Cunningham Correction Factor at D_{Physical} .

CCF_{Aero} = the Cunningham Correction Factor at D_{Aero} .

12.4 Presentation of Results. For a given arrestor, results will be presented for:

- Triplicate arrestor tests with the liquid-phase challenge aerosol.
- Triplicate arrestor tests with the solid-phase challenge aerosol.
- Triplicate 100 percent penetration tests with the liquid-phase challenge aerosol.

- Triplicate 100 percent penetration tests with the solid-phase challenge aerosol, and

- One 0 percent filter test (using either the liquid-phase or solid-phase aerosol and performed at least monthly).

12.4.1 Results for the paint arrestor test must be presented in both graphical and tabular form. The X-axis of the graph will be a logarithmic scale of aerodynamic diameter from 0.1 to 100 μm . The Y-axis will be efficiency (%) on a linear scale from 0 to 100. Plots for each individual run and a plot of the average of triplicate solid-phase and of the average triplicate liquid-phase tests must be prepared. All plots are to be based

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on point-to-point plotting (i.e., no curve fitting is to be used). The data are to be plotted based on the geometric mean diameter of each of the OPC's sizing channels.

12.4.2 Tabulated data from each test must be provided. The data must include the upper and lower diameter bound and geometric mean diameter of each of the OPC sizing channels, the background particle counts for each channel for each sample, the upstream particle counts for each channel for each sample, the downstream particle counts for each channel for each sample, the 100 percent penetration values computed for each channel, and the 0 percent penetration values computed for each channel.

13.0 Pollution Prevention

13.1 The quantities of materials to be aerosolized should be prepared in accord with the amount needed for the current tests so as to prevent wasteful excess.

14.0 Waste Management

14.1 Paint arrestors may be returned to originator, if requested, or disposed of with regular laboratory waste.

15.0 References

1. Hanley, J.T., D.D. Smith and L. Cox. "Fractional Penetration of Paint Overspray Arrestors, Draft Final Report," EPA Cooperative Agreement CR-817083-01-0, January 1994.

2. Hanley, J.T., D.D. Smith, and D.S. Ensor. "Define a Fractional Efficiency Test Method that is Compatible with Particulate Removal Air Cleaners Used in General Ventilation," Final Report, 671-RP, American Society of Heating, Refrigerating, and Air-Conditioning Engineers, Inc., December 1993.

3. "Project Work and Quality Assurance Plan: Fractional Penetration of Paint Overspray Arrestors, Category II," EPA Cooperative Agreement No. CR-817083, July 1994.

TEST METHOD 320—MEASUREMENT OF VAPOR PHASE ORGANIC AND INORGANIC EMISSIONS BY EXTRACTIVE FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

1.0 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

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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 and 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 of this method are met.

1.1 Scope and Applicability

1.1 *Analytes.* Analytes include hazardous air pollutants (HAPs) 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 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 used to determine 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.

1.2 *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.

1.2.1 For any optical configuration the analytical range is between the absorbance values of about 0.01 (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.)

1.2.2 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 (A) limit ($A = 0.01$) depends on the root mean square deviation (RMSD) noise in the analytical region.

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

1.2.3.1 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.

1.2.3.2 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 gas, the presence of other interferants, and losses in the sampling system.

1.3 *Sensitivity.* The limit of sensitivity for an optical configuration and integration time is determined using appendix D of the 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 shall be determined by executing Protocol pre-test procedures in appendices B to H of the protocol and post-test procedures in appendices I and J of the protocol.

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

1.4.2 An instrumental configuration shall be selected. An estimate of gas composition shall be made based on previous test data, data from a similar source or information gathered in a pre-test site survey. Spectral interferants shall be identified using the selected DL_i and AU_i , and band areas from reference spectra and interferant spectra. The baseline noise of the system shall be measured in each analytical region to determine the MAU of the instrument configuration for each analyte and interferant (MIU_i).

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

1.4.4 The MAU is the minimum analyte concentration for which the 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 through 7 provide background material on infrared spectro-

copy and quantitative analysis. A summary is given in this section.

2.1.1 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).

2.1.2 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.

2.1.3 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 determine compound concentration in a sample mixture.

2.1.4 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.

2.1.5 This method is self-validating provided that the results meet the performance requirement of the QA spike in sections 8.6.2 and 9.0 of this method, 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 gas from the exhaust of the affected source and transport the sample to the FTIR gas cell. Typically, the sampling apparatus is similar to that used for single-component continuous emission monitor (CEM) measurements.

2.2.1 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,

$$A_i = a_i b c_i \quad (1)$$

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.

2.2.2 Analyte spiking is used for quality assurance (QA). In this procedure (section 8.6.2

of this method) 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 Protocol.

2.4 Operator Requirements. The FTIR analyst shall 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.

2.4.1 The spectral analysis shall be supervised by someone familiar with EPA FTIR Protocol procedures.

2.4.2 A technician trained in instrumental 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 Protocol for definitions relating to infrared spectroscopy. Additional definitions are given in sections 3.1 through 3.29.

3.1 Analyte. A compound that this method is used 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 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 to the addendum of this method). 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 the 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 discrete, 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

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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 sections 13.0 through 13.4 of this method. 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. The 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 to obtain information about important sample characteristics such as moisture, temperature, and interferences. Screening results are semi-quantitative (estimated concentrations) or qualitative (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 of this method) 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 of this method) 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

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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 Interference. 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 shall be classified as known interferants (FTIR Protocol, section 4.9 and appendix B). Water vapor and CO₂ 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, CO₂ 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 shall 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 ensure that gases are properly vented and that the gas handling system is leak free. (Always perform a leak check with the sys-

tem under maximum vacuum and, again, with the system at greater than ambient pressure.) Refer to section 8.2 of this method 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

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

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, polytetrafluoroethane, 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 bypass 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

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probe upstream of the out-of-stack particulate filter and the FTIR analytical system.

6.7 Mass Flow Meter (MFM). These are used for measuring analyte spike flow. The MFM shall 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 Polytetrafluoroethane Tubing. Diameter (e.g., $\frac{3}{8}$ in.) and length suitable to connect cylinder regulators to gas standard manifold.

6.10 Sample Pump. A leak-free pump (e.g., KNP™), with by-pass valve, capable of producing a sample flow rate of at least 10 L/min 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 L/min 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 shall 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 $\pm 2^{\circ}\text{C}$.

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.

6.17.1 The analyte spike procedure of section 9.2 of this method, the QA spike procedure of section 8.6.2 of this method, and the validation procedure of section 13 of this method 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.

6.17.2 Another option is sample dilution. The dilution factor measurement must be documented and accounted for in the reported concentrations. An alternative to di-

lution 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 containing all of the analyte(s) at concentrations within ± 2 percent of the emission source levels (expressed in ppm-meter/K). If practical, the analyte standard cylinder shall 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 National Institute of Standards and Technology (NIST) traceable gravimetric standard of the CTS (± 2 percent).

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 of this method. Determine the purpose(s) of the FTIR test. Test requirements include: (a) AU_i, DL_i, overall fractional uncertainty, OFU_i, maximum expected concentration (C_{MAX})_i, and t_{AN} for each, (b) potential interferants, (c) sampling system factors, e.g., minimum absolute cell pressure, (P_{min}), FTIR cell volume (V_{ss}), estimated sample absorption pathlength, L_s, estimated sample pressure, P_s, T_s, signal integration time (t_{ss}), minimum instrumental linewidth, MIL, fractional error, and (d) analytical regions, e.g., m = 1 to M, lower wavenumber position, FLM_m, center wavenumber position, FC_m, and upper wavenumber position, FU_m, plus interferants, upper wavenumber position of the CTS absorption band, FFU_m, lower wavenumber position of the CTS absorption band, FFL_m, wavenumber range FNU to FNL. 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. Sections 8.1 through 8.11 of this method 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

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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 (DL_i) and the maximum permissible analytical uncertainty (AU_i) for each analyte (labeled from 1 to i). Estimate, if possible, the maximum expected concentration for each analyte, C_{MAX_i} . The expected measurement range is fixed by DL_i and C_{MAX_i} 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 para-xylene 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 <AU. Appendix E of the protocol 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_3 (cts1101b - cts1031a), and S_4 [(cts1101b + cts1031a)/2]. The RMSD (SRMS) is calculated in the subtracted baseline, S_3 , 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_4 .

8.1.5 *Known Interferants.* Use appendix B of the EPA FTIR Protocol.

8.1.6 Calculate the Minimum Analyte Uncertainty, MAU (section 1.3 of this method 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 interferants. Reference spectra of additional compounds shall also be included in the program if their presence (even if transient) in the samples is considered possible. The program output shall be in ppm (or ppb) and shall 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

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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 ≤ 200 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 ΔP_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 ΔP_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 ΔP_{max} , i.e., the larger of ΔP_v or ΔP_p , as follows:

$$\%V_L = 50t_{SS} \frac{\Delta P_{max}}{P_{SS}} \quad (2)$$

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 procedures of sections 8.3.1 through 8.3.3 to verify that the detector response is linear. If the detector response is not linear, decrease the 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 shall 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 again.

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 $\frac{1}{2}$ its original intensity. Collect a second CTS spectrum. Use another filter to attenuate the infrared beam to approximately $\frac{1}{4}$ its original intensity. Collect a third background and CTS spectrum. Compare the CTS spectra. CTS band areas shall agree to within the uncertainty of the cylinder standard and the RMSD noise in the system.

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.

8.5.2 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, 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 method has been validated for at least some of the target analytes at the source. For emissions testing perform a QA 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 of this method. Record spectra of at least three independent (section 3.22 of this method) spiked samples. Calculate the spiked component of the analyte concentration. If 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 of this appendix validation test (not the result from the QA spike).

8.7 *Sampling.* If analyte concentrations vary rapidly with time, continuous sampling is preferable using the smallest cell volume, fastest sampling rate and fastest spectra collection rate possible. Continuous sampling requires the least operator intervention even without an automated sampling system. For continuous monitoring at one location over long periods, continuous 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 ensures that each spectrum measures a discreet (and unique) sample volume. Continuous static (and continuous) sampling provide a very stable background over long periods. Like batch sampling, continuous static sampling also ensures that each spectrum measures a unique sample volume. It is essential that the leak check procedure under vacuum (section 8.2 of this method) is passed if the batch sampling procedure is used. It is essential that the leak check procedure

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under positive pressure is passed if the continuous static or continuous sampling procedures are used. The sampling techniques are described in sections 8.7.1 through 8.7.2 of this method.

8.7.1 *Batch Sampling.* Evacuate the absorbance cell to ≤ 5 mmHg absolute pressure. Fill the cell with exhaust 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 eight 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.

8.8 Sampling QA and Reporting

8.8.1 Sample Integration times shall 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 percent or more (absorbance = -.02 to .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 of this method) to verify that 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 FTIR Protocol.

9.2 *Spiking Procedure.* QA spiking (section 8.6.2 of this method) is a calibration procedure used before testing. QA spiking involves following the spike procedure of sections 9.2.1 through 9.2.3 of this method to obtain at least three spiked samples. The analyte concentrations in the spiked samples shall be compared to the expected spike concentration to verify that the sampling/analytical 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/analytical conditions are being duplicated. If the QA spike fails then the sampling/analytical system shall be repaired before testing proceeds. The method validation procedure (section 13.0 of this method) involves a more extensive use of the analyte spike procedure of sections 9.2.1 through 9.2.3 of this method. 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 of this appendix, then a correction factor shall be applied to the analytical results. If the systematic bias is greater than the allowed limits, this 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, when possible.

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 percent), 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 by continuously collecting 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 twice the duration of the RT, then collect spectra of two independent spiked gas samples. 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 Where:
the tracer gas as follows: where:

$$DF = \frac{SF_{6(spk)}}{SF_{6(dir)}} \quad (3)$$

$$CS = DF * Spike_{dir} + Unspike (1 - DF) \quad (4)$$

DF = Dilution factor of the spike gas; this value shall be ≥ 10 .

$SF_{6(und)}$ = SF₆ (or tracer gas) concentration measured directly in undiluted spike gas.

$SF_{6(spk)}$ = Diluted SF₆ (or tracer gas) concentration measured in a spiked sample.

$Spike_{dir}$ = Concentration of the analyte in the spike standard measured by filling the FTIR cell directly.

CS = Expected concentration of the spiked samples.

Unspike = Native concentration of analytes in unspiked samples.

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 ≤ 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 ≤ 5 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 VSS, including that of the connecting tubing, as follows:

$$V_{SS} = \frac{V_m \frac{P_m}{T_m}}{\left[\frac{P_f - P_i}{T_f - T_i} \right]} \quad (5)$$

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 of this method) by truncating the original reference sample and background interferograms. Appendix K of the FTIR Protocol gives specific de-resolution 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 the calculated concentrations in the sample spectra for differences in absorption path length and temperature between the reference and sample spectra using equation 6.

$$C_{corr} = \left(\frac{L_r}{L_s} \right) \left(\frac{T_s}{T_r} \right) \left(\frac{P_r}{P_s} \right) C_{calc} \quad (6)$$

Where:

C_{corr} = Concentration, corrected for path length.

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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.
 P_s = Sample cell pressure.
 P_r = Reference spectrum sample pressure.

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 of this method, the QA spike of section 8.6.2 of this method, and the validation procedure of section 13 of this method 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 of this method 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. Factors which can be controlled to provide better accuracy in the spiking procedure are listed in sections 12.2.1 through 12.2.4 of this method.

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

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

12.2.3 *Temperature.* Temperature measurements of the cell shall 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.

12.2.4 *Pressure.* Accuracy depends on the accuracy of the barometer, but fluctuations in pressure throughout a day may be as much as 2.5 percent due to 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

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the analytes in a gas matrix. Validation at one source may also apply to another type of source, if it can be shown that the exhaust gas characteristics are similar at both sources.

13.1 Section 6.0 of Method 301 (40 CFR part 63, appendix A), the Analyte Spike procedure, is used with these modifications. The statistical analysis of the results follows section 12.0 of EPA Method 301. Section 3 of this method defines terms that are not defined in Method 301.

13.1.1 The analyte spike is performed dynamically. This means the spike flow is continuous and constant as spiked samples are measured.

13.1.2 The spike gas is introduced at the back of the sample probe.

13.1.3 Spiked effluent is carried through all sampling components downstream of the probe.

13.1.4 A single FTIR system (or more) may be used to collect and analyze spectra (not quadruplicate integrated sampling trains).

