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Measurement of Volatile Organic Compounds

EPA-450/2-78-041

OAQPS No. 1.2-115

Measurement of Volatile Organic Compounds

Emissions Measurement Branch
Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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OAQPS GUIDELINE SERIES

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PREFACE

Emphasis on the control of volatile organic compounds through the State Implementation Plans, new source performance standards, and national emission standards for hazardous air pollutants has created a need for standardized test procedures. In setting national performance standards for new sources and national emission standards for hazardous air pollutants, the Environmental Protection Agency has followed a policy of establishing a reference method for each regulated source category and pollutant. Under the State Implementation Plan process, however, test methods and erocedures are defined by the States. Thus, the case-by-case approach used by the Environmental Protection Agency for national standards could conflict with State established methods. In addition, the case-by-case approach does not provide sufficient guidance to the States in their efforts to develop regulations for a large number of sources and organic compounds.

The purpose of this document, therefore, is to provide guidance to the States on the measurement of volatile organic compounds from a diversity of sources and pollutants that is consistent with the methodology being applied by the Environmental Protection Agency as it develops regulations for specific sources and pollutants.

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METHODS FOR DETERMINING VOLATILE ORGANIC COMPOUNDS AS CARBON IN STATIONARY SOURCES

Introduction

Volatile organic compound (VOC) emission control regulations are being developed by EPA and by State and local agencies to meet the oxidant control needs. In some cases, the regulations are in terms of the volatile organic content of solvents. In other cases, they cover organic volume or mass concentrations, mass emission rates, and control equipment efficiencies. Regardless of the approach taken in the regulation, consideration must be given to the expression of emission limits in terms of what can be measured, and to the cost and practicality of the test methods.

One concept of volatile organic emission measurement is the determination of organic carbon mass concentration. The rationale for selecting this concept and conceptual approach for writing regulations in terms of volatile organic carbon are discussed herein, and two specific test methods are presented to implement the recommended approach.

Rationale for Selecting Organic Carbon

In considering volatile organic compound test methods one must recognize that organic emissions normally consist of a mixture of compounds and that there is presently no detection technique having an inherent, quantitative response to the total molecular structure of the mixture. Several detection techniques respond to organic compounds; however, the response can vary widely from compound to compound and may, therefore, not be proportional to the total organic mass or volume in a mixture.

Such is the case of the flame ionization detector (FID), the most commonly used detector for organic measurements. The FID response can vary from compound to compound because it is a function of the number of carbon atoms, the type of bonds, and the elements present in the organic molecules. Thus, if the volatile organic emission limit is expressed in terms that require the measurement of the total molecular structure of the organic emissions, the variable response of the flame ionization detector must be overcome by one of the methods described below.

1. Gas Chromatograph/Flame Ionization Detector. This method involves the separation of the organic components into discrete compounds using gas chromatography (GC). The compounds are identified, and the FID is calibrated for each of the identified compounds. The compounds are then measured individually, and the total mass concentration is determined by adding the individual mass concentration values; methane can be identified and excluded from the results. This method may be eractical where only two or three compounds are emitted, such as in maleic anhydride plants; but if it is applied to sources that emit numerous organics, the time and expense would be formidable. For example, over 20 peaks were noted in a preliminary study of emissions from the manufacture of nitrobenzene.
2. Direct Flame Ionization Detector with Emission Stream Characterization. This method involves direct measurement with an FID analyzer,

with prior characterization of the gas stream and knowledge that the detector responds predictably to the organic components in the stream. If present, methane will, of course, also be measured.

In practice, this method can be applied to the determination of the mass concentration of the total molecular structure of the organic emissions under the following limited conditions: (1) where only one compound is known to exist, (2) when the organic compounds consist of only hydrogen and carbon, (3) where the relative percentage of the compounds is known or can be determined, and the FID response to the compounds is known; (4) where a consistent mixture of compounds exists before and after emission control and only the relative concentrations are to be assessed, or (5) where the FID can be calibrated against mass standards of the emissions (solvent emissions, for example).

In the case of volatile organic solvents, accurate measurements by direct FID analyzers without calibration with solvent standards are seldom possible because these solvents are often a mixture of multiple unknown compounds. Even if the emissions can be separated and identified using a GC, accurate determination of the average FID response is often impractical. In addition, the emissions may be altered as they pass through a control device: for example, they may be partially oxidized in an incinerator or selectively retained in an adsorber. In such cases the measurement is more difficult and cannot be corrected with

solvent standards; therefore even the determination of percent control efficiency can be a difficult problem.

