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METHOD 308—PROCEDURE FOR DETERMINATION OF METHANOL EMISSION FROM STATIONARY SOURCES

1.0   Scope and Application

1.1   Analyte. Methanol. Chemical Abstract Service (CAS) No. 67-56-1.

1.2   Applicability. This method applies to the measurement of methanol emissions from specified stationary sources.

2.0   Summary of Method

A gas sample is extracted from the sampling point in the stack. The methanol is collected in deionized distilled water and adsorbed on silica gel. The sample is returned to the laboratory where the methanol in the water fraction is separated from other organic compounds with a gas chromatograph (GC) and is then measured by a flame ionization detector (FID). The fraction adsorbed on silica gel is extracted with an aqueous solution of n-propanol and is then separated and measured by GC/FID.

3.0   Definitions [Reserved]

4.0   Interferences [Reserved]

5.0   Safety

5.1   Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations before performing this test method.

5.2   Methanol Characteristics. Methanol is flammable and a dangerous fire and explosion risk. It is moderately toxic by ingestion and inhalation.

6.0   Equipment and Supplies

6.1   Sample Collection. The following items are required for sample collection:

6.1.1   Sampling Train. The sampling train is shown in Figure 308-1 and component parts are discussed below.

6.1.1.1   Probe. Teflon®, approximately 6-millimeter (mm) (0.24 inch) outside diameter.

6.1.1.2   Impinger. A 30-milliliter (ml) midget impinger. The impinger must be connected with leak-free glass connectors. Silicone grease may not be used to lubricate the connectors.

6.1.1.3   Adsorbent Tube. Glass tubes packed with the required amount of the specified adsorbent.

6.1.1.4   Valve. Needle valve, to regulate sample gas flow rate.

6.1.1.5   Pump. Leak-free diaphragm pump, or equivalent, to pull gas through the sampling train. Install a small surge tank between the pump and rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

6.1.1.6   Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of up to 1000 milliliter per minute (ml/min). Alternatively, the tester may use a critical orifice to set the flow rate.

6.1.1.7   Volume Meter. Dry gas meter (DGM), sufficiently accurate to measure the sample volume to within 2 percent, calibrated at the selected flow rate and conditions actually encountered during sampling, and equipped with a temperature sensor (dial thermometer, or equivalent) capable of measuring temperature accurately to within 3 °C (5.4 °F).

6.1.1.8   Barometer. Mercury (Hg), aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 inch) Hg. See the NOTE in Method 5 (40 CFR part 60, appendix A), section 6.1.2.

6.1.1.9   Vacuum Gauge and Rotameter. At least 760-mm (30-inch) Hg gauge and 0- to 40-ml/min rotameter, to be used for leak-check of the sampling train.

6.2   Sample Recovery. The following items are required for sample recovery:

6.2.1   Wash Bottles. Polyethylene or glass, 500-ml, two.

6.2.2   Sample Vials. Glass, 40-ml, with Teflon®-lined septa, to store impinger samples (one per sample).

6.2.3   Graduated Cylinder. 100-ml size.

6.3   Analysis. The following are required for analysis:

6.3.1   Gas Chromatograph. GC with an FID, programmable temperature control, and heated liquid injection port.

6.3.2   Pump. Capable of pumping 100 ml/min. For flushing sample loop.

6.3.3   Flow Meter. To monitor accurately sample loop flow rate of 100 ml/min.

6.3.4   Regulators. Two-stage regulators used on gas cylinders for GC and for cylinder standards.

6.3.5   Recorder. To record, integrate, and store chromatograms.

6.3.6   Syringes. 1.0- and 10-microliter (l) size, calibrated, for injecting samples.

6.3.7   Tubing Fittings. Stainless steel, to plumb GC and gas cylinders.

6.3.8   Vials. Two 5.0-ml glass vials with screw caps fitted with Teflon®-lined septa for each sample.

6.3.9   Pipettes. Volumetric type, assorted sizes for preparing calibration standards.

6.3.10   Volumetric Flasks. Assorted sizes for preparing calibration standards.

6.3.11   Vials. Glass 40-ml with Teflon®-lined septa, to store calibration standards (one per standard).

7.0   Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

7.1   Sampling. The following are required for sampling:

7.1.1   Water. Deionized distilled to conform to the American Society for Testing and Materials (ASTM) Specification D 1193-77, Type 3. At the option of the analyst, the potassium permanganate ($KMnO_4$) test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.1.2   Silica Gel. Deactivated chromatographic grade 20/40 mesh silica gel packed in glass adsorbent tubes. The silica gel is packed in two sections. The front section contains 520 milligrams (mg) of silica gel, and the back section contains 260 mg.