13.1.5 All of the validation measurements are performed sequentially in a single "run" (section 3.26 of this method).

13.1.6 The measurements analyzed statistically are each independent (section 3.22 of this method).

13.1.7 A validation data set can consist of more than 12 spiked and 12 unspiked measurements.

13.2 *Batch Sampling.* The procedure in sections 13.2.1 through 13.2.2 may be used for stable processes. If process emissions are highly variable, the procedure in section 13.2.3 shall be used.

13.2.1 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.

13.2.2 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.)

13.2.3 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

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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.

13.3 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 shall be similar, if possible. The sampling configurations shall be the same. One sampling system and FTIR analyzer shall be used to measure spiked effluent. The other sampling system and FTIR analyzer shall be used to measure unspiked flue gas. Both systems shall use the same sampling procedure (i.e., batch or continuous).

13.3.1 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).

13.3.2 If continuous sampling is used, 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. $TC_1 = TC_2$).

13.4 Statistical Treatment. The statistical procedure of EPA Method 301 of this appendix, section 12.0 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.

13.4.1 Bias. Determine the bias (defined by EPA Method 301 of this appendix, section 12.1.1) using equation 7:

$$B = S_m - CS$$

Where:

B = Bias at spike level.

S_m = Mean concentration of the analyte spiked samples.

CS = Expected concentration of the spiked samples.

13.4.2 Correction Factor. Use section 6.3.2.2 of Method 301 of this appendix 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 $0.7 \leq CF \leq 1.3$. If it is determined that the bias is significant and $CF > \pm 30$ percent, then the test method is considered to "not valid."

13.4.3 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 1.6×10^{-4} to 3.2×10^{-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 L/min, 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

1. "Field Validation Test Using Fourier Transform Infrared (FTIR) Spectrometry To Measure Formaldehyde, Phenol and Methanol at a Wool Fiberglass Production Facility." Draft. U.S. Environmental Protection Agency Report, EPA Contract No. 68D20163, Work Assignment I-32, September 1994.
2. "FTIR Method Validation at a Coal-Fired Boiler". Prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No.: EPA-454/R95-004, NTIS No.: PB95-193199. July, 1993.
3. "Method 301—Field Validation of Pollutant Measurement Methods from Various Waste Media," 40 CFR part 63, appendix A.
4. "Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra," E. Bright Wilson, J.C. Decius, and P.C. Cross, Dover Publications, Inc., 1980. For a less intensive treatment of molecular rotational-vibrational spectra see, for example, "Physical Chemistry," G.M. Barrow, chapters 12, 13, and 14, McGraw Hill, Inc., 1979.
5. "Fourier Transform Infrared Spectrometry," Peter R. Griffiths and James de Haseth, Chemical Analysis, 83, 16-25,(1986), P.J. Elving, J.D. Winefordner and L.M. Kolthoff (ed.), John Wiley and Sons.
6. "Computer-Assisted Quantitative Infrared Spectroscopy," Gregory L. McClure (ed.), ASTM Special Publication 934 (ASTM), 1987.
7. "Multivariate Least-Squares Methods Applied to the Quantitative Spectral Analysis of Multicomponent Mixtures," Applied Spectroscopy, 39(10), 73-84. 1985.

TABLE 1—EXAMPLE PRESENTATION OF SAMPLING DOCUMENTATION

Sample time	Spectrum file name	Background file name	Sample conditioning	Process condition			
Sample time	Spectrum file	Interferogram	Resolution	Scans	Apodization	Gain	CTS Spectrum

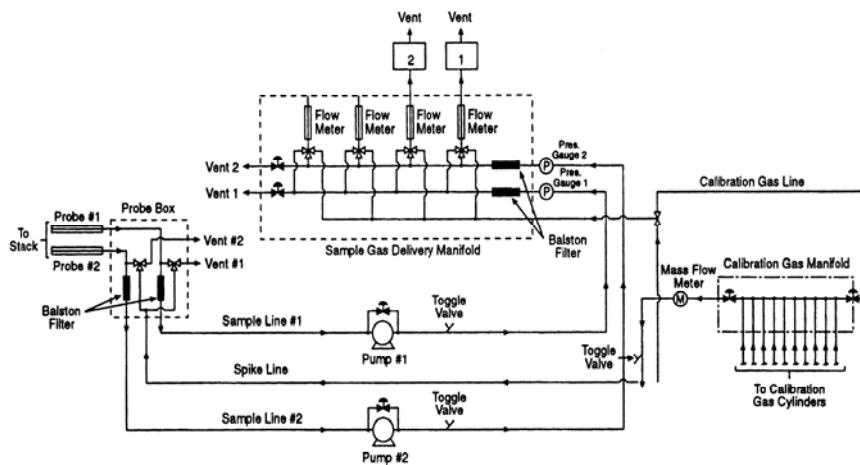


Figure 1. Extractive FTIR sampling system.

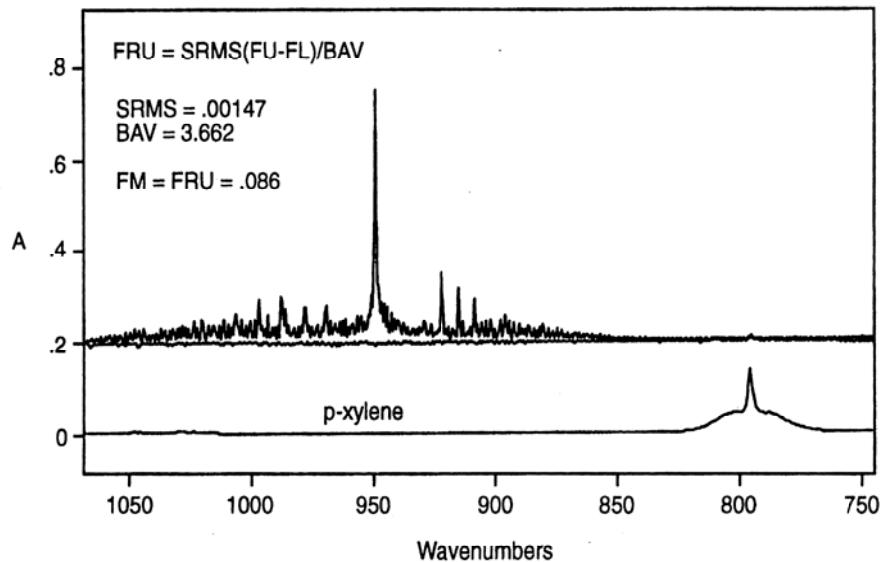


Figure 2. Fractional Reproducibility. Top: average of cts1031a and cts1101b. Bottom: Reference spectrum of p-xylene.

ADDENDUM TO TEST METHOD 320—PROTOCOL FOR THE USE OF EXTRACTIVE FOURIER TRANSFORM INFRARED (FTIR) SPECTROMETRY FOR THE ANALYSES OF GASEOUS EMISSIONS FROM STATIONARY SOURCES

1.0 Introduction

The purpose of this addendum is to set general guidelines for the use of modern FTIR spectroscopic methods for the analysis of gas samples extracted from the effluent of stationary emission sources. This addendum outlines techniques for developing and evaluating such methods and sets basic requirements for reporting and quality assurance procedures.

1.1 Nomenclature

1.1.1 Appendix A to this addendum lists definitions of the symbols and terms used in this Protocol, many of which have been taken directly from American Society for Testing and Materials (ASTM) publication E 131-90a, entitled "Terminology Relating to Molecular Spectroscopy."

1.1.2 Except in the case of background spectra or where otherwise noted, the term "spectrum" refers to a double-beam spectrum in units of absorbance vs. wavenumber (cm^{-1}).

1.1.3 The term "Study" in this addendum refers to a publication that has been subjected to EPA- or peer-review.

2.0 Applicability and Analytical Principle

2.1 *Applicability.* This Protocol applies to the determination of compound-specific concentrations in single- and multiple-component gas phase samples using double-beam absorption spectroscopy in the mid-infrared band. It does not specifically address other FTIR applications, such as single-beam spectroscopy, analysis of open-path (non-enclosed) samples, and continuous measurement techniques. If multiple spectrometers, absorption cells, or instrumental linewidths are used in such analyses, each distinct operational configuration of the system must be evaluated separately according to this Protocol.

2.2 Analytical Principle

2.2.1 In the mid-infrared band, most molecules exhibit characteristic gas phase absorption spectra that may be recorded by FTIR systems. Such systems consist of a source of mid-infrared radiation, an interferometer, an enclosed sample cell of known absorption pathlength, an infrared detector, optical elements for the transfer of infrared radiation between components, and gas flow control and measurement components. Adjunct and integral computer systems are used for controlling the instrument, processing the signal, and for performing both Fourier transforms and quantitative analyses of spectral data.

2.2.2 The absorption spectra of pure gases and of mixtures of gases are described by a linear absorbance theory referred to as Beer's Law. Using this law, modern FTIR systems use computerized analytical programs to quantify compounds by comparing the absorption spectra of known (reference) gas samples to the absorption spectrum of the sample gas. Some standard mathematical techniques used for comparisons are classical least squares, inverse least squares, cross-correlation, factor analysis, and partial least squares. Reference A describes several of these techniques, as well as additional techniques, such as differentiation methods, linear baseline corrections, and non-linear absorbance corrections.

3.0 General Principles of Protocol Requirements

The characteristics that distinguish FTIR systems from gas analyzers used in instrumental gas analysis methods (e.g., Methods 6C and 7E of appendix A to part 60 of this chapter) are: (1) Computers are necessary to obtain and analyze data; (2) chemical concentrations can be quantified using previously recorded infrared reference spectra; and (3) analytical assumptions and results, including possible effects of interfering compounds, can be evaluated after the quantitative analysis. The following general principles and requirements of this Protocol are based on these characteristics.

3.1 *Verifiability and Reproducibility of Results.* Store all data and document data analysis techniques sufficient to allow an independent agent to reproduce the analytical results from the raw interferometric data.

3.2 *Transfer of Reference Spectra.* To determine whether reference spectra recorded under one set of conditions (e.g., optical bench, instrumental linewidth, absorption pathlength, detector performance, pressure, and temperature) can be used to analyze sample spectra taken under a different set of conditions, quantitatively compare "calibration transfer standards" (CTS) and reference spectra as described in this Protocol.

NOTE: The CTS may, but need not, include analytes of interest). To effect this, record the absorption spectra of the CTS (a) immediately before and immediately after recording reference spectra and (b) immediately after recording sample spectra.

3.3 *Evaluation of FTIR Analyses.* The applicability, accuracy, and precision of FTIR measurements are influenced by a number of interrelated factors, which may be divided into two classes:

3.3.1 *Sample-Independent Factors.* Examples are system configuration and performance (e.g., detector sensitivity and infrared source output), quality and applicability of reference absorption spectra, and type of mathematical analyses of the spectra. These

factors define the fundamental limitations of FTIR measurements for a given system configuration. These limitations may be estimated from evaluations of the system before samples are available. For example, the detection limit for the absorbing compound under a given set of conditions may be estimated from the system noise level and the strength of a particular absorption band. Similarly, the accuracy of measurements may be estimated from the analysis of the reference spectra.

3.3.2 *Sample-Dependent Factors.* Examples are spectral interferences (e.g., water vapor and CO₂) or the overlap of spectral features of different compounds and contamination deposits on reflective surfaces or transmitting windows. To maximize the effectiveness of the mathematical techniques used in spectral analysis, identification of interferences (a standard initial step) and analysis of samples (includes effect of other analytical errors) are necessary. Thus, the Protocol requires post-analysis calculation of measurement concentration uncertainties for the detection of these potential sources of measurement error.

4.0 Pre-Test Preparations and Evaluations

Before testing, demonstrate the suitability of FTIR spectrometry for the desired application according to the procedures of this section.

4.1 *Identify Test Requirements.* Identify and record the test requirements described in sections 4.1.1 through 4.1.4 of this addendum. These values set the desired or required goals of the proposed analysis; the description of methods for determining whether these goals are actually met during the analysis comprises the majority of this Protocol.

4.1.1 *Analyses (specific chemical species) of interest.* Label the analytes from i = 1 to I.

4.1.2 *Analytical uncertainty limit (AU_i).* The AU_i is the maximum permissible fractional uncertainty of analysis for the ith analyte concentration, expressed as a fraction of the analyte concentration in the sample.

4.1.3 *Required detection limit for each analyte (DL_i, ppm).* The detection limit is the lowest concentration of an analyte for which its overall fractional uncertainty (OFU_i) is required to be less than its analytical uncertainty limit (AU_i).

4.1.4 *Maximum expected concentration of each analyte (CMAX_i, ppm).*

4.2 *Identify Potential Interferants.* Considering the chemistry of the process or results of previous studies, identify potential interferants, i.e., the major effluent constituents and any relatively minor effluent constituents that possess either strong absorption characteristics or strong structural similarities to any analyte of interest. Label them 1 through N_j, where the subscript "j"

pertains to potential interferants. Estimate the concentrations of these compounds in the effluent (CPOT_i, ppm).

4.3 Select and Evaluate the Sampling System. Considering the source, e.g., temperature and pressure profiles, moisture content, analyte characteristics, and particulate concentration, select the equipment for extracting gas samples. Recommended are a particulate filter, heating system to maintain sample temperature above the dew point for all sample constituents at all points within the sampling system (including the filter), and sample conditioning system (e.g., coolers, water-permeable membranes that remove water or other compounds from the sample, and dilution devices) to remove spectral interferers or to protect the sampling and analytical components. Determine the minimum absolute sample system pressure (P_{min} , mmHg) and the infrared absorption cell volume (V_{ss} , liter). Select the techniques and/or equipment for the measurement of sample pressures and temperatures.

4.4 Select Spectroscopic System. Select a spectroscopic configuration for the application. Approximate the absorption pathlength (L_s' , meter), sample pressure (P_s' , kPa), absolute sample temperature T_s' , and signal integration period (t_{ss} , seconds) for the analysis. Specify the nominal minimum instrumental linewidth (MIL) of the system. Verify that the fractional error at the approximate values P_s' and T_s' is less than one half the smallest value AU_i (see section 4.1.2 of this addendum).

4.5 Select Calibration Transfer Standards (CTS's). Select CTS's that meet the criteria listed in sections 4.5.1, 4.5.2, and 4.5.3 of this addendum.