Another applicable measurement technique involves an oxidation-reduction analysis; however, the results of this technique are in terms of organic carbon and not a mass concentration of the total molecular structure. In this approach, the nonmethane organic compounds are separated from other carbon compounds and are then oxidized to CO_2. The resultant CO_2 is subsequently reduced to methane, which is then measured with an FID. The CO_2 from the combustion step can also be measured with a nondispersive infrared (NDIR) analyzer; however, the NDIR is not as sensitive as the FID and is therefore limited to high concentration levels. One limitation to the oxidation-reduction analysis is that the equipment required is somewhat complex and is unlikely to be made available in a portable form.

Consideration of the various measurement approaches indicates that organic emission regulations expressed in terms of the measurement of organic carbon could be applied to a wide range of volatile compounds. The measurement of organic carbon can be used to assess directly the efficiency of control devices such as incinerators or adsorbers. By performing volumetric flow rate measurements, one can then determine organic carbon emission rates. Organic carbon content can also be related to volatile

content of solvents or surface coatings.

Costs, logistics, and other practicalities of source testing may, under limited conditions, make other test methods more desirable for routine compliance determinations. Three distinct categories of test methods are therefore recommended for use with volatile organic compound regulations expressed in terms of organic carbon: a reference method, alternate methods, and screening methods. These categories are described as follows:

1. Reference Method. This method would be applicable to all regulated sources and would be accurate in reference to the emission standard. OAQPS recommends that the reference method be based on the oxidation-reduction method of analysis to measure organic carbon.
2. Alternate Methods. These are methods not necessarily demonstrated to be equivalent to the reference method, but demonstrated to the satisfaction of the control agency to produce results adequate for determining compliance, in specific applications. Methods involving direct measurement with flame ionization detectors would be primary candidates for alternate methods.
3. Screening Methods. These alternative methods may produce biased or imprecise results, but they have been demonstrated to the satisfaction of the control agency to be adequate for determining compliance, provided that any bias or imprecision is taken into account. These

methods are normally characterized by portability of equipment, procedural simplicity, and low cost. Methods based on thermal conductivity or low-cost portable FID analyzers would be candidates for approval as screening methods.

Recommended Reference Method

A reference method that involves indirect measurement of volatile organic carbon by an oxidation-reduction is recommended. This necessitates that the emission limits be expressed in terms of organic carbon. If the emission limits and a universal reference method are both based on organic carbon, the volatile organic standard will be expressed in clear, unambiguous terms. No other known practical test method could accomplish this objective for a wide range of volatile organic compounds.

A draft "Reference Method for Determination of Total Gaseous Nonmethane Organic Emissions as Carbon" is included as Attachment 1. The method requires a system for separating total nonmethane organics from other carbon compounds, converting the total nonmethane organics to methane, and analysis of the methane by a flame ionization detector. Other than requiring this general equipment, the method provides performance specifications designed to assure correct performance of the separation-detection system. Depending on the organic carbon concentration, the method may allow the use of the NDIR to detect the CO_2 formed by the initial oxidation step.

The concept upon which the method is based has been utilized for many years in Los Angeles County, where it has been demonstrated to be valid and effective for compliance determinations.

There is at least one private laboratory that is able to perform the analysis on a fee basis. The oxidation-reduction analysis concept for measurement of gaseous nonmethane organic compounds is also offered commercially by at least one instrument vendor. Although the availability of instruments is admittedly very limited, there is no serious technical impediment that would prevent additional vendors from designing and producing acceptable instruments.

Because of the somewhat limited use potential for the Los Angeles laboratory-oriented procedure and the present limited production of commerical instruments for field use, the OAQPS recommendation of the oxidation-reduction reference method for the definition of organic emissions is recognized as leading the technology. Wide acceptance of the organic carbon reference method will, however, procide the needed inducement for additional vendors to enter the market and thereby increase the supply and variety of organic carbon analysis instruments.

A draft of the Los Angeles procedure is included as Attachment 2. Although the detail is considerable, some agencies may wish to assemble the laboratory apparatus. The Emission Measurement Branch of OAQPS is working to refine the operating details of the procedure; as information becomes available, it will be incorporated into the method.

Alternate Methods

An "Alternate method" may have only limited applicability or other deficiencies that prevent its designation as a reference method. Such methods may offer practical advantages and produce results adequate for determining compliance in certain applications. Where such methods are applicable, the results may be accepted in lieu of reference method results.

As a specific example, methods based on direct measurement with flame ionization detectors are often practical for hydrocarbon compounds, and, in addition, the equipment is widely available. An FID analyzer will be less costly and may be less complicated for field application that an oxidation-reduction analyzer; therefore, for those applications where such methods can be made to produce accurate results, approval of them as alternate methods is desirable.

