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Background Chapter: 4

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Title: Determination of Total Gaseous
Organic Concentration Using a Flame
Ionization Analyzer

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METHOD 25A—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A FLAME IONIZATION ANALYZER

1. Applicability and Principle

1.1 **Applicability.** This method applies to the measurement of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

1.2 **Principle.** A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a flame ionization analyzer (FIA). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

2. Definitions

2.1 **Measurement System.** The total equipment required for the determination of the gas concentration. The system consists of the following major subsystems:

2.1.1 **Sample Interface.** That portion of the system that is used for one or more of the following: sample acquisition, sample transportation, sample conditioning, or protection of the analyzer from the effects of the stack effluent.

2.1.2 **Organic Analyzer.** That portion of the system that senses organic concentration and generates an output proportional to the gas concentration.

2.2 **Span Value.** The upper limit of a gas concentration measurement range that is specified for affected source categories in the

applicable part of the regulations. The span value is established in the applicable regulation and is usually 1.5 to 2.5 times the applicable emission limit. If no span value is provided, use a span value equivalent to 1.5 to 2.5 times the expected concentration. For convenience, the span value should correspond to 100 percent of the recorder scale.

2.3 **Calibration Gas.** A known concentration of a gas in an appropriate diluent gas.

2.4 **Zero Drift.** The difference in the measurement system response to a zero level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

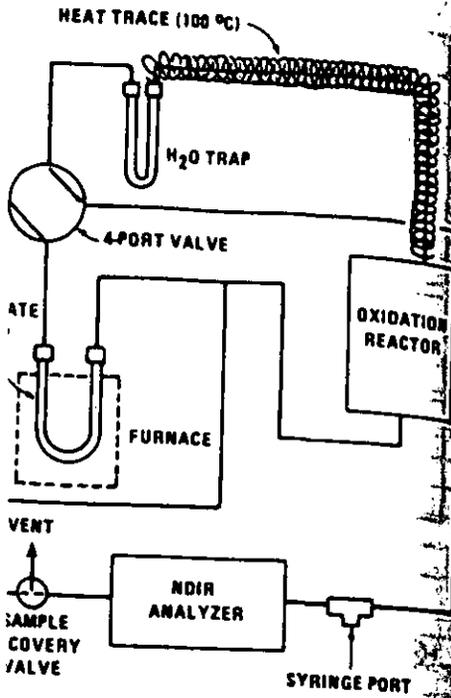
2.5 **Calibration Drift.** The difference in the measurement system response to a mid-level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair or adjustment took place.

2.6 **Response Time.** The time interval from a step change in pollutant concentration at the inlet to the emission measurement system to the time at which 95 percent of the corresponding final value is reached as displayed on the recorder.

2.7 **Calibration Error.** The difference between the gas concentration indicated by the measurement system and the known concentration of the calibration gas.

3. Apparatus

A schematic of an acceptable measurement system is shown in Figure 25A-1. The essential components of the measurement system are described below:



/ system, collection of trap organics.

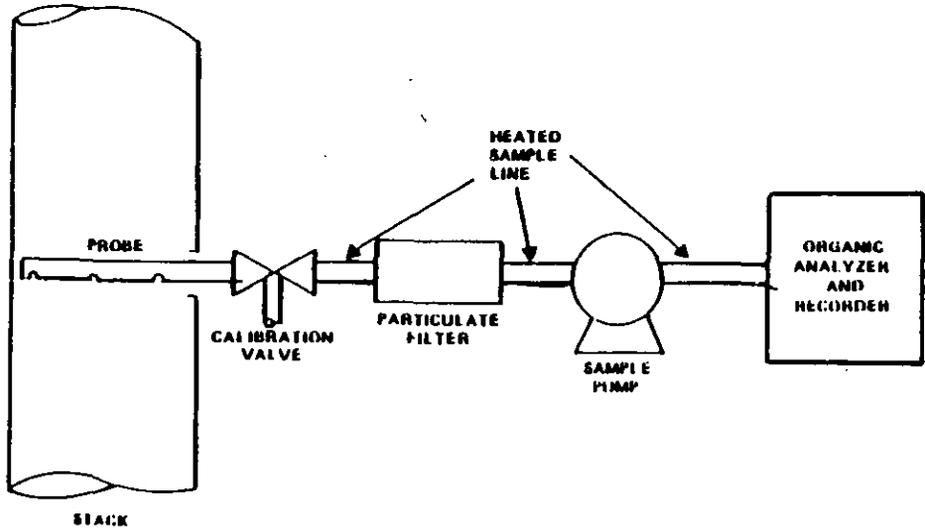


Figure 25A 1. Organic Concentration Measurement System.