NOTE: It may be necessary to choose preliminary analytical regions (see section 4.7 of this addendum), identify the minimum analyte linewidths, or estimate the system noise level (see section 4.12 of this addendum) before selecting the CTS. More than one compound may be needed to meet the criteria; if so, obtain separate cylinders for each compound.

4.5.1 The central wavenumber position of each analytical region shall lie within 25 percent of the wavenumber position of at least one CTS absorption band.

4.5.2 The absorption bands in section 4.5.1 of this addendum shall exhibit peak absorbances greater than ten times the value RMS_{EST} (see section 4.12 of this addendum) but less than 1.5 absorbance units.

4.5.3 At least one absorption CTS band within the operating range of the FTIR instrument shall have an instrument-independent linewidth no greater than the narrowest analyte absorption band. Perform and document measurements or cite Studies to determine analyte and CTS compound linewidths.

4.5.4 For each analytical region, specify the upper and lower wavenumber positions (FFU_m and FFL_m, respectively) that bracket the CTS absorption band or bands for the associated analytical region. Specify the wavenumber range, FNU to FNL, containing the absorption band that meets the criterion of section 4.5.3 of this addendum.

4.5.5 Associate, whenever possible, a single set of CTS gas cylinders with a set of reference spectra. Replacement CTS gas cylinders shall contain the same compounds at concentrations within 5 percent of that of the original CTS cylinders; the entire absorption spectra (not individual spectral segments) of the replacement gas shall be scaled by a factor between 0.95 and 1.05 to match the original CTS spectra.

4.6 Prepare Reference Spectra

NOTE: Reference spectra are available in a permanent soft copy from the EPA spectral library on the EMTIC (Emission Measurement Technical Information Center) computer bulletin board; they may be used if applicable.

4.6.1 Select the reference absorption pathlength (L_R) of the cell.

4.6.2 Obtain or prepare a set of chemical standards for each analyte, potential and known spectral interferants, and CTS. Select the concentrations of the chemical standards to correspond to the top of the desired range.

4.6.2.1 Commercially-Prepared Chemical Standards. Chemical standards for many compounds may be obtained from independent sources, such as a specialty gas manufacturer, chemical company, or commercial laboratory. These standards (accurate to within ± 2 percent) shall be prepared according to EPA Traceability Protocol (see Reference D) or shall be traceable to NIST standards. Obtain from the supplier an estimate of the stability of the analyte concentration. Obtain and follow all of the supplier's recommendations for recertifying the analyte concentration.

4.6.2.2 Self-Prepared Chemical Standards. Chemical standards may be prepared by diluting certified commercially prepared chemical gases or pure analytes with ultrapure carrier (UPC) grade nitrogen according to the barometric and volumetric techniques generally described in Reference A, section A4.6.

4.6.3 Record a set of the absorption spectra of the CTS {R1}, then a set of the reference spectra at two or more concentrations in duplicate over the desired range (the top of the range must be less than 10 times that of the bottom), followed by a second set of CTS spectra {R2}. (If self-prepared standards are used, see section 4.6.5 of this addendum before disposing of any of the standards.) The maximum accepted standard concentration-pathlength product (ASCPP) for each compound shall be higher than the

maximum estimated concentration-pathlength products for both analytes and known interferants in the effluent gas. For each analyte, the minimum ASCPP shall be no greater than ten times the concentration-pathlength product of that analyte at its required detection limit.

4.6.4 Permanently store the background and interferograms in digitized form. Document details of the mathematical process for generating the spectra from these interferograms. Record the sample pressure (P_R), sample temperature (T_R), reference absorption pathlength (L_R), and interferogram signal integration period (t_{SR}). Signal integration periods for the background interferograms shall be $\geq t_{SR}$. Values of P_R , L_R , and t_{SR} shall not deviate by more than ± 1 percent from the time of recording [R1] to that of recording [R2].

4.6.5 If self-prepared chemical standards are employed and spectra of only two concentrations are recorded for one or more compounds, verify the accuracy of the dilution technique by analyzing the prepared standards for those compounds with a secondary (non-FTIR) technique in accordance with sections 4.6.5.1 through 4.6.5.4 of this addendum.

4.6.5.1 Record the response of the secondary technique to each of the four standards prepared.

4.6.5.2 Perform a linear regression of the response values (dependent variable) versus the accepted standard concentration (ASC) values (independent variable), with the regression constrained to pass through the zero-response, zero ASC point.

4.6.5.3 Calculate the average fractional difference between the actual response values and the regression-predicted values (those calculated from the regression line using the four ASC values as the independent variable).

4.6.5.4 If the average fractional difference value calculated in section 4.6.5.3 of this addendum is larger for any compound than the corresponding AU_i, the dilution technique is not sufficiently accurate and the reference spectra prepared are not valid for the analysis.

4.7 *Select Analytical Regions.* Using the general considerations in section 7 of Reference A and the spectral characteristics of the analytes and interferants, select the analytical regions for the application. Label them m = 1 to M. Specify the lower, center and upper wavenumber positions of each analytical region (FL_m, FC_m, and FU_m, respectively). Specify the analytes and interferants which exhibit absorption in each region.

4.8 *Determine Fractional Reproducibility Uncertainties.* Using appendix E of this addendum, calculate the fractional reproducibility uncertainty for each analyte (FRU_i) from a comparison of [R1] and [R2]. If FRU_i > AU_i for any analyte, the reference spectra generated

in accordance with section 4.6 of this addendum are not valid for the application.

4.9 *Identify Known Interferants.* Using appendix B of this addendum, determine which potential interferants affect the analyte concentration determinations. Relabel these potential interferants as "known" interferants, and designate these compounds from k = 1 to K. Appendix B to this addendum also provides criteria for determining whether the selected analytical regions are suitable.

4.10 *Prepare Computerized Analytical Programs*

4.10.1 Choose or devise mathematical techniques (e.g., classical least squares, inverse least squares, cross-correlation, and factor analysis) based on equation 4 of Reference A that are appropriate for analyzing spectral data by comparison with reference spectra.

4.10.2 Following the general recommendations of Reference A, prepare a computer program or set of programs that analyzes all of the analytes and known interferants, based on the selected analytical regions (section 4.7 of this addendum) and the prepared reference spectra (section 4.6 of this addendum). Specify the baseline correction technique (e.g., determining the slope and intercept of a linear baseline contribution in each analytical region) for each analytical region, including all relevant wavenumber positions.

4.10.3 Use programs that provide as output [at the reference absorption pathlength (L_R), reference gas temperature (T_R), and reference gas pressure (P_R)] the analyte concentrations, the known interferant concentrations, and the baseline slope and intercept values. If the sample absorption pathlength (L_S), sample gas temperature (T_S), or sample gas pressure (P_S) during the actual sample analyses differ from L_R , T_R , and P_R , use a program or set of programs that applies multiplicative corrections to the derived concentrations to account for these variations, and that provides as output both the corrected and uncorrected values. Include in the report of the analysis (see section 7.0 of this addendum) the details of any transformations applied to the original reference spectra (e.g., differentiation), in such a fashion that all analytical results may be verified by an independent agent from the reference spectra and data spectra alone.

4.11 *Determine the Fractional Calibration Uncertainty.* Calculate the fractional calibration uncertainty for each analyte (FCU_i) according to appendix F of this addendum, and compare these values to the fractional uncertainty limits (AU_i; see section 4.1.2 of this addendum). If FCU_i > AU_i, either the reference spectra or analytical programs for that analyte are unsuitable.

4.12 *Verify System Configuration Suitability.* Using appendix C of this addendum, measure or obtain estimates of the noise level (RMS_{EST}, absorbance) of the FTIR system.

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Alternatively, construct the complete spectrometer system and determine the values RMS_m using appendix G of this addendum. Estimate the minimum measurement uncertainty for each analyte (MAU_i, ppm) and known interferant (MIU_k, ppm) using appendix D of this addendum. Verify that (a) MAU_i < (AU_i)(DL_i), FRU_i < AU_i, and FCU_i < AU_i for each analyte and that (b) the CTS chosen meets the requirements listed in sections 4.5.1 through 4.5.5 of this addendum.

5.0 Sampling and Analysis Procedure

5.1 Analysis System Assembly and Leak-Test. Assemble the analysis system. Allow sufficient time for all system components to reach the desired temperature. Then, determine the leak-rate (L_R) and leak volume (V_L), where $V_L = L_R t_{ss}$. Leak volumes shall be ≤ 4 percent of V_{ss} .

5.2 Verify Instrumental Performance. Measure the noise level of the system in each analytical region using the procedure of appendix G of this addendum. If any noise level is higher than that estimated for the system in section 4.12 of this addendum, repeat the calculations of appendix D of this addendum and verify that the requirements of section 4.12 of this addendum are met; if they are not, adjust or repair the instrument and repeat this section.

5.3 Determine the Sample Absorption Pathlength

Record a background spectrum. Then, fill the absorption cell with CTS at the pressure P_R and record a set of CTS spectra [R3]. Store the background and unscaled CTS single beam interferograms and spectra. Using appendix H of this addendum, calculate the sample absorption pathlength (L_S) for each analytical region. The values L_S shall not differ from the approximated sample pathlength L_S' (see section 4.4 of this addendum) by more than 5 percent.

5.4 Record Sample Spectrum. Connect the sample line to the source. Either evacuate the absorption cell to an absolute pressure below 5 mmHg before extracting a sample from the effluent stream into the absorption cell, or pump at least ten cell volumes of sample through the cell before obtaining a sample. Record the sample pressure P_S . Generate the absorbance spectrum of the sample. Store the background and sample single beam interferograms, and document the process by which the absorbance spectra are generated from these data. (If necessary, apply the spectral transformations developed in section 5.6.2 of this addendum). The resulting sample spectrum is referred to below as S_S .

NOTE: Multiple sample spectra may be recorded according to the procedures of section 5.4 of this addendum before performing sections 5.5 and 5.6 of this addendum.

5.5 Quantify Analyte Concentrations. Calculate the unscaled analyte concentrations RUA_i and unscaled interferant concentrations RUI_k using the programs developed in section 4 of this addendum. To correct for pathlength and pressure variations between the reference and sample spectra, calculate the scaling factor, R_{LPS} using equation A.1,

$$R_{LPS} = (L_R P_R T_S) / (L_S P_S T_R) \quad (A.1)$$

Calculate the final analyte and interferant concentrations RSA_i and RSI_k using equations A.2 and A.3,

$$RSA_i = R_{LPS} RUA_i \quad (A.2)$$

$$RSI_k = R_{LPS} RUI_k \quad (A.3)$$

5.6 Determine Fractional Analysis Uncertainty. Fill the absorption cell with CTS at the pressure P_S . Record a set of CTS spectra [R4]. Store the background and CTS single beam interferograms. Using appendix H of this addendum, calculate the fractional analysis uncertainty (FAU) for each analytical region. If the FAU indicated for any analytical region is greater than the required accuracy requirements determined in sections 4.1.1 through 4.1.4 of this addendum, then comparisons to previously recorded reference spectra are invalid in that analytical region, and the analyst shall perform one or both of the procedures of sections 5.6.1 through 5.6.2 of this addendum.

5.6.1 Perform instrumental checks and adjust the instrument to restore its performance to acceptable levels. If adjustments are made, repeat sections 5.3, 5.4 (except for the recording of a sample spectrum), and 5.5 of this addendum to demonstrate that acceptable uncertainties are obtained in all analytical regions.

5.6.2 Apply appropriate mathematical transformations (e.g., frequency shifting, zero-filling, apodization, smoothing) to the spectra (or to the interferograms upon which the spectra are based) generated during the performance of the procedures of section 5.3 of this addendum. Document these transformations and their reproducibility. Do not apply multiplicative scaling of the spectra, or any set of transformations that is mathematically equivalent to multiplicative scaling. Different transformations may be applied to different analytical regions. Frequency shifts shall be less than one-half the minimum instrumental linewidth, and must be applied to all spectral data points in an analytical region. The mathematical transformations may be retained for the analysis if they are also applied to the appropriate analytical regions of all sample spectra recorded, and if all original sample spectra are digitally stored. Repeat sections 5.3, 5.4 (except the recording of a sample spectrum), and 5.5 of this addendum to demonstrate

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that these transformations lead to acceptable calculated concentration uncertainties in all analytical regions.

6.0 Post-Analysis Evaluations

Estimate the overall accuracy of the analyses performed in accordance with sections 5.1 through 5.6 of this addendum using the procedures of sections 6.1 through 6.3 of this addendum.

6.1 Qualitatively Confirm the Assumed Matrix. Examine each analytical region of the sample spectrum for spectral evidence of unexpected or unidentified interferants. If found, identify the interfering compounds (see Reference C for guidance) and add them to the list of known interferants. Repeat the procedures of section 4 of this addendum to include the interferants in the uncertainty calculations and analysis procedures. Verify that the MAU and FCU values do not increase beyond acceptable levels for the application requirements. Re-calculate the analyte concentrations (section 5.5 of this addendum) in the affected analytical regions.

6.2 Quantitatively Evaluate Fractional Model Uncertainty (FMU). Perform the procedures of either section 6.2.1 or 6.2.2 of this addendum:

6.2.1 Using appendix I of this addendum, determine the fractional model error (FMU) for each analyte.

6.2.2 Provide statistically determined uncertainties FMU for each analyte which are equivalent to two standard deviations at the 95 percent confidence level. Such determinations, if employed, must be based on mathematical examinations of the pertinent sample spectra (not the reference spectra alone). Include in the report of the analysis (see section 7.0 of this addendum) a complete description of the determination of the concentration uncertainties.

6.3 Estimate Overall Concentration Uncertainty (OCU). Using appendix J of this addendum, determine the overall concentration uncertainty (OCU) for each analyte. If the OCU is larger than the required accuracy for any analyte, repeat sections 4 and 6 of this addendum.

7.0 Reporting Requirements

[Documentation pertaining to virtually all the procedures of sections 4, 5, and 6 will be required. Software copies of reference spectra and sample spectra will be retained for some minimum time following the actual testing.]

8.0 References

(A) Standard Practices for General Techniques of Infrared Quantitative Analysis (American Society for Testing and Materials, Designation E 168-88).

40 CFR Ch. I (7-1-17 Edition)

(B) The Coblenz Society Specifications for Evaluation of Research Quality Analytical Infrared Reference Spectra (Class II); Anal. Chemistry 47, 945A (1975); Appl. Spectroscopy 44, pp. 211-215, 1990.