The Office of Air Quality Planning and Standards, EPA,has drafted an "Alternate Test Method for Direct Measurement of Total Gaseous Organic Compounds Using a Flame Ionization Detector," which is included as Attachment 3. This method outlines the known characteristics and limitations of FID techniques and provides procedures needed to assure its proper operation. The method does not and is not intended to indicate specific applications where the method can (or cannot) be used or correction factors to be applied to the results. Such determinations must be made on a case-by-case basis founded on knowledge of

the contents of the stream under test and the limitations of the detector.

Screening Methods

In addition to the limitations associated with alternate methods, screening methods may also lack precision. In spite of such shortcomings, screening methods may play an important role in any volatile organic control program. As a practical matter, the cost of applying a reference or alternate method to all or even a majority of the regulated effluent streams in a jurisdiction may be unreasonable; therefore, less expensive, simpler testing techniques will be needed.

To date, OAQPS has made effective use of an explosimeter to detect vapor leaks in gasoline marketing operations. In addition, an inexpensive hydrocarbon monitor using a solid-state ionization detector was designed by OAQPS and has been used successfully as an emissions breakthrough detector on the exit of a carbon adsorber. More recently, OAQPS has initiated a test program associated with the development of new source standards, using portable analyzers to detect leaks occurring in unit operations in the petroleum industry. Two analyzers will be employed in this program, one involving a combustion/thermal-conductivity-type detector and the other a low-cost FID.

Another example of a screening method would be the case of an FID analyzer applied to an unknown gas stream. In such case there is often enough information available to provide a rough estimate of the analyzer accuracy, but a more exact determination would be prohibitive. In such an

event the FID may be used as an alternative method for determining compliance, provided that sufficient buffer is included to account for the possible inaccuracy.

Regulatory Language

Examples of how general regulations may be expressed in terms of the reference method that measures organic carbon concentration are as follows:

1. To regulate concentration:

   "Emissions of organic carbon shall not exceed _____ grams carbon per cubic meter."

2. To regulate mass rate:

   "Emissions of organic carbon shall not exceed _____ grams carbon per hour" or "Emissions of organic carbon shall not exceed _____grams carbon per kilogram of solvent used."

To protect the analytical instrument from contamination from particulates and condensation, a filter and heated sample line (temperature defined) must also be included in the emission regulations.

ATTACHMENT 1. REFERENCE METHOD FOR DETERMINATION OF TOTAL GASEOUS NONMETHANE ORGANIC EMISSIONS AS CARBON--AUTOMATED ANALYZER VERSION

1. Principle and Applicability

1.1 Principle. Conditioned stack gas is transported to and analyzed by a semiportable gas chromatograph (GC) equipped with a flame ionization detector (FID). The total gaseous nonmethane organic (TGNMO) fraction is separated by means of various GC columns from the other constituents, oxidized to CO_2 and then reduced to methane (CH_4) before it is introduced to the FID. In this manner, the variable response of the FID associated with different types of organics is eliminated, and a count of TGNMO carbon atoms is obtained.

1.2 Applicability. The method is applicable to the semicontinuous measurement of total gaseous nonmethane organics in source emissions.

2. Range and Sensitivity

2.1 Range. Signal attenuators shall be available so that a minimum signal response of 10 percent of full scale can be produced when analyzing calibration gas or sample.

2.2 Sensitivity. The detector sensitivity shall be equal to or better than 2.0 percent of the full scale setting, with a minimum full scale setting of 10 ppm (methane or carbon equivalent).

3. Interferences

None.

4. Apparatus

4.1 TGNMO analyzers are available commercially or can be constructed from available components by a qualified instrument laboratory. The

primary components of the analyzer are an FID preceded by a GC column to achieve the necessary separation of TGNMO from other carbon compounds. Oxidation and reduction catalysts then convert the TGNMO to CH_4 prior to detection. The analyzer shall be accompanied by an instruction manual (supplied by the manufacturer if the analyzer was commercially produced) describing proper operation and maintenance procedures. In addition to the specific procedures required by this method, the analyzer shall be demonstrated prior to initial use to be capable of proper separation, oxidation, and reduction. As a minimum this demonstration shall include measurement of a known TGNMO concentration present in a mixture that also contains similar amounts of CH_4, CO_2, and CO. Certification of such demonstration by the manufacturer is acceptable.