3.1 Organic Concentration Analyzer. A flame ionization analyzer (FIA) capable of meeting or exceeding the specifications in this method.

3.2 Sample Probe. Stainless steel, or equivalent, three-hole rake type. Sample holes shall be 4 mm in diameter or smaller and located at 16.7, 50, and 83.3 percent of the equivalent stack diameter. Alternatively, a single opening probe may be used so that a gas sample is collected from the centrally located 10 percent area of the stack cross-section.

3.3 Sample Line. Stainless steel or Teflon® tubing to transport the sample gas to the analyzer. The sample line should be heated, if necessary, to prevent condensation in the line.

3.4 Calibration Valve Assembly. A three-way valve assembly to direct the zero and calibration gases to the analyzers is recommended. Other methods, such as quick-connect lines, to route calibration gas to the analyzers are applicable.

3.5 Particulate Filter. An in-stack or an out-of-stack glass fiber filter is recommended if exhaust gas particulate loading is significant. An out-of-stack filter should be heated to prevent any condensation.

3.6 Recorder. A strip-chart recorder, analog computer, or digital recorder for recording measurement data. The minimum data recording requirement is one measurement value per minute. Note: This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

4. Calibration and Other Gases

Gases used for calibrations, fuel, and combustion air (if required) are contained in compressed gas cylinders. Preparation of calibration gases shall be done according to the procedure in Protocol No. 1, listed in Citation 2 of Bibliography. Additionally, the manufacturer of the cylinder should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change more than ± 2 percent from the certified value. For calibration gas values not generally available (i.e., organics between 1 and 10 percent by volume), alternative methods for preparing calibration gas mixtures, such as dilution systems, may be used with prior approval of the Administrator.

Calibration gases usually consist of propane in air or nitrogen and are determined in terms of the span value. Organic compounds other than propane can be used following the above guidelines and making the appropriate corrections for response factor.

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

4.1 Fuel. A 40 percent H₂/60 percent He or 40 percent H₂/60 percent N₂ gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

4.2 Zero Gas. High purity air with less than 0.1 parts per million by volume (ppmv) of organic material (propane or carbon equivalent) or less than 0.1 percent of the span value, whichever is greater.

4.3 Low-level Calibration Gas. An organic calibration gas with a concentration equivalent to 25 to 35 percent of the applicable span value.

4.4 Mid-level Calibration Gas. An organic calibration gas with a concentration equivalent to 45 to 55 percent of the applicable span value.

4.5 High-level Calibration Gas. An organic calibration gas with a concentration equivalent to 80 to 90 percent of the applicable span value.

5. Measurement System Performance Specifications

5.1 Zero Drift. Less than ± 3 percent of the span value.

5.2 Calibration Drift. Less than ± 3 percent of span value.

5.3 Calibration Error. Less than ± 5 percent of the calibration gas value.

6. Pretest Preparations

6.1 Selection of Sampling Site. The location of the sampling site is generally specified by the applicable regulation or purpose of the test; i.e., exhaust stack, inlet line, etc. The sample port shall be located at least 1.5 meters or 2 equivalent diameters upstream of the gas discharge to the atmosphere.

6.2 Location of Sample Probe. Install the sample probe so that the probe is centrally located in the stack, pipe, or duct and is sealed tightly at the stack port connection.

6.3 Measurement System Preparation. Prior to the emission test, assemble the measurement system following the manufacturer's written instructions in preparing the sample interface and the organic analyzer. Make the system operable.

FIA equipment can be calibrated for almost any range of total organics concentrations. For high concentrations of organics (>1.0 percent by volume as propane) modifications to most commonly available analyzers are necessary. One accepted method of equipment modification is to decrease the size of the sample to the analyzer through the use of a smaller diameter sample capillary. Direct and continuous measurement of organic concentration is a necessary consideration when determining any modification design.

6.4 Calibration Error Test. Immediately prior to the test series, (within 2 hours of the start of the test) introduce zero gas and high-level calibration gas at the calibration valve assembly. Adjust the analyzer output

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Fuel. A 40 percent H₂/60 percent N₂ gas mixture is recommended to avoid an oxygen synergetic effect that reportedly occurs when oxygen concentration varies significantly from the nominal value.

Zero Gas. High purity air with a concentration of 0.1 parts per million by volume (ppmv) of organic material (propane or carbon monoxide) or less than 0.1 percent of the total value, whichever is greater.

Low-level Calibration Gas. An organic calibration gas with a concentration equivalent to 25 to 35 percent of the applicable span.

Mid-level Calibration Gas. An organic calibration gas with a concentration equivalent to 45 to 55 percent of the applicable span.

High-level Calibration Gas. An organic calibration gas with a concentration equivalent to 80 to 90 percent of the applicable span.