(C) Standard Practices for General Techniques for Qualitative Infrared Analysis. American Society for Testing and Materials, Designation E 1252-88.

(D) "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards," U.S. Environmental Protection Agency Publication No. EPA/600/R-93/224. December 1993.

APPENDIX A TO ADDENDUM TO METHOD 320— DEFINITIONS OF TERMS AND SYMBOLS

A.1 Definitions of Terms. All terms used in this method that are not defined below have the meaning given to them in the CAA and in subpart A of this part.

Absorption band means a contiguous wavenumber region of a spectrum (equivalently, a contiguous set of absorbance spectrum data points) in which the absorbance passes through a maximum or a series of maxima.

Absorption pathlength means the distance in a spectrophotometer, measured in the direction of propagation of the beam of radiant energy, between the surface of the specimen on which the radiant energy is incident and the surface of the specimen from which it is emergent.

Analytical region means a contiguous wavenumber region (equivalently, a contiguous set of absorbance spectrum data points) used in the quantitative analysis for one or more analytes.

NOTE: The quantitative result for a single analyte may be based on data from more than one analytical region.

Apodization means modification of the ILS function by multiplying the interferogram by a weighing function whose magnitude varies with retardation.

Background spectrum means the single beam spectrum obtained with all system components without sample present.

Baseline means any line drawn on an absorption spectrum to establish a reference point that represents a function of the radiant power incident on a sample at a given wavelength.

Beers's law means the direct proportionality of the absorbance of a compound in a homogeneous sample to its concentration.

Calibration transfer standard (CTS) gas means a gas standard of a compound used to achieve and/or demonstrate suitable quantitative agreement between sample spectra and the reference spectra; see section 4.5.1 of this addendum.

Compound means a substance possessing a distinct, unique molecular structure.

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Concentration (c) means the quantity of a compound contained in a unit quantity of sample. The unit "ppm" (number, or mole, basis) is recommended.

Concentration-pathlength product means the mathematical product of concentration of the species and absorption pathlength. For reference spectra, this is a known quantity; for sample spectra, it is the quantity directly determined from Beer's law. The units "centimeters-ppm" or "meters-ppm" are recommended.

Derivative absorption spectrum means a plot of rate of change of absorbance or of any function of absorbance with respect to wavelength or any function of wavelength.

Double beam spectrum means a transmission or absorbance spectrum derived by dividing the sample single beam spectrum by the background spectrum.

NOTE: The term "double-beam" is used elsewhere to denote a spectrum in which the sample and background interferograms are collected simultaneously along physically distinct absorption paths. Here, the term denotes a spectrum in which the sample and background interferograms are collected at different times along the same absorption path.

Fast Fourier transform (FFT) means a method of speeding up the computation of a discrete FT by factoring the data into sparse matrices containing mostly zeros.

Flyback means interferometer motion during which no data are recorded.

Fourier transform (FT) means the mathematical process for converting an amplitude-time spectrum to an amplitude-frequency spectrum, or vice versa.

Fourier transform infrared (FTIR) spectrometer means an analytical system that employs a source of mid-infrared radiation, an interferometer, an enclosed sample cell of known absorption pathlength, an infrared detector, optical elements that transfer infrared radiation between components, and a computer system. The time-domain detector response (interferogram) is processed by a Fourier transform to yield a representation of the detector response vs. infrared frequency.

NOTE: When FTIR spectrometers are interfaced with other instruments, a slash should be used to denote the interface; e.g., GC/FTIR; HPCL/FTIR, and the use of FTIR should be explicit; i.e., FTIR not IR.

Frequency, v means the number of cycles per unit time.

Infrared means the portion of the electromagnetic spectrum containing wavelengths from approximately 0.78 to 800 microns.

Interferogram, I(σ) means record of the modulated component of the interference signal measured as a function of retardation by the detector.

Interferometer means device that divides a beam of radiant energy into two or more paths, generates an optical path difference between the beams, and recombines them in order to produce repetitive interference maxima and minima as the optical retardation is varied.

Linewidth means the full width at half maximum of an absorption band in units of wavenumbers (cm^{-1}).

Mid-infrared means the region of the electromagnetic spectrum from approximately 400 to 5000 cm^{-1} .

Reference spectra means absorption spectra of gases with known chemical compositions, recorded at a known absorption pathlength, which are used in the quantitative analysis of gas samples.

Retardation, σ means optical path difference between two beams in an interferometer; also known as "optical path difference" or "optical retardation."

Scan means digital representation of the detector output obtained during one complete motion of the interferometer's moving assembly or assemblies.

Scaling means application of a multiplicative factor to the absorbance values in a spectrum.

Single beam spectrum means Fourier-transformed interferogram, representing the detector response vs. wavenumber.

NOTE: The term "single-beam" is used elsewhere to denote any spectrum in which the sample and background interferograms are recorded on the same physical absorption path; such usage differentiates such spectra from those generated using interferograms recorded along two physically distinct absorption paths (see "double-beam spectrum" above). Here, the term applies (for example) to the two spectra used directly in the calculation of transmission and absorbance spectra of a sample.

Standard reference material means a reference material, the composition or properties of which are certified by a recognized standardizing agency or group.

NOTE: The equivalent ISO term is "certified reference material."

Transmittance, T means the ratio of radiant power transmitted by the sample to the radiant power incident on the sample. Estimated in FTIR spectroscopy by forming the ratio of the single-beam sample and background spectra.

Wavenumber, ν means the number of waves per unit length.

NOTE: The usual unit of wavenumber is the reciprocal centimeter, cm^{-1} . The wavenumber is the reciprocal of the wavelength, $λ$, when $λ$ is expressed in centimeters.

Zero-filling means the addition of zero-valued points to the end of a measured interferogram.

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NOTE: Performing the FT of a zero-filled interferogram results in correctly interpolated points in the computed spectrum.

A.2 Definitions of Mathematical Symbols. The symbols used in equations in this protocol are defined as follows:

(1) A, absorbance = the logarithm to the base 10 of the reciprocal of the transmittance (T).

$$A = \log_{10} \left(\frac{1}{T} \right) = -\log_{10} T$$

(2) AAI_{im} = band area of the i^{th} analyte in the m^{th} analytical region, at the concentration (CL_i) corresponding to the product of its required detection limit (DL_i) and analytical uncertainty limit (AU_i).

(3) AAV_{im} = average absorbance of the i^{th} analyte in the m^{th} analytical region, at the concentration (CL_i) corresponding to the product of its required detection limit (DL_i) and analytical uncertainty limit (AU_i).

(4) ASC, accepted standard concentration = the concentration value assigned to a chemical standard.

(5) ASCPP, accepted standard concentration-pathlength product = for a chemical standard, the product of the ASC and the sample absorption pathlength. The units "centimeters-ppm" or "meters-ppm" are recommended.

(6) AU_i , analytical uncertainty limit = the maximum permissible fractional uncertainty of analysis for the i^{th} analyte concentration, expressed as a fraction of the analyte concentration determined in the analysis.

(7) AVT_m = average estimated total absorbance in the m^{th} analytical region.

(8) $CKWN_k$ = estimated concentration of the k^{th} known interferant.

(9) $CMAX_i$ = estimated maximum concentration of the i^{th} analyte.

(10) $CPOT_j$ = estimated concentration of the j^{th} potential interferant.

(11) DL_i , required detection limit = for the i^{th} analyte, the lowest concentration of the analyte for which its overall fractional uncertainty (OFU_i) is required to be less than the analytical uncertainty limit (AU_i).

(12) FC_m = center wavenumber position of the m^{th} analytical region.

(13) FAU_i , fractional analytical uncertainty = calculated uncertainty in the measured concentration of the i^{th} analyte because of errors in the mathematical comparison of reference and sample spectra.

(14) FCU_i , fractional calibration uncertainty = calculated uncertainty in the measured concentration of the i^{th} analyte because of errors in Beer's law modeling of the reference spectra concentrations.

(15) FFL_m = lower wavenumber position of the CTS absorption band associated with the m^{th} analytical region.

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(16) FFU_m = upper wavenumber position of the CTS absorption band associated with the m^{th} analytical region.

(17) FL_m = lower wavenumber position of the m^{th} analytical region.

(18) FMU_i , fractional model uncertainty = calculated uncertainty in the measured concentration of the i^{th} analyte because of errors in the absorption model employed.

(19) FN_L = lower wavenumber position of the CTS spectrum containing an absorption band at least as narrow as the analyte absorption bands.

(20) FN_U = upper wavenumber position of the CTS spectrum containing an absorption band at least as narrow as the analyte absorption bands.

(21) FRU_i , fractional reproducibility uncertainty = calculated uncertainty in the measured concentration of the i^{th} analyte because of errors in the reproducibility of spectra from the FTIR system.

(22) FU_m = upper wavenumber position of the m^{th} analytical region.

(23) IAI_{jm} = band area of the j^{th} potential interferant in the m^{th} analytical region, at its expected concentration ($CPOT_j$).

(24) IAV_{jm} = average absorbance of the i^{th} analyte in the m^{th} analytical region, at its expected concentration ($CPOT_j$).

(25) $ISC_{i \text{ or } k}$, indicated standard concentration = the concentration from the computerized analytical program for a single-compound reference spectrum for the i^{th} analyte or k^{th} known interferant.

(26) kPa = kilo-Pascal (see Pascal).

(27) L_s' = estimated sample absorption pathlength.

(28) L_R = reference absorption pathlength.

(29) L_s = actual sample absorption pathlength.

(30) MAU_i = mean of the MAU_{im} over the appropriate analytical regions.

(31) MAU_{im} , minimum analyte uncertainty = the calculated minimum concentration for which the analytical uncertainty limit (AU_i) in the measurement of the i^{th} analyte, based on spectral data in the m^{th} analytical region, can be maintained.

(32) MIU_j = mean of the MIU_{jm} over the appropriate analytical regions.

(33) MIU_{jm} , minimum interferant uncertainty = the calculated minimum concentration for which the analytical uncertainty limit $CPOT_j/20$ in the measurement of the j^{th} interferant, based on spectral data in the m^{th} analytical region, can be maintained.

(34) MIL , minimum instrumental linewidth = the minimum linewidth from the FTIR system, in wavenumbers.

NOTE: The MIL of a system may be determined by observing an absorption band known (through higher resolution examinations) to be narrower than indicated by the system. The MIL is fundamentally limited by the retardation of the interferometer, but

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is also affected by other operational parameters (e.g., the choice of apodization).

- (35) N_i = number of analytes.
- (36) N_j = number of potential interferants.
- (37) N_k = number of known interferants.
- (38) N_{scan} = the number of scans averaged to obtain an interferogram.
- (39) OFU_i = the overall fractional uncertainty in an analyte concentration determined in the analysis ($\text{OFU}_i = \text{MAX}[\text{FRU}_i, \text{FCU}_i, \text{FAU}_i, \text{FMU}_i]$).
- (40) Pascal (Pa) = metric unit of static pressure, equal to one Newton per square meter; one atmosphere is equal to 101,325 Pa; 1/760 atmosphere (one Torr, or one millimeter Hg) is equal to 133.322 Pa.
- (41) P_{min} = minimum pressure of the sampling system during the sampling procedure.
- (42) P_s' = estimated sample pressure.
- (43) P_R = reference pressure.
- (44) P_s = actual sample pressure.
- (45) RMS_{Sm} = measured noise level of the FTIR system in the m^{th} analytical region.
- (46) RMSD , root mean square difference = a measure of accuracy determined by the following equation:

$$\text{RMSD} = \sqrt{\left(\frac{1}{n}\right) \sum_{i=1}^n e_i^2}$$

Where:

- n = the number of observations for which the accuracy is determined.
- e_i = the difference between a measured value of a property and its mean value over the n observations.

NOTE: The RMSD value "between a set of n contiguous absorbance values (A_i) and the mean of the values" (A_M) is defined as

$$\text{RMSD} = \sqrt{\left(\frac{1}{n}\right) \sum_{i=1}^n (A_i - A_M)^2}$$

- (47) RSA_i = the (calculated) final concentration of the i^{th} analyte.

- (48) RSI_k = the (calculated) final concentration of the k^{th} known interferant.

- (49) t_{scan} , scan time = time used to acquire a single scan, not including flyback.

- (50) t_s , signal integration period = the period of time over which an interferogram is averaged by addition and scaling of individual scans. In terms of the number of scans N_{scan} and scan time t_{scan} , $t_s = N_{\text{scan}} t_{\text{scan}}$.

- (51) t_{SR} = signal integration period used in recording reference spectra.

- (52) t_{SS} = signal integration period used in recording sample spectra.

- (53) T_R = absolute temperature of gases used in recording reference spectra.

- (54) T_S = absolute temperature of sample gas as sample spectra are recorded.

- (55) TP, Throughput = manufacturer's estimate of the fraction of the total infrared

power transmitted by the absorption cell and transfer optics from the interferometer to the detector.

(56) V_{ss} = volume of the infrared absorption cell, including parts of attached tubing.

(57) W_k = weight used to average over analytical regions k for quantities related to the analyte i ; see appendix D of this addendum.

APPENDIX B TO ADDENDUM TO METHOD 320— IDENTIFYING SPECTRAL INTERFERANTS

B.1 General

B.1.1 Assume a fixed absorption pathlength equal to the value L_s' .

B.1.2 Use band area calculations to compare the relative absorption strengths of the analytes and potential interferants. In the m^{th} analytical region (FL_m to FU_m), use either rectangular or trapezoidal approximations to determine the band areas described below (see Reference A, sections A.3.1 through A.3.3). Document any baseline corrections applied to the spectra.

B.1.3 Use the average total absorbance of the analytes and potential interferants in each analytical region to determine whether the analytical region is suitable for analyte concentration determinations.

NOTE: The average absorbance in an analytical region is the band area divided by the width of the analytical region in wavenumbers. The average total absorbance in an analytical region is the sum of the average absorbances of all analytes and potential interferants.

B.2 Calculations

B.2.1 Prepare spectral representations of each analyte at the concentration $CL_i = (DL_i)(AU_i)$, where DL_i is the required detection limit and AU_i is the maximum permissible analytical uncertainty. For the m^{th} analytical region, calculate the band area (AAI_{im}) and average absorbance (AAV_{im}) from these scaled analyte spectra.

B.2.2 Prepare spectral representations of each potential interferant at its expected concentration ($CPOT_i$). For the m^{th} analytical region, calculate the band area (IAI_{jm}) and average absorbance (IAV_{jm}) from these scaled potential interferant spectra.