7.2   Analysis. The following are required for analysis:

7.2.1   Water. Same as specified in section 7.1.1.

7.2.2   n-Propanol, 3 Percent. Mix 3 ml of n-propanol with 97 ml of water.

7.2.3   Methanol Stock Standard. Prepare a methanol stock standard by weighing 1 gram of methanol into a 100-ml volumetric flask. Dilute to 100 ml with water.

7.2.3.1   Methanol Working Standard. Prepare a methanol working standard by pipetting 1 ml of the methanol stock standard into a 100-ml volumetric flask. Dilute the solution to 100 ml with water.

7.2.3.2   Methanol Standards For Impinger Samples. Prepare a series of methanol standards by pipetting 1, 2, 5, 10, and 25 ml of methanol working standard solution respectively into five 50-ml volumetric flasks. Dilute the solutions to 50 ml with water. These standards will have 2, 4, 10, 20, and 50 µg/ml of methanol, respectively. After preparation, transfer the solutions to 40-ml glass vials capped with Teflon® septa and store the vials under refrigeration. Discard any excess solution.

7.2.3.3   Methanol Standards for Adsorbent Tube Samples. Prepare a series of methanol standards by first pipetting 10 ml of the methanol working standard into a 100-ml volumetric flask and diluting the contents to exactly 100 ml with 3 percent n-propanol solution. This standard will contain 10 µg/ml of methanol. Pipette 5, 15, and 25 ml of this standard, respectively, into four 50-ml volumetric flasks. Dilute each solution to 50 ml with 3 percent n-propanol solution. These standards will have 1, 3, and 5 µg/ml of methanol, respectively. Transfer all four standards into 40-ml glass vials capped with Teflon®-lined septa and store under refrigeration. Discard any excess solution.

7.2.4   GC Column. Capillary column, 30 meters (100 feet) long with an inside diameter (ID) of 0.53 mm (0.02 inch), coated with DB 624 to a film thickness of 3.0 micrometers, (µm) or an equivalent column. Alternatively, a 30-meter capillary column coated with polyethylene glycol to a film thickness of 1 µm such as AT-WAX or its equivalent.

7.2.5   Helium. Ultra high purity.

7.2.6   Hydrogen. Zero grade.

7.2.7   Oxygen. Zero grade.

8.0   Procedure

8.1   Sampling. The following items are required for sampling:

8.1.1   Preparation of Collection Train. Measure 20 ml of water into the midget impinger. The adsorbent tube must contain 520 mg of silica gel in the front section and 260 mg of silica gel in the backup section. Assemble the train as shown in Figure 308-1. An optional, second impinger that is left empty may be placed in front of the water-containing impinger to act as a condensate trap. Place crushed ice and water around the impinger.
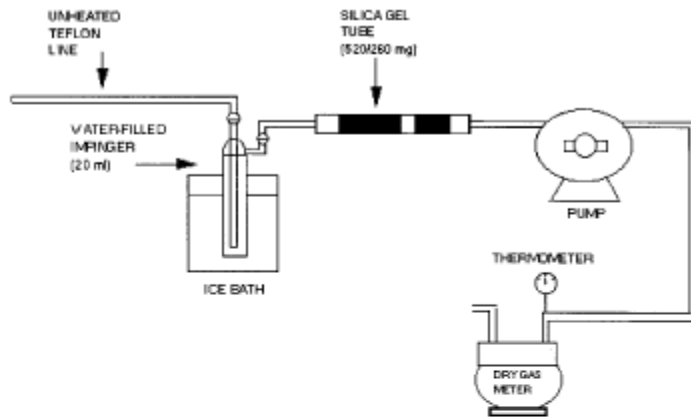
Figure 308.1. Sampling train schematic

8.1.2 Leak Check. A leak check prior to the sampling run is optional; however, a leak check after the sampling run is mandatory. The leak-check procedure is as follows:

Temporarily attach a suitable (e.g., 0-to 40-ml/min) rotameter to the outlet of the DGM, and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm (10 inch) Hg, and note the flow rate as indicated by the rotameter. A leakage rate not in excess of 2 percent of the average sampling rate is acceptable.