Measurement System Performance Specifications

Zero Drift. Less than ±3 percent of the nominal value.

Calibration Drift. Less than ±3 percent of the nominal value.

Calibration Error. Less than ±5 percent of the calibration gas value.

Test Preparations

Selection of Sampling Site. The location of the sampling site is generally specified by the applicable regulation or purpose of the test; i.e., exhaust stack, inlet line, etc. The sample port shall be located at least 10 or 2 equivalent diameters upstream from the discharge to the atmosphere.

Location of Sample Probe. Install the probe so that the probe is centrally located in the stack, pipe, or duct and is held tightly at the stack port connection.

Measurement System Preparation. Prior to the emission test, assemble the measurement system following the manufacturer's written instructions in preparing the interface and the organic analyzer. The system is operable.

The equipment can be calibrated for a wide range of total organics concentrations (or high concentrations of organic material) by volume as propane) modification is most commonly available analysis modification is to decrease the size of the sample to the analyzer through the use of a smaller diameter sample capillary. Discontinuous measurement of organic material is a necessary consideration in determining any modification design.

Calibration Error Test. Immediately before the test series, (within 2 hours of the test) introduce zero gas and a low-level calibration gas at the calibration assembly. Adjust the analyzer output

to the appropriate levels, if necessary. Calculate the predicted response for the low-level and mid-level gases based on a linear response line between the zero and high-level responses. Then introduce low-level and mid-level calibration gases successively to the measurement system. Record the analyzer responses for low-level and mid-level calibration gases and determine the differences between the measurement system responses and the predicted responses. These differences must be less than 5 percent of the respective calibration gas value. If not, the measurement system is not acceptable and must be replaced or repaired prior to testing. No adjustments to the measurement system shall be conducted after the calibration and before the drift check (Section 7.3). If adjustments are necessary before the completion of the test series, perform the drift checks prior to the required adjustments and repeat the calibration following the adjustments. If multiple electronic ranges are to be used, each additional range must be checked with a mid-level calibration gas to verify the multiplication factor.

6.5 Response Time Test. Introduce zero gas into the measurement system at the calibration valve assembly. When the system output has stabilized, switch quickly to the high-level calibration gas. Record the time from the concentration change to the measurement system response equivalent to 95 percent of the step change. Repeat the test three times and average the results.

7. Emission Measurement Test Procedure

7.1 Organic Measurement. Begin sampling at the start of the test period, recording time and any required process information as appropriate. In particular, note on the recording chart periods of process interruption or cyclic operation.

7.2 Drift Determination. Immediately following the completion of the test period and hourly during the test period, reintroduce the zero and mid-level calibration gases, one at a time, to the measurement system at the calibration valve assembly. (Make no adjustments to the measurement system until after both the zero and calibration drift checks are made.) Record the analyzer response. If the drift values exceed the specified limits, invalidate the test results preceding the check and repeat the test following corrections to the measurement system. Alternatively, recalibrate the test measurement system as in Section 6.4 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period).

8. Organic Concentration Calculations

Determine the average organic concentration in terms of ppmv as propane or other calibration gas. The average shall be determined by the integration of the output re-

ording over the period specified in the applicable regulation.

If results are required in terms of ppmv as carbon, adjust measured concentrations using Equation 25A-1.

$$C_c = K C_{meas} \quad \text{Eq. 25A-1}$$

Where:

C_c = Organic concentration as carbon, ppmv.
 C_{meas} = Organic concentration as measured, ppmv.

K = Carbon equivalent correction factor.

$K=2$ for ethane.

$K=3$ for propane.

$K=4$ for butane.

K = Appropriate response factor for other organic calibration gases.

9. Bibliography

1. Measurement of Volatile Organic Compounds—Guideline Series. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA-450/2-78-041. June 1978. p. 46-54.

2. Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Continuous Source Emission Monitors (Protocol No. 1). U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Research Triangle Park, NC. June 1978.

3. Gasoline Vapor Emission Laboratory Evaluation—Part 2. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. EMB Report No. 75-GAS-6. August 1975.

METHOD 25B—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A NONDISPERSIVE INFRARED ANALYZER

1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of total gaseous organic concentration of vapors consisting primarily of alkanes. (Other organic materials may be measured using the general procedure in this method, the appropriate calibration gas, and an analyzer set to the appropriate absorption band.) The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

1.2 Principle. A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a nondispersive infrared analyzer (NDIR). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

2. Definitions

The terms and definitions are the same as for Method 25A.

3. Apparatus

The apparatus is the same as for Method 25A with the exception of the following:

3.1 Organic Concentration Analyzer. A nondispersive infrared analyzer designed to