B.2.3 Repeat the calculation for each analytical region, and record the band area results in matrix form as indicated in Figure B.1.

B.2.4 If the band area of any potential interferant in an analytical region is greater than the one-half the band area of any analyte (i.e., $IAI_{jm} > 0.5 AAI_{im}$ for any pair ij and any m), classify the potential interferant as a known interferant. Label the known interferants $k = 1$ to K . Record the results in matrix form as indicated in Figure B.2.

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B.2.5 Calculate the average total absorbance (AVT_m) for each analytical region and record the values in the last row of the matrix described in Figure B.2. Any analytical region where $AVT_m > 2.0$ is unsuitable.

FIGURE B.1 Presentation of Potential Interferant Calculations.

Analytical Regions	
	1 . . . M
<hr/>	
Analyte Labels	
1	AAI ₁₁ . . . AAI _{1M}
.	.
.	.
I	AAI _{I1} . . . AAI _{IM}
<hr/>	
Potential Interferant Labels	
1	IAI ₁₁ . . . IAI _{1M}
.	.
.	.
J	IAI _{J1} . . . IAI _{JM}

FIGURE B.2 Presentation of Known Interferant Calculations

Analytical Regions	
	1 . . . M
<hr/>	
Analyte Labels	
1	AAI ₁₁ . . . AAI _{1M}
.	.
.	.
I	AAI _{I1} . . . AAI _{IM}
<hr/>	
Known Interferant Labels	
1	IAI ₁₁ . . . IAI _{1M}
.	.
.	.
K	IAI _{K1} . . . IAI _{KM}
<hr/>	
Total Average Absorbance	
	AVT ₁ AVT _M

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APPENDIX C TO ADDENDUM TO METHOD 320— ESTIMATING NOISE LEVELS

C.1 General

C.1.1 The root-mean-square (RMS) noise level is the standard measure of noise in this addendum. The RMS noise level of a contiguous segment of a spectrum is defined as the RMS difference (RMSD) between the absorbance values which form the segment and the mean value of that segment (see appendix A of this addendum).

C.1.2 The RMS noise value in double-beam absorbance spectra is assumed to be inversely proportional to: (a) the square root of the signal integration period of the sample single beam spectra from which it is formed, and (b) the total infrared power transmitted through the interferometer and absorption cell.

C.1.3 Practically, the assumption of C.1.2 allows the RMS noise level of a complete system to be estimated from the quantities described in sections C.1.3.1 through C.1.3.4:

C.1.3.1 RMS_{MAN} , the noise level of the system (in absorbance units), without the absorption cell and transfer optics, under those conditions necessary to yield the specified minimum instrumental linewidth, e.g., Jacquinot stop size.

C.1.3.2 t_{MAN} , the manufacturer's signal integration time used to determine RMS_{MAN} .

C.1.3.3 t_{ss} , the signal integration time for the analyses.

C.1.3.4 TP, the manufacturer's estimate of the fraction of the total infrared power transmitted by the absorption cell and transfer optics from the interferometer to the detector.

C.2 Calculations

C.2.1 Obtain the values of RMS_{MAN} , t_{MAN} , and TP from the manufacturers of the equipment, or determine the noise level by direct measurements with the completely constructed system proposed in section 4 of this addendum.

C.2.2 Calculate the noise value of the system (RMS_{EST}) using equation C.1.

$$RMS_{EST} = RMS_{MAN} \sqrt{\frac{t_{ss}}{t_{MAN}}} \quad (C.1)$$

APPENDIX D TO ADDENDUM TO METHOD 320— ESTIMATING MINIMUM CONCENTRATION MEASUREMENT UNCERTAINTIES (MAU AND MIU)

D.1 General

Estimate the minimum concentration measurement uncertainties for the i^{th} analyte (MAU_i) and j^{th} interferant (MIU_j) based on the spectral data in the m^{th} analytical region by comparing the analyte band area in the analytical region (AAI_{im}) and estimating or measuring the noise level of the system (RMS_{EST} or RMS_{SM}).

NOTE: For a single analytical region, the MAU or MIU value is the concentration of the analyte or interferant for which the band

area is equal to the product of the analytical region width (in wavenumbers) and the noise level of the system (in absorbance units). If data from more than one analytical region are used in the determination of an analyte concentration, the MAU or MIU is the mean of the separate MAU or MIU values calculated for each analytical region.

D.2 Calculations

D.2.1 For each analytical region, set $RMS = RMS_{SM}$ if measured (appendix G of this addendum), or set $RMS = RMS_{EST}$ if estimated (appendix C of this addendum).

D.2.2 For each analyte associated with the analytical region, calculate MAU_{im} using equation D.1.

$$MAU_{im} = (RMS) (DL_i) (AU_i) \frac{(FU_m - FL_m)}{AAI_{im}} \quad (D.1)$$

D.2.3 If only the m^{th} analytical region is used to calculate the concentration of the i^{th} analyte, set $MAU_i = MAU_{im}$.

D.2.4 If more than one analytical region is used to calculate the concentration of the i^{th}

analyte, set MAU_i equal to the weighted mean of the appropriate MAU_{im} values calculated above; the weight for each term in the mean is equal to the fraction of the total wavenumber range used for the calculation

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represented by each analytical region. Mathematically, if the set of analytical regions employed is $\{m'\}$, then the MAU for each analytical region is given by equation D.2.

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$$MAU_i = \sum_{k \in \{m'\}} W_{ik} MAU_{ik} \quad (D.2)$$

where the weight W_{ik} is defined for each term in the sum as

$$W_{ik} = (FM_k - FL_k) \left(\sum_{p \in \{m'\}} [FM_p - FL_p] \right)^{-1} \quad (D.3)$$

D.2.5 Repeat sections D.2.1 through D.2.4 of this appendix to calculate the analogous values MIU_j for the interferants $j = 1$ to J . Replace the value $(AU_i)(DL_i)$ in equation D.1 with CPOT/20; replace the value AAI_m in equation D.1 with IAI_m .

APPENDIX E TO ADDENDUM TO METHOD 320—DETERMINING FRACTIONAL REPRODUCIBILITY UNCERTAINTIES (FRU)

E.1 General

To estimate the reproducibility of the spectroscopic results of the system, compare the CTS spectra recorded before and after preparing the reference spectra. Compare the difference between the spectra to their average band area. Perform the calculation for each analytical region on the portions of the CTS spectra associated with that analytical region.

E.2 Calculations

E.2.1 The CTS spectra {R1} consist of N spectra, denoted by S_{ii} , $i = 1, N$. Similarly, the CTS spectra {R2} consist of N spectra,

denoted by S_{2i} , $i = 1, N$. Each S_{ki} is the spectrum of a single compound, where i denotes the compound and k denotes the set $\{i\}$ of which S_{ki} is a member. Form the spectra S_3 according to $S_{3i} = S_{2i} - S_{ii}$ for each i . Form the spectra S_4 according to $S_{4i} = [S_{2i} + S_{ii}]/2$ for each i .

E.2.2 Each analytical region m is associated with a portion of the CTS spectra S_{2i} and S_{1i} , for a particular i , with lower and upper wavenumber limits FFL_m and FFU_m , respectively.

E.2.3 For each m and the associated i , calculate the band area of S_{4i} in the wavenumber range FFU_m to FFL_m . Follow the guidelines of section B.1.2 of this addendum for this band area calculation. Denote the result by BAV_m .

E.2.4 For each m and the associated i , calculate the RMSD of S_{3i} between the absorbance values and their mean in the wavenumber range FFU_m to FFL_m . Denote the result by $SRMS_m$.

E.2.5 For each analytical region m , calculate FM_m using equation E.1,

$$FM_m = SRMS_m (FFU_m - FFL_m) / BAV_m \quad (E.1)$$

E.2.6 If only the m^{th} analytical region is used to calculate the concentration of the i^{th} analyte, set $FRU_i = FM_m$.

E.2.7 If a number p of analytical regions are used to calculate the concentration of the i^{th} analyte, set FRU_i equal to the weighted mean of the appropriate FM_m values calculated according to section E.2.5. Mathematically, if the set of analytical regions employed is $\{m'\}$, then FRU_i is given by equation E.2.

$$FRU_i = \sum_{k \in \{m'\}} W_{ik} FM_k \quad (E.2)$$

where the W_{ik} are calculated as described in appendix D of this addendum.

APPENDIX F OF ADDENDUM TO METHOD 320—DETERMINING FRACTIONAL CALIBRATION UNCERTAINTIES (FCU)

F.1 General

F.1.1 The concentrations yielded by the computerized analytical program applied to each single-compound reference spectrum are defined as the indicated standard concentrations (ISC's). The ISC values for a single compound spectrum should ideally equal the accepted standard concentration (ASC) for one analyte or interferant, and should ideally be zero for all other compounds. Variations from these results are caused by errors in the ASC values, variations from the Beer's law (or modified Beer's law) model

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used to determine the concentrations, and noise in the spectra. When the first two effects dominate, the systematic nature of the errors is often apparent and the analyst shall take steps to correct them.

F.1.2 When the calibration error appears non-systematic, apply the procedures of sections F.2.1 through F.2.3 of this appendix to estimate the fractional calibration uncertainty (FCU) for each compound. The FCU is defined as the mean fractional error between the ASC and the ISC for all reference spectra with non-zero ASC for that compound. The FCU for each compound shall be less than the required fractional uncertainty specified in section 4.1 of this addendum.

F.1.3 The computerized analytical programs shall also be required to yield acceptably low concentrations for compounds with ISC = 0 when applied to the reference spectra. The ISC of each reference spectrum for each analyte or interferant shall not exceed that compound's minimum measurement uncertainty (MAU or MIU).

FIGURE F.1—PRESENTATION OF ACCEPTED STANDARD CONCENTRATIONS (ASC'S) AND INDICATED STANDARD CONCENTRATIONS (ISC'S)

Compound name	Reference spectrum file name	ASC (ppm)	ISC (ppm)							
			Analytes				Interferants			
			i = 1	i = 2	j = 1	j = 2	I	J	K	L

FIGURE F.2—PRESENTATION OF FRACTIONAL CALIBRATION UNCERTAINTIES (FCU'S) AND ANALYTICAL UNCERTAINTIES (AU'S)

Analyte name	FCU (%)	AU (%)

**APPENDIX G TO ADDENDUM TO METHOD 320—
MEASURING NOISE LEVELS**

G.1 General

The root-mean-square (RMS) noise level is the standard measure of noise. The RMS noise level of a contiguous segment of a spectrum is the RMSD between the absorbance values that form the segment and the mean value of the segment (see appendix A of this addendum).

G.2 Calculations

G.2.1 Evacuate the absorption cell or fill it with UPC grade nitrogen at approximately one atmosphere total pressure.

G.2.2 Record two single beam spectra of signal integration period t_{SS} .

G.2.3 Form the double beam absorption spectrum from these two single beam spectra, and calculate the noise level RMS_{SM} in the M analytical regions.

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APPENDIX H OF ADDENDUM TO METHOD 320—DETERMINING SAMPLE ABSORPTION PATHLENGTH (L_S) AND FRACTIONAL ANALYTICAL UNCERTAINTY (FAU)

H.1 General

Reference spectra recorded at absorption pathlength (L_R), gas pressure (P_R), and gas absolute temperature (T_R) may be used to determine analyte concentrations in samples whose spectra are recorded at conditions different from that of the reference spectra, i.e., at absorption pathlength (L_S), absolute temperature (T_S), and pressure (P_S). This appendix describes the calculations for estimating the fractional uncertainty (FAU) of this practice. It also describes the calculations for determining the sample absorption pathlength from comparison of CTS spectra, and for preparing spectra for further instrumental and procedural checks.

H.1.1 Before sampling, determine the sample absorption pathlength using least squares analysis. Determine the ratio L_S/L_R by comparing the spectral sets {R1} and {R3}, which are recorded using the same CTS at L_S and L_R , and T_S and T_R , but both at P_R .

H.1.2 Determine the fractional analysis uncertainty (FAU) for each analyte by comparing a scaled CTS spectral set, recorded at L_S , T_S , and P_S , to the CTS reference spectra of the same gas, recorded at L_R , T_R , and P_R . Perform the quantitative comparison after

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recording the sample spectra, based on band areas of the spectra in the CTS absorbance band associated with each analyte.

H.2 Calculations

H.2.1 *Absorption Pathlength Determination.* Perform and document separate linear baseline corrections to each analytical region in the spectral sets {R1} and {R3}. Form a one-dimensional array A_R containing the absorbance values from all segments of {R1} that are associated with the analytical regions; the members of the array are A_{Ri} , $i = 1, n$. Form a similar one-dimensional array A_S from the absorbance values in the spectral set {R3}; the members of the array are A_{Si} , $i = 1, n$. Based on the model $A_S = rA_R + E$, determine the least-squares estimate of r , the value of r which minimizes the square error E^2 . Calculate the sample absorption pathlength, L_S , using equation H.1,

$$L_S = r'(T_S/T_R)L_R \quad (H.1)$$

H.2.2 *Fractional Analysis Uncertainty.* Perform and document separate linear baseline corrections to each analytical region in the spectral sets {R1} and {R4}. Form the arrays A_S and A_R as described in section H.2.1 of this appendix, using values from {R1} to form A_R , and values from {R4} to form A_S . Calculate NRMS_E and IA_{AV} using equations H.2 and H.3,

$$\text{NRMS}_E = \sqrt{\sum_{i=1}^n \left[A_{Si} - \left(\frac{T_R}{T_S} \right) \left(\frac{L_S}{L_R} \right) \left(\frac{P_S}{P_R} \right) A_{Ri} \right]^2} \quad (H.2)$$

$$IA_{AV} = \frac{1}{2} \sum_{i=1}^n \left[A_{Si} + \left(\frac{T_R}{T_S} \right) \left(\frac{L_S}{L_R} \right) \left(\frac{P_S}{P_R} \right) A_{Ri} \right] \quad (H.3)$$

The fractional analytical uncertainty, FAU, is given by equation H.4.

$$FAU = \frac{\text{NRMS}_E}{IA_{AV}} \quad (H.4)$$

APPENDIX I TO ADDENDUM TO METHOD 320—DETERMINING FRACTIONAL MODEL UNCERTAINTIES (FMU)

I.1 General

To prepare analytical programs for FTIR analyses, the sample constituents must first be assumed. The calculations in this appendix, based upon a simulation of the sample spectrum, shall be used to verify the appropriateness of these assumptions. The simu-

lated spectra consist of the sum of single compound reference spectra scaled to represent their contributions to the sample absorbance spectrum; scaling factors are based on the indicated standard concentrations (ISC) and measured (sample) analyte and interferant concentrations, the sample and reference absorption pathlengths, and the sample and reference gas pressures. No band-shape correction for differences in the temperature of the sample and reference spectra gases is made; such errors are included in the FMU estimate. The actual and simulated sample spectra are quantitatively compared to determine the fractional model uncertainty; this comparison uses the reference

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spectra band areas and residuals in the difference spectrum formed from the actual and simulated sample spectra.