NOTE: Carefully release the probe inlet plug before turning off the pump.

8.1.3 Sample Collection. Record the initial DGM reading and barometric pressure. To begin sampling, position the tip of the Teflon® tubing at the sampling point, connect the tubing to the impinger, and start the pump. Adjust the sample flow to a constant rate between 200 and 1000 ml/min as indicated by the rotameter. Maintain this constant rate (±10 percent) during the entire sampling run. Take readings (DGM, temperatures at DGM and at impinger outlet, and rate meter) at least every 5 minutes. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 20 °C (68 °F) or less. At the conclusion of each run, turn off the pump, remove the Teflon® tubing from the stack, and record the final readings. Conduct a leak check as in section 8.1.2. (This leak check is mandatory.) If a leak is found, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for the leakage.

8.2 Sample Recovery. The following items are required for sample recovery:

8.2.1   Impinger. Disconnect the impinger. Pour the contents of the midget impinger into a graduated cylinder. Rinse the midget impinger and the connecting tubes with water, and add the rinses to the graduated cylinder. Record the sample volume. Transfer the sample to a glass vial and cap with a Teflon® septum. Discard any excess sample. Place the samples in an ice chest for shipment to the laboratory.

8.2.2.   Adsorbent Tubes. Seal the silica gel adsorbent tubes and place them in an ice chest for shipment to the laboratory.

9.0   Quality Control

9.1   Miscellaneous Quality Control Measures. The following quality control measures are required:

Section	Quality control measure	Effect
8.1.2, 8.1.3, 10.1	Sampling equipment leak check and calibration	Ensures accurate measurement of sample volume.
10.2	GC calibration	Ensures precision of GC analysis.

10.0   Calibration and Standardization

10.1   Metering System. The following items are required for the metering system:

10.1.1   Initial Calibration.

10.1.1.1   Before its initial use in the field, first leak-check the metering system (drying tube, needle valve, pump, rotameter, and DGM) as follows: Place a vacuum gauge at the inlet to the drying tube, and pull a vacuum of 250 mm (10 inch) Hg; plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum shall remain stable for at least 30 seconds. Carefully release the vacuum gauge before releasing the flow meter end.

10.1.1.2   Next, remove the drying tube, and calibrate the metering system (at the sampling flow rate specified by the method) as follows: Connect an appropriately sized wet test meter (e.g., 1 liter per revolution (0.035 cubic feet per revolution)) to the inlet of the drying tube. Make three independent calibrations runs, using at least five revolutions of the DGM per run. Calculate the calibration factor, Y (wet test meter calibration volume divided by the DGM volume, both volumes adjusted to the same reference temperature and pressure), for each run, and average the results. If any Y-value deviates by more than 2 percent from the average, the metering system is unacceptable for use. Otherwise, use the average as the calibration factor for subsequent test runs.

10.1.2   Posttest Calibration Check. After each field test series, conduct a calibration check as in section 10.1.1 above, except for the following variations: (a) The leak check is not to be conducted, (b) three, or more revolutions of the DGM may be used, and (c) only two independent runs need be made. If the calibration factor does not deviate by more than 5 percent

from the initial calibration factor (determined in section 10.1.1), then the DGM volumes obtained during the test series are acceptable. If the calibration factor deviates by more than 5 percent, recalibrate the metering system as in section 10.1.1, and for the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

10.1.3   Temperature Sensors. Calibrate against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.1.4   Rotameter. The rotameter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instruction.

10.1.5   Barometer. Calibrate against a mercury barometer.

10.2   Gas Chromatograph. The following procedures are required for the gas chromatograph:

10.2.1   Initial Calibration. Inject 1 µl of each of the standards prepared in sections 7.2.3.3 and 7.2.3.4 into the GC and record the response. Repeat the injections for each standard until two successive injections agree within 5 percent. Using the mean response for each calibration standard, prepare a linear least squares equation relating the response to the mass of methanol in the sample. Perform the calibration before analyzing each set of samples.

10.2.2   Continuing Calibration. At the beginning of each day, analyze the mid level calibration standard as described in section 10.5.1. The response from the daily analysis must agree with the response from the initial calibration within 10 percent. If it does not, the initial calibration must be repeated.