1.2 Calculations

1.2.1 For each analyte (with scaled concentration RSA_i), select a reference spectrum SA_i with indicated standard concentration ISC_i. Calculate the scaling factors, RA_i, using equation I.1,

$$RA_i = \frac{T_R L_S P_S RSA_i}{T_S L_R P_R ISC_i} \quad (I.1)$$

Form the spectra SAC_i by scaling each SA_i by the factor RA_i.

1.2.2 For each interferant, select a reference spectrum SI_k with indicated standard concentration ISC_k. Calculate the scaling factors, RI_k, using equation I.2,

$$RI_k = \frac{T_R L_S P_S RSI_k}{T_S L_R P_R ISC_k} \quad (I.2)$$

Form the spectra SIC_k by scaling each SI_k by the factor RI_k.

1.2.3 For each analytical region, determine by visual inspection which of the spectra SAC_i and SIC_k exhibit absorbance bands within the analytical region. Subtract each spectrum SAC_i and SIC_k exhibiting absorbance from the sample spectrum S_S to form the spectrum SUB_S. To save analysis time and to avoid the introduction of unwanted noise into the subtracted spectrum, it is recommended that the calculation be made (1) only for those spectral data points within the analytical regions, and (2) for each analytical region separately using the original spectrum S_S.

1.2.4 For each analytical region m, calculate the RMSD of SUB_S between the absorbance values and their mean in the region FFU_m to FFL_m. Denote the result by RMSS_m.

1.2.5 For each analyte i, calculate FM_m, using equation I.3,

$$FM_m = \frac{RMSS_m(FFU_m - FFL_m)AU_i DL_i}{AA_i RSA_i} \quad (I.3)$$

for each analytical region associated with the analyte.

1.2.6 If only the mth analytical region is used to calculate the concentration of the ith analyte, set FMU_i = FM_m.

1.2.7 If a number of analytical regions are used to calculate the concentration of the ith analyte, set FM_i equal to the weighted mean of the appropriate FM_m values calculated using equation I.3. Mathematically, if the set of analytical regions employed is {m'}, then the fractional model uncertainty, FMU, is given by equation I.4,

$$FMU_i = \sum_{k \in \{m'\}} W_{ik} FM_k \quad (I.4)$$

where W_{ik} is calculated as described in appendix D of this addendum.

APPENDIX J OF ADDENDUM TO METHOD 320—DETERMINING OVERALL CONCENTRATION UNCERTAINTIES (OCU)

The calculations in this addendum estimate the measurement uncertainties for various FTIR measurements. The lowest possible overall concentration uncertainty (OCU) for an analyte is its MAU value, which is an estimate of the absolute concentration uncertainty when spectral noise dominates the measurement error. However, if the product of the largest fractional concentration

uncertainty (FRU, FCU, FAU, or FMU) and the measured concentration of an analyte exceeds the MAU for the analyte, then the OCU is this product. In mathematical terms, set OFU_i = MAX{FRU_i, FCU_i, FAU_i, FMU_i} and OCU_i = MAX{RSA_i*OFU_i, MAU_i}.

TEST METHOD 321—MEASUREMENT OF GASEOUS HYDROGEN CHLORIDE EMISSIONS AT PORTLAND CEMENT KILNS BY FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

1.0 Introduction

This method should be performed by those persons familiar with the operation of Fourier Transform Infrared (FTIR) instrumentation in the application to source sampling. This document describes the sampling procedures for use in the application of FTIR spectrometry for the determination of vapor phase hydrogen chloride (HCl) concentrations both before and after particulate matter control devices installed at portland cement kilns. A procedure for analyte spiking is included for quality assurance. This method is considered to be self validating provided that the requirements listed in section 9 of this method are followed. The analytical procedures for interpreting infrared spectra from emission measurements are described in the "Protocol For The Use of Extractive

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Fourier Transform Infrared (FTIR) Spectrometry in Analyses of Gaseous Emissions From Stationary Industrial Sources", included as an addendum to proposed Method 320 of this appendix (hereafter referred to as the "FTIR Protocol"). References 1 and 2 describe the use of FTIR spectrometry in field measurements. Sample transport presents the principal difficulty in directly measuring HCl emissions. This identical problem must be overcome by any extractive measurement method. HCl is reactive and water soluble. The sampling system must be adequately designed to prevent sample condensation in the system.

1.1 Scope and Application

This method is specifically designed for the application of FTIR Spectrometry in extractive measurements of gaseous HCl con-

centrations in portland cement kiln emissions.

1.2 Applicability

This method applies to the measurement of HCl [CAS No. 7647-01-0]. This method can be applied to the determination of HCl concentrations both before and after particulate matter control devices installed at portland cement manufacturing facilities. This method applies to either continuous flow through measurement (with isolated sample analysis) or grab sampling (batch analysis). HCl is measured using the mid-infrared spectral region for analysis (about 400 to 4000 cm^{-1} or 25 to 2.5 μm). Table 1 lists the suggested analytical region for quantification of HCl taking the interference from water vapor into consideration.

TABLE 1—EXAMPLE ANALYTICAL REGION FOR HCl

Compound	Analytical region (cm^{-1})	Potential interferants
Hydrogen chloride	2679-2840	Water.

1.3 Method Range and Sensitivity

1.3.1 The analytical range is determined by the instrumental design and the composition of the gas stream. For practical purposes there is no upper limit to the range because the pathlength may be reduced or the sample may be diluted. The lower detection range depends on (1) the absorption coefficient of the compound in the analytical frequency region, (2) the spectral resolution, (3) the interferometer sampling time, (4) the detector sensitivity and response, and (5) the absorption pathlength.

1.3.2 The practical lower quantification range is usually higher than that indicated by the instrument performance in the laboratory, and is dependent upon (1) the presence of interfering species in the exhaust gas (notably H_2O), (2) the optical alignment of the gas cell and transfer optics, and (3) the quality of the reflective surfaces in the cell (cell throughput). Under typical test conditions (moisture content of up to 30 percent, 10 meter absorption path length, liquid nitrogen-cooled IR detector, 0.5 cm^{-1} resolution, and an interferometer sampling time of 60 seconds) a typical lower quantification range for HCl is 0.1 to 1.0 ppm.

1.4 Data Quality Objectives

1.4.1 In designing or configuring the analytical system, data quality is determined by measuring the root mean square deviation (RMSD) of the absorbance values within a chosen spectral (analytical) region. The RMSD provides an indication of the signal-to-noise ratio (S/N) of the spectral baseline. Appendix D of the FTIR Protocol (the addendum to Method 320 of this appendix) presents

a discussion of the relationship between the RMSD, lower detection limit, DL_{L} , and analytical uncertainty, AU_{L} . It is important to consider the target analyte quantification limit when performing testing with FTIR instrumentation, and to optimize the system to achieve the desired detection limit.

1.4.2 Data quality is determined by measuring the root mean square (RMS) noise level in each analytical spectral region (appendix C of the FTIR Protocol). The RMS noise is defined as the root mean square deviation (RMSD) of the absorbance values in an analytical region from the mean absorbance value in the same region. Appendix D of the FTIR Protocol defines the minimum analyte uncertainty (MAU), and how the RMSD is used to calculate the MAU. The MAU_{m} is the minimum concentration of the i th analyte in the m th analytical region for which the analytical uncertainty limit can be maintained. Table 2 presents example values of AU and MAU using the analytical region presented in Table 1.

TABLE 2—EXAMPLE PRE-TEST PROTOCOL CALCULATIONS FOR HYDROGEN CHLORIDE

	HCl
Reference concentration (ppm-meters)/K	11.2
Reference Band area	2.881
DL (ppm-meters)/K	0.1117
AU	0.2
CL (DL \times AU)	0.02234
FL (cm^{-1})	2679.83
FU (cm^{-1})	2840.93
FC (cm^{-1})	2760.38
AAI (ppm-meters)/K	0.06435

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TABLE 2—EXAMPLE PRE-TEST PROTOCOL CALCULATIONS FOR HYDROGEN CHLORIDE—Continued

	HCl
RMSD	2.28E-03
MAU (ppm-meters)/K	1.28E-01
MAU ppm at 22 meters and 250 °F02284

2.0 Summary of Method

2.1 Principle

See Method 320 of this appendix. HCl can also undergo rotation transitions by absorbing energy in the far-infrared spectral region. The rotational transitions are superimposed on the vibrational fundamental to give a series of lines centered at the fundamental vibrational frequency, 2885 cm⁻¹. The frequencies of absorbance and the pattern of rotational/vibrational lines are unique to HCl. When this distinct pattern is observed in an infrared spectrum of an unknown sample, it unequivocally identifies HCl as a component of the mixture. The infrared spectrum of HCl is very distinctive and cannot be confused with the spectrum of any other compound. See Reference 6.

2.2 Sampling and Analysis. See Method 320 of this appendix.

2.3 Operator Requirements. The analyst must have knowledge of spectral patterns to choose an appropriate absorption path length or determine if sample dilution is necessary. The analyst should also understand FTIR instrument operation well enough to choose instrument settings that are consistent with the objectives of the analysis.

3.0 Definitions

See appendix A of the FTIR Protocol.

4.0 Interferences

This method will not measure HCl under conditions: (1) where the sample gas stream can condense in the sampling system or the instrumentation, or (2) where a high moisture content sample relative to the analyte concentrations imparts spectral interference due to the water vapor absorbance bands. For measuring HCl the first (sampling) consideration is more critical. Spectral interference from water vapor is not a significant problem except at very high moisture levels and low HCl concentrations.

4.1 Analytical Interferences. See Method 320 of this appendix.

4.1.1 Background Interferences. See Method 320 of this appendix.

4.1.2 Spectral interferences. Water vapor can present spectral interference for FTIR gas analysis of HCl. Therefore, the water vapor in the spectra of kiln gas samples must be accounted for. This means preparing at least one spectrum of a water vapor sam-

ple where the moisture concentration is close to that in the kiln gas.

4.2 Sampling System Interferences. The principal sampling system interferant for measuring HCl is water vapor. Steps must be taken to ensure that no condensation forms anywhere in the probe assembly, sample lines, or analytical instrumentation. Cold spots anywhere in the sampling system must be avoided. The extent of sampling system bias in the FTIR analysis of HCl depends on concentrations of potential interferants, moisture content of the gas stream, temperature of the gas stream, temperature of sampling system components, sample flow rate, and reactivity of HCl with other species in the gas stream (e.g., ammonia). For measuring HCl in a wet gas stream the temperatures of the gas stream, sampling components, and the sample flow rate are of primary importance. Analyte spiking with HCl is performed to demonstrate the integrity of the sampling system for transporting HCl vapor in the flue gas to the FTIR instrument. See section 9 of this method for a complete description of analyte spiking.

5.0 Safety

5.1 Hydrogen chloride vapor is corrosive and can cause irritation or severe damage to respiratory system, eyes and skin. Exposure to this compound should be avoided.

5.2 This method may involve sampling at locations having high positive or negative pressures, or high concentrations of hazardous or toxic pollutants, and can not address all safety problems encountered under these diverse sampling conditions. It is the responsibility of the tester(s) to ensure proper safety and health practices, and to determine the applicability of regulatory limitations before performing this test method. Leak-check procedures are outlined in section 8.2 of Method 320 of this appendix.

6.0 Equipment and Supplies

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1 FTIR Spectrometer and Detector. An FTIR Spectrometer system (interferometer, transfer optics, gas cell and detector) having the capability of measuring HCl to the predetermined minimum detectable level required (see section 4.1.3 of the FTIR Protocol). The system must also include an accurate means to control and/or measure the temperature of the FTIR gas analysis cell, and a personal computer with compatible software that provides real-time updates of the spectral profile during sample and spectral collection.

6.2 Pump. Capable of evacuating the FTIR cell volume to 1 Torr (133.3 Pascals) within two minutes (for batch sample analysis).

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6.3 *Mass Flow Meters/Controllers.* To accurately measure analyte spike flow rate, having the appropriate calibrated range and a stated accuracy of ± 2 percent of the absolute measurement value. This device must be calibrated with the major component of the calibration/spike gas (e.g., nitrogen) using an NIST traceable bubble meter or equivalent. Single point calibration checks should be performed daily in the field. When spiking HCl, the mass flow meter/controller should be thoroughly purged before and after introduction of the gas to prevent corrosion of the interior parts.

6.4 *Polytetrafluoroethane tubing.* Diameter and length suitable to connect cylinder regulators.

6.5 *Stainless Steel tubing.* Type 316 of appropriate length and diameter for heated connections.

6.6 *Gas Regulators.* Purgeable HCl regulator.

6.7 *Pressure Gauge.* Capable of measuring pressure from 0 to 1000 Torr (133.3 Pa = 1 Torr) within ± 5 percent.

6.8 *Sampling Probe.* Glass, stainless steel or other appropriate material of sufficient length and physical integrity to sustain heating, prevent adsorption of analytes and capable of reaching gas sampling point.

6.9 *Sampling Line.* Heated 180 °C (360 °F) and fabricated of either stainless steel, polytetrafluoroethane or other material that prevents adsorption of HCl and transports effluent to analytical instrumentation. The extractive sample line must have the capability to transport sample gas to the analytical components as well as direct heated calibration spike gas to the calibration assembly located at the sample probe. It is important to minimize the length of heated sample line.

6.10 *Particulate Filters.* A sintered stainless steel filter rated at 20 microns or greater may be placed at the inlet of the probe (for removal of large particulate matter). A heated filter (Balston or equivalent) rated at 1 micron is necessary for primary particulate matter removal, and shall be placed immediately after the heated probe. The filter/filter holder temperature should be maintained at 180 °C (360 °F).

6.11 *Calibration/Analyte Spike Assembly.* A heated three-way valve assembly (or equivalent) to introduce surrogate spikes into the sampling system at the outlet of the probe before the primary particulate filter.

6.12 *Sample Extraction Pump.* A leak-free heated head pump (KNF Neuberger or equivalent) capable of extracting sample effluent through entire sampling system at a rate which prevents analyte losses and minimizes analyzer response time. The pump should have a heated by-pass and may be placed either before the FTIR instrument or after. If the sample pump is located upstream of the FTIR instrument, it must be fabricated from

materials non-reactive to HCl. The sampling system and FTIR measurement system shall allow the operator to obtain at least six sample spectra during a one-hour period.

6.13 *Barometer.* For measurement of barometric pressure.

6.14 *Gas Sample Manifold.* A distribution manifold having the capabilities listed in sections 6.14.1 through 6.14.4:

6.14.1 Delivery of calibration gas directly to the analytical instrumentation;

6.14.2 Delivery of calibration gas to the sample probe (system calibration or analyte spike) via a heated traced sample line;

6.14.3 Delivery of sample gas (kiln gas, spiked kiln gas, or system calibrations) to the analytical instrumentation;

6.14.4 Delivery (optional) of a humidified nitrogen sample stream.

6.15 *Flow Measurement Device.* Type S Pitot tube (or equivalent) and Magnahelic set for measurement of volumetric flow rate.

7.0 Reagents and Standards

HCl can be purchased in a standard compressed gas cylinder. The most stable HCl cylinder mixture available has a concentration certified at ± 5 percent. Such a cylinder is suitable for performing analyte spiking because it will provide reproducible samples. The stability of the cylinder can be monitored over time by periodically performing direct FTIR analysis of cylinder samples. It is recommended that a 10–50 ppm cylinder of HCl be prepared having from 2–5 ppm SF₆ as a tracer compound. (See sections 7.1 through 7.3 of Method 320 of this appendix for a complete description of the use of existing HCl reference spectra. See section 9.1 of Method 320 of this appendix for a complete discussion of standard concentration selection.)

8.0 Sample Collection, Preservation and Storage

See also Method 320 of this appendix.

8.1 *Pretest.* A screening test is ideal for obtaining proper data that can be used for preparing analytical program files. Information from literature surveys and source personnel is also acceptable. Information about the sampling location and gas stream composition is required to determine the optimum sampling system configuration for measuring HCl. Determine the percent moisture of the kiln gas by Method 4 of appendix A to part 60 of this chapter or by performing a wet bulb/dry bulb measurement. Perform a preliminary traverse of the sample duct or stack and select the sampling point(s). Acquire an initial spectrum and determine the optimum operational pathlength of the instrument.

8.2 *Leak-Check.* See Method 320 of this appendix, section 8.2 for direction on performing leak-checks.

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8.3 *Background Spectrum.* See Method 320 of this appendix, section 8.5 for direction in background spectral acquisition.

8.4 *Pre-Test Calibration Transfer Standard (Direct Instrument Calibration).* See Method 320 of this appendix, section 8.3 for direction in CTS spectral acquisition.

8.5 *Pre-Test System Calibration.* See Method 320 of this appendix, sections 8.6.1 through 8.6.2 for direction in performing system calibration.

8.6 Sampling

8.6.1 *Extractive System.* An extractive system maintained at 180 °C (360 °F) or higher which is capable of directing a total flow of at least 12 L/min to the sample cell is required (References 1 and 2). Insert the probe into the duct or stack at a point representing the average volumetric flow rate and 25 percent of the cross sectional area. Co-locate an appropriate flow monitoring device with the sample probe so that the flow rate is recorded at specified time intervals during emission testing (e.g., differential pressure measurements taken every 10 minutes during each run).

8.6.2 *Batch Samples.* Evacuate the absorbance cell to 5 Torr (or less) absolute pressure before taking first sample. Fill the cell with kiln gas to ambient pressure and record the infrared spectrum, then evacuate the cell until there is no further evidence of infrared absorption. Repeat this procedure, collecting a total of six separate sample spectra within a 1-hour period.

8.6.3 *Continuous Flow Through Sampling.* Purge the FTIR cell with kiln gas for a time period sufficient to equilibrate the entire sampling system and FTIR gas cell. The time required is a function of the mechanical response time of the system (determined by performing the system calibration with the CTS gas or equivalent), and by the chemical reactivity of the target analytes. If the effluent target analyte concentration is not variable, observation of the spectral up-date of the flowing gas sample should be performed until equilibration of the sample is achieved. Isolate the gas cell from the sample flow by directing the purge flow to vent. Record the spectrum and pressure of the sample gas. After spectral acquisition, allow the sample gas to purge the cell with at least three volumes of kiln gas. The time required to adequately purge the cell with the required volume of gas is a function of (1) cell volume, (2) flow rate through the cell, and (3) cell design. It is important that the gas introduction and vent for the FTIR cell provides a complete purge through the cell.

8.6.4 *Continuous Sampling.* In some cases it is possible to collect spectra continuously while the FTIR cell is purged with sample gas. The sample integration time, t_{int} , the sample flow rate through the gas cell, and the sample integration time must be chosen so that the collected data consist of at least

10 spectra with each spectrum being of a separate cell volume of flue gas. Sampling in this manner may only be performed if the native source analyte concentrations do not affect the test results.

8.7 Sample Conditioning

8.7.1 *High Moisture Sampling.* Kiln gas emitted from wet process cement kilns may contain 3- to 40 percent moisture. Zinc selenide windows or the equivalent should be used when attempting to analyze hot/wet kiln gas under these conditions to prevent dissolution of water soluble window materials (e.g., KBr).

8.7.2 *Sample Dilution.* The sample may be diluted using an in-stack dilution probe, or an external dilution device provided that the sample is not diluted below the instrument's quantification range. As an alternative to using a dilution probe, nitrogen may be dynamically spiked into the effluent stream in the same manner as analyte spiking. A constant dilution rate shall be maintained throughout the measurement process. It is critical to measure and verify the exact dilution ratio when using a dilution probe or the nitrogen spiking approach. Calibrating the system with a calibration gas containing an appropriate tracer compound will allow determination of the dilution ratio for most measurement systems. The tester shall specify the procedures used to determine the dilution ratio, and include these calibration results in the report.

8.8 *Sampling QA, Data Storage and Reporting.* See the FTIR Protocol. Sample integration times shall be sufficient to achieve the required signal-to-noise ratio, and all sample spectra should have unique file names. Two copies of sample interferograms and processed spectra will be stored on separate computer media. For each sample spectrum the analyst must 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, integration time), and the spectral file name. A hard copy of these data must be maintained until the test results are accepted.

8.9 *Signal Transmittance.* Monitor the signal transmittance through the instrumental system. If signal transmittance (relative to the background) drops below 95 percent in any spectral region where the sample does not absorb infrared energy, then a new background spectrum must be obtained.

8.10 *Post-test CTS.* After the sampling run completion, record the CTS spectrum. Analysis of the spectral band area used for quantification from pre- and post-test CTS spectra should agree to within ± 5 percent or corrective action must be taken.

8.11 *Post-test QA.* The sample spectra shall be inspected immediately after the run to verify that the gas matrix composition was

close to the assumed gas matrix, (this is necessary to account for the concentrations of the interferants for use in the analytical analysis programs), and to confirm that the sampling and instrumental parameters were appropriate for the conditions encountered.

9.0 Quality Control

Use analyte spiking to verify the effectiveness of the sampling system for the target compounds in the actual kiln gas matrix. QA spiking shall be performed before and after each sample run. QA spiking shall be performed after the pre- and post-test CTS direct and system calibrations. The system biases calculated from the pre- and post-test dynamic analyte spiking shall be within ± 30 percent for the spiked surrogate analytes for the measurements to be considered valid. See sections 9.3.1 through 9.3.2 for the requisite calculations. Measurement of the undiluted spike (direct-to-cell measurement) involves sending dry, spike gas to the FTIR cell, filling the cell to 1 atmosphere and obtaining the spectrum of this sample. The direct-to-cell measurement should be performed before each analyte spike so that the recovery of the dynamically spiked analytes may be calculated. Analyte spiking is only effective for assessing the integrity of the sampling system when the concentration of HCl in the source does not vary substantially. Any attempt to quantify an analyte recovery in a variable concentration matrix will result in errors in the expected concentration of the spiked sample. If the kiln gas target analyte concentrations vary by more than ± 5 percent (or 5 ppm, whichever is greater) in the time required to acquire a sample spectrum, it may be necessary to: (1) Use a dual sample probe approach, (2) use two independent FTIR measurement systems, (3) use alternate QA/QC procedures, or (4) postpone testing until stable emission concentrations are achieved. (See section 9.2.3 of this method). It is recommended that a laboratory evaluation be performed before attempting to employ this method under actual field conditions. The laboratory evaluation shall include (1) performance of all applicable calculations in section 4 of the FTIR Protocol; (2) simulated analyte spiking experiments in dry (ambient) and humidified sample matrices using HCl; and (3) performance of bias (recovery) calculations from analyte spiking experiments. It is not necessary to perform a laboratory evaluation before every field test. The purpose of the laboratory study is to demonstrate that the actual instrument and sampling system configuration used in field testing meets the requirements set forth in this method.

9.1 *Spike Materials.* Perform analyte spiking with an HCl standard to demonstrate the integrity of the sampling system.

9.1.1 An HCl standard of approximately 50 ppm in a balance of ultra pure nitrogen is recommended. The SF₆ (tracer) concentration shall be 2 to 5 ppm depending upon the measurement pathlength. The spike ratio (spike flow/total flow) shall be no greater than 1:10, and an ideal spike concentration should approximate the native effluent concentration.

9.1.2 The ideal spike concentration may not be achieved because the target concentration cannot be accurately predicted prior to the field test, and limited calibration standards will be available during testing. Therefore, practical constraints must be applied that allow the tester to spike at an anticipated concentration. For these tests, the analyte concentration contributed by the HCl standard spike should be 1 to 5 ppm or should more closely approximate the native concentration if it is greater.

9.2 Spike Procedure

9.2.1 A spiking/sampling apparatus is shown in Figure 2. Introduce the spike/tracer gas mixture at a constant flow (± 2 percent) rate at approximately 10 percent of the total sample flow. (For example, introduce the surrogate spike at 1 L/min 20 cc/min, into a total sample flow rate of 10 L/min). The spike must be pre-heated before introduction into the sample matrix to prevent a localized condensation of the gas stream at the spike introduction point. A heated sample transport line(s) containing multiple transport tubes within the heated bundle may be used to spike gas up through the sampling system to the spike introduction point. Use a calibrated flow device (e.g., mass flow meter/controller), to monitor the spike flow as indicated by a calibrated flow meter or controller, or alternately, the SF₆ tracer ratio may be calculated from the direct measurement and the diluted measurement. It is often desirable to use the tracer approach in calculating the spike/total flow ratio because of the difficulty in accurately measuring hot/wet total flow. The tracer technique has been successfully used in past validation efforts (Reference 1).

9.2.2 Perform a direct-to-cell measurement of the dry, undiluted spike gas. Introduce the spike directly to the FTIR cell, bypassing the sampling system. Fill cell to 1 atmosphere and collect the spectrum of this sample. Ensure that the spike gas has equilibrated to the temperature of the measurement cell before acquisition of the spectra. Inspect the spectrum and verify that the gas is dry and contains negligible CO₂. Repeat the process to obtain a second direct-to-cell measurement. Analysis of spectral band areas for HCl from these duplicate measurements should agree to within ± 5 percent of the mean.

9.2.3 *Analyte Spiking.* Determine whether the kiln gas contains native concentrations

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of HCl by examination of preliminary spectra. Determine whether the concentration varies significantly with time by observing a continuously up-dated spectrum of sample gas in the flow-through sampling mode. If the concentration varies by more than ± 5 percent during the period of time required to acquire a spectra, then an alternate approach should be used. One alternate approach uses two sampling lines to convey sample to the gas distribution manifold. One of the sample lines is used to continuously extract unspiked kiln gas from the source. The other sample line serves as the analyte spike line. One FTIR system can be used in this arrangement. Spiked or unspiked sample gas may be directed to the FTIR system from the gas distribution manifold, with the need to purge only the components between the manifold and the FTIR system. This approach minimizes the time required to acquire an equilibrated sample of spiked or unspiked kiln gas. If the source varies by more than ± 5 percent (or 5 ppm, whichever is greater) in the time it takes to switch from the unspiked sample line to the spiked sample line, then analyte spiking may not be a feasible means to determine the effectiveness of the sampling system for the HCl in the sample matrix. A second alternative is to use two completely independent FTIR measurement systems. One system would measure unspiked samples while the other system would measure the spiked samples. As a last option, (where no other alternatives can be used) a humidified nitrogen stream may be generated in the field which approximates the moisture content of the kiln gas. Analyte spiking into this humidified stream can be employed to assure that the sampling system is adequate for transporting the HCl to the FTIR instrumentation.

9.2.3.1 Adjust the spike flow rate to approximately 10 percent of the total flow by metering spike gas through a calibrated mass flowmeter or controller. Allow spike flow to equilibrate within the sampling system before analyzing the first spiked kiln gas samples. A minimum of two consecutive spikes are required. Analysis of the spectral band area used for quantification should agree to within ± 5 percent or corrective action must be taken.

9.2.3.2 After QA spiking is completed, the sampling system components shall be purged with nitrogen or dry air to eliminate traces of the HCl compound from the sampling system components. Acquire a sample spectra of the nitrogen purge to verify the absence of the calibration mixture.

9.2.3.3 Analyte spiking procedures must be carefully executed to ensure that meaningful measurements are achieved. The requirements of sections 9.2.3.1 through 9.2.3.4 shall be met.

9.2.3.3.1 The spike must be in the vapor phase, dry, and heated to (or above) the kiln

gas temperature before it is introduced to the kiln gas stream.

9.2.3.3.2 The spike flow rate must be constant and accurately measured.

9.2.3.3.3 The total flow must also be measured continuously and reliably or the dilution ratio must otherwise be verified before and after a run by introducing a spike of a non-reactive, stable compound (i.e., tracer).

9.2.3.3.4 The tracer must be inert to the sampling system components, not contained in the effluent gas, and readily detected by the analytical instrumentation. Sulfur hexafluoride (SF_6) has been used successfully (References 1 and 2) for this purpose.