11.0   Analytical Procedure

11.1   Gas Chromatograph Operating Conditions. The following operating conditions are required for the GC:

11.1.1   Injector. Configured for capillary column, splitless, 200 °C (392 °F).

11.1.2   Carrier. Helium at 10 ml/min.

11.1.3   Oven. Initially at 45 °C for 3 minutes; then raise by 10 °C to 70 °C; then raise by 70 °C/min to 200 °C.

11.2   Impinger Sample. Inject 1 µl of the stored sample into the GC. Repeat the injection and average the results. If the sample response is above that of the highest calibration standard, either dilute the sample until it is in the measurement range of the calibration line or prepare additional calibration standards. If the sample response is below that of the lowest calibration standard, prepare additional calibration standards. If additional calibration standards are prepared, there shall be at least two that bracket the response of the sample. These standards should produce approximately 50 percent and 150 percent of the response of the sample.

11.3   Silica Gel Adsorbent Sample. The following items are required for the silica gel adsorbent samples:

11.3.1   Preparation of Samples. Extract the front and backup sections of the adsorbent tube separately. With a file, score the glass adsorbent tube in front of the first section of silica gel. Break the tube open. Remove and discard the glass wool. Transfer the first section of the silica gel to a 5-ml glass vial and stopper the vial. Remove the spacer between the first and second section of the adsorbent tube and discard it. Transfer the second section of silica gel to a separate 5-ml glass vial and stopper the vial.

11.3.2   Desorption of Samples. Add 3 ml of the 10 percent n-propanol solution to each of the stoppered vials and shake or vibrate the vials for 30 minutes.

11.3.3   Inject a 1-µl aliquot of the diluted sample from each vial into the GC. Repeat the injection and average the results. If the sample response is above that of the highest calibration standard, either dilute the sample until it is in the measurement range of the calibration line or prepare additional calibration standards. If the sample response is below that of the lowest calibration standard, prepare additional calibration standards. If additional calibration standards are prepared, there shall be at least two that bracket the response of the sample. These standards should produce approximately 50 percent and 150 percent of the response of the sample.

12.0   Data Analysis and Calculations

12.1   Nomenclature.

C_{af} = Concentration of methanol in the front of the adsorbent tube, µg/ml.

C_{ab} = Concentration of methanol in the back of the adsorbent tube, µg/ml.

C_i = Concentration of methanol in the impinger portion of the sample train, µg/ml.

E=Mass emission rate of methanol, µg/hr (lb/hr).

M_{tot} = Total mass of methanol collected in the sample train, µg.

P_{bar} = Barometric pressure at the exit orifice of the DGM, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

Q_{std} = Dry volumetric stack gas flow rate corrected to standard conditions, dscm/hr (dscf/hr).

T_m = Average DGM absolute temperature, degrees K (°R).

T_{std} = Standard absolute temperature, 293 degrees K (528 °R).

V_{af} = Volume of front half adsorbent sample, ml.

V_{ab} = Volume of back half adsorbent sample, ml.

V_i = Volume of impinger sample, ml.

V_m = Dry gas volume as measured by the DGM, dry cubic meters (dcm), dry cubic feet (dcf).

$V_{m(std)}$ = Dry gas volume measured by the DGM, corrected to standard conditions, dry standard cubic meters (dscm), dry standard cubic feet (dscf).

12.2   Mass of Methanol. Calculate the total mass of methanol collected in the sampling train using Equation 308-1.

$$M_{tot} = V_i C_i + V_{qf} C_{qf} + V_{ab} C_{ab}$$ Equation 308-1

12.3   Dry Sample Gas Volume, Corrected to Standard Conditions. Calculate the volume of gas sampled at standard conditions using Equation 308-2.

$$V_m(std) = \frac{V_m Y \, T_{std} P_{bar}}{T_m P_{std}}$$ Equation 308-2

12.4   Mass Emission Rate of Methanol. Calculate the mass emission rate of methanol using Equation 308-3.

$$E = \frac{M_{tot} Q_{sd}}{V_{m(std)}}$$ Equation 308-3

13.0   Method Performance [Reserved]

14.0   Pollution Prevention [Reserved]

15.0   Waste Management [Reserved]

16.0   Bibliography

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17.0   Tables, Diagrams, Flowcharts, and Validation Data [Reserved]