9.3 Calculations

9.3.1 *Recovery.* Calculate the percent recovery of the spiked analytes using equations 1 and 2.

$$\%R = 100 \times \frac{S_m - S_u(1 - DF)}{DF \times C_s} \quad (1)$$

S_m = Mean concentration of the analyte spiked effluent samples (observed).

$$C_e = DF \times C_s + S_u(1 - DF) \quad (2)$$

C_e = Expected concentration of the spiked samples (theoretical).

DF = Dilution Factor (Total flow/Spike flow). Total flow = spike flow plus effluent flow.

C_s = cylinder concentration of spike gas.

S_u = native concentration of analytes in unspiked samples.

The spike dilution factor may be confirmed by measuring the total flow and the spike flow directly. Alternately, the spike dilution can be verified by comparing the concentration of the tracer compound in the spiked samples (diluted) to the tracer concentration in the direct (undiluted) measurement of the spike gas.

If SF_6 is the tracer gas, then

$$D_f = [SF_6]_{\text{spike}} / [SF_6]_{\text{direct}} \quad (3)$$

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

$[SF_6]_{\text{direct}}$ = the SF_6 concentration measured directly.

9.3.2 *Bias.* The bias may be determined by the difference between the observed spike value and the expected response (i.e., the equivalent concentration of the spiked material plus the analyte concentration adjusted for spike dilution). Bias is defined by section 6.3.1 of EPA Method 301 of this appendix (Reference 8) as,

$$B = S_m - C_e \quad (4)$$

Where:

B = Bias at spike level.

S_m = Mean concentration of the analyte spiked samples.

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C_e = Expected concentration of the analyte in spiked samples.

Acceptable recoveries for analyte spiking are ± 30 percent. Application of correction factors to the data based upon bias and recovery calculations is subject to the approval of the Administrator.

10.0 Calibration and Standardization

10.1 *Calibration transfer standards (CTS).* The EPA Traceability Protocol gases or NIST traceable standards, with a minimum accuracy of ± 2 percent shall be used. For other requirements of the CTS, see the FTIR Protocol section 4.5.

10.2 *Signal-to-Noise Ratio (S/N).* The S/N shall be less than the minimum acceptable measurement uncertainty in the analytical regions to be used for measuring HCl.

10.3 *Absorbance Pathlength.* Verify the absorbance path length by comparing CTS spectra to reference spectra of the calibration gasses.

10.4 *Instrument Resolution.* Measure the line width of appropriate CTS band(s) to verify instrumental resolution.

10.5 *Apodization Function.* Choose the appropriate apodization function. Determine any appropriate mathematical transformations that are required to correct instrumental errors by measuring the CTS.

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Any mathematical transformations must be documented and reproducible. Reference 9 provides additional information about FTIR instrumentation.

11.0 Analytical Procedure

A full description of the analytical procedures is given in sections 4.6–4.11, sections 5, 6, and 7, and the appendices of the FTIR Protocol. Additional description of quantitative spectral analysis is provided in References 10 and 11.

12.0 Data Analysis and Calculations

Data analysis is performed using appropriate reference spectra whose concentrations can be verified using CTS spectra. Various analytical programs (References 10 and 11) are available to relate sample absorbance to a concentration standard. Calculated concentrations should be verified by analyzing spectral baselines after mathematically subtracting scaled reference spectra from the sample spectra. A full description of the data analysis and calculations may be found in the FTIR Protocol (sections 4.0, 5.0, 6.0 and appendices).

12.1 Calculated concentrations in sample spectra are corrected for differences in absorption pathlength between the reference and sample spectra by

$$C_{corr} = \left(L_r / L_s \right) \times \left(T_s / T_r \right) \times (C_{calc}) \quad (5)$$

Where:

C_{corr} = The pathlength corrected concentration.

C_{calc} = The initial calculated concentration (output of the multicomponent analysis program designed for the compound).

L_r = The pathlength associated with the reference spectra.

L_s = The pathlength associated with the sample spectra.

T_s = The absolute temperature (K) of the sample gas.

T_r = The absolute temperature (K) at which reference spectra were recorded.

12.2 The temperature correction in equation 5 is a volumetric correction. It does not account for temperature dependence of rotational-vibrational relative line intensities. Whenever possible, the reference spectra used in the analysis should be collected at a temperature near the temperature of the FTIR cell used in the test to minimize the calculated error in the measurement (FTIR Protocol, appendix D). Additionally, the analytical region chosen for the analysis should be sufficiently broad to minimize errors caused by small differences in relative line

intensities between reference spectra and the sample spectra.

13.0 Method Performance

A description of the method performance may be found in the FTIR Protocol. This method is self validating provided the results meet the performance specification of the QA spike in sections 9.0 through 9.3 of this method.

14.0 Pollution Prevention

This is a gas phase measurement. Gas is extracted from the source, analyzed by the instrumentation, and discharged through the instrument vent.

15.0 Waste Management

Gas standards of HCl are handled according to the instructions enclosed with the material safety data sheet.

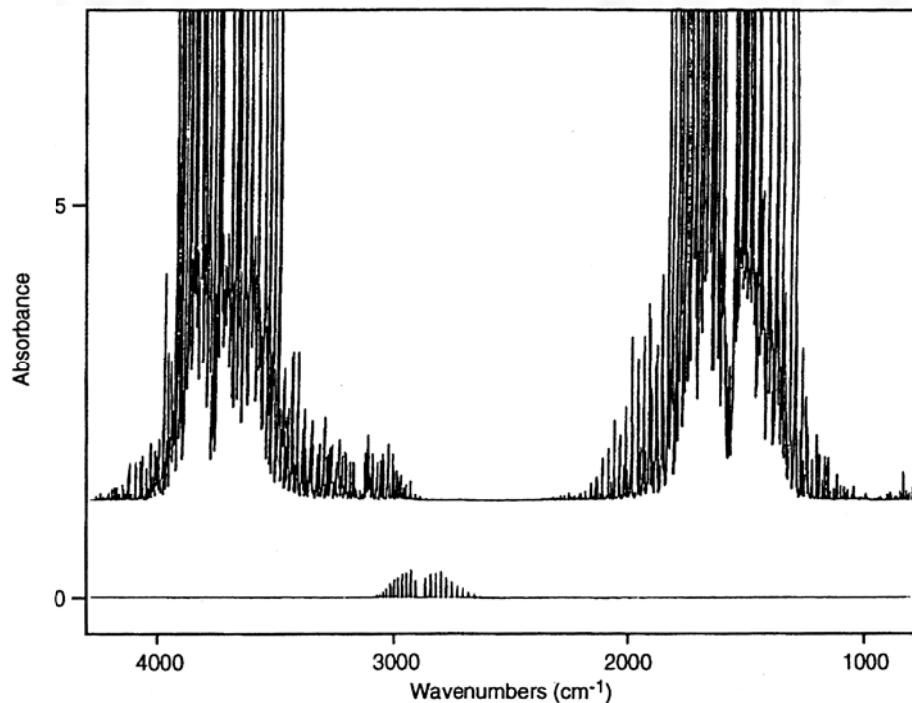
16.0 References

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Top, water vapor (194hsub); Bottom, HCl at 11.4 (ppm-M)/K.

Figure 1. FTIR Spectra of HCl and Water.

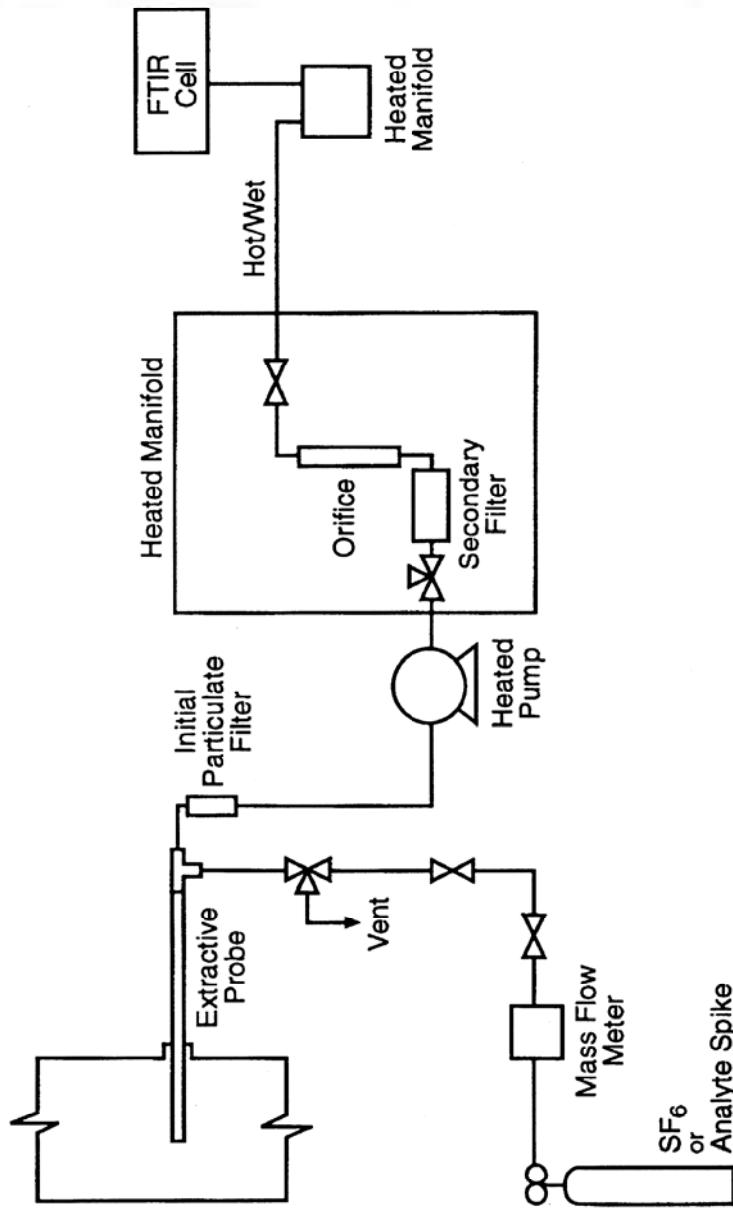


Figure 2. FTIR Sampling/Spiking System.

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40 CFR Ch. I (7-1-17 Edition)

METHOD 323—MEASUREMENT OF FORMALDEHYDE EMISSIONS FROM NATURAL GAS-FIRED STATIONARY SOURCES—ACETYL ACETONE DERIVITIZATION METHOD

1.0 Introduction. This method describes the sampling and analysis procedures of the acetyl acetone colorimetric method for measuring formaldehyde emissions in the exhaust of natural gas-fired, stationary combustion sources. This method, which was prepared by the Gas Research Institute (GRI), is based on the Chilled Impinger Train Method for Methanol, Acetone, Acetaldehyde, Methyl Ethyl Ketone, and Formaldehyde (Technical Bulletin No. 684) developed and published by the National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI). However, this method has been prepared specifically for formaldehyde and does not include specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) for methanol, acetone, acetaldehyde, and methyl ethyl ketone. To obtain reliable results, persons using this method should have a thorough knowledge of at least Methods 1 and 2 of 40 CFR part 60, appendix A-1; Method 3 of 40 CFR part 60, appendix A-2; and Method 4 of 40 CFR part 60, appendix A-3.

1.1 Scope and Application

1.1.1 Analytes. The only analyte measured by this method is formaldehyde (CAS Number 50-00-0).

1.1.2 Applicability. This method is for analyzing formaldehyde emissions from uncontrolled and controlled natural gas-fired, stationary combustion sources.

1.1.3 Data Quality Objectives. If you adhere to the quality control and quality assurance requirements of this method, then you and future users of your data will be able to assess the quality of the data you obtain and estimate the uncertainty in the measurements.

2.0 Summary of Method. An emission sample from the combustion exhaust is drawn through a midget impinger train containing chilled reagent water to absorb formaldehyde. The formaldehyde concentration in the impinger is determined by reaction with acetyl acetone to form a colored derivative which is measured colorimetrically.

3.0 Definitions

[Reserved]

4.0 Interferences. The presence of acetaldehyde, amines, polymers of formaldehyde, periodate, and sulfites can cause interferences with the acetyl acetone procedure which is used to determine the formaldehyde concentration. However, based on experience gained from extensive testing of natural gas-fired combustion sources using FTIR to measure a variety of compounds, GRI expects only acetaldehyde to be potentially

present when combusting natural gas. Acetaldehyde has been reported to be a significant interference only when present at concentrations above 50 ppmv. However, GRI reports that the concentration of acetaldehyde from gas-fired sources is very low (typically below the FTIR detection limit of around 0.5 ppmv); therefore, the potential positive bias due to acetaldehyde interference is expected to be negligible.

5.0 Safety

5.1 Prior to applying the method in the field, a site-specific Health and Safety Plan should be prepared. General safety precautions include the use of steel-toed boots, safety glasses, hard hats, and work gloves. In certain cases, facility policy may require the use of fire-resistant clothing while on-site. Since the method involves testing at high-temperature sampling locations, precautions must be taken to limit the potential for exposure to high-temperature gases and surfaces while inserting or removing the sample probe. In warm locations, precautions must also be taken to avoid dehydration.

5.2 Potential chemical hazards associated with sampling include formaldehyde, nitrogen oxides (NO_x), and carbon monoxide (CO). Formalin solution, used for field spiking, is an aqueous solution containing formaldehyde and methanol. Formaldehyde is a skin, eye, and respiratory irritant and a carcinogen, and should be handled accordingly. Eye and skin contact and inhalation of formaldehyde vapors should be avoided. Natural gas-fired combustion sources can potentially emit CO at toxic concentrations. Care should be taken to minimize exposure to the sample gas while inserting or removing the sample probe. If the work area is enclosed, personal CO monitors should be used to insure that the concentration of CO in the work area is maintained at safe levels.

5.3 Potential chemical hazards associated with the analytical procedures include acetyl acetone and glacial acetic acid. Acetyl acetone is an irritant to the skin and respiratory system, as well as being moderately toxic. Glacial acetic acid is highly corrosive and is an irritant to the skin, eyes, and respiratory system. Eye and skin contact and inhalation of vapors should be avoided. Acetyl acetone and glacial acetic acid have flash points of 41 °C (105.8 °F) and 43 °C (109.4 °F), respectively. Exposure to heat or flame should be avoided.

6.0 Equipment and Supplies

6.1 Sampling Probe. Quartz glass probe with stainless steel sheath or stainless steel probe.

6.2 Teflon Tubing. Teflon tubing to connect the sample probe to the impinger train. A heated sample line is not needed since the sample transfer system is rinsed to recover