4.2 Sample Conditioning or Interface System (see Figure 1). Probe with filter, 6.4 mm O.D. Teflon[1] sample line, Teflon-coated diaphragm pump, and Teflon flow control valves. A heating system capable of maintaining all components at 120°C or greater shall be included. The pump shall be sized so that the sample residence time from the probe to the instrument will not exceed 15 seconds.

4.3 Potentiometric Recorder (optional). Strip chart recorder with a voltage output compatible with the analyzer.

5. Reagents

5.1 Combustion Gas. Air containing less than 2 ppm organics (methane or carbon equivalent).

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[1]Mention of trade names on specific products does not constitute endorsement by the Environmental Protection Agency.

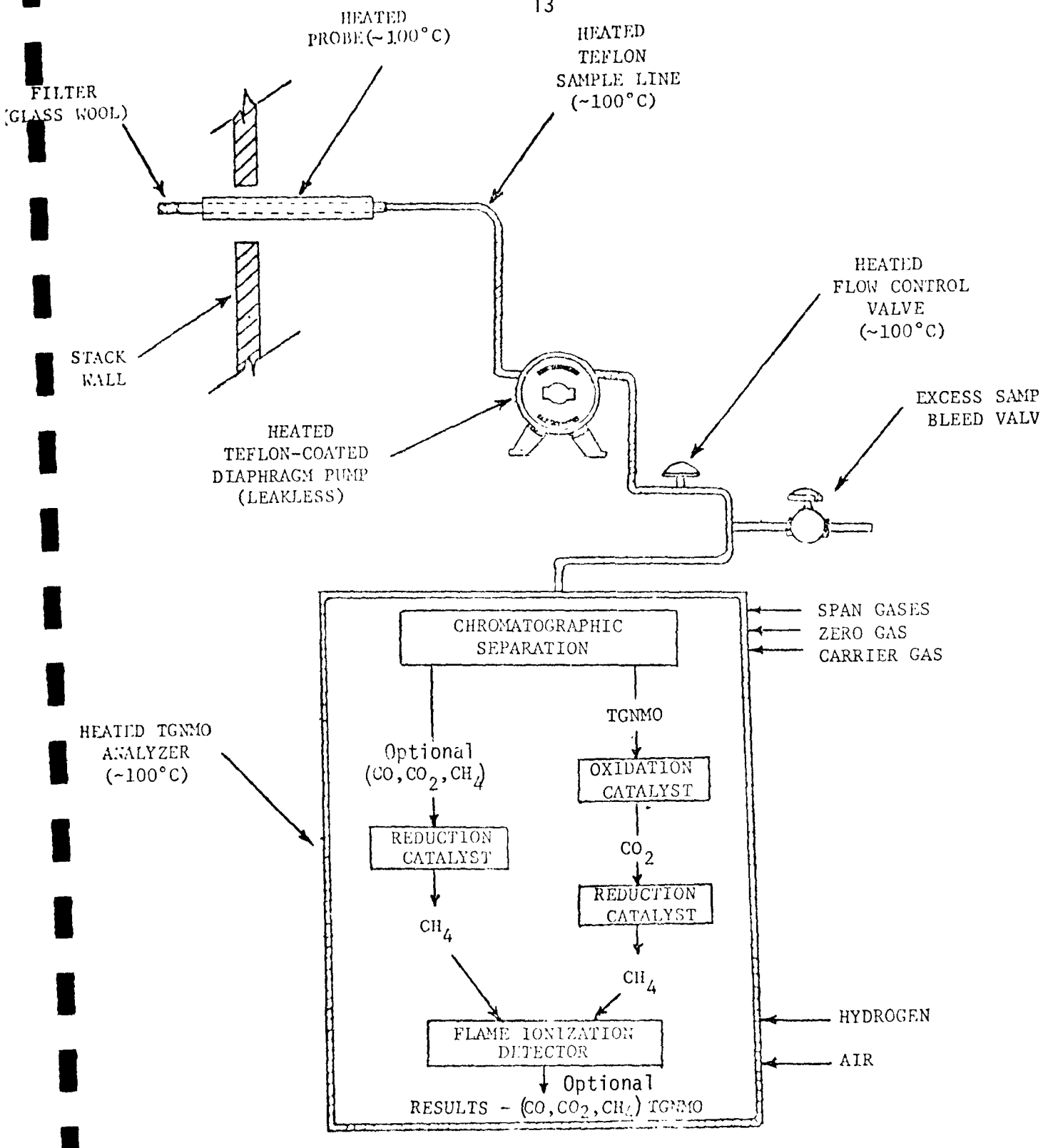


FIGURE 1. On-site Application of TGNMO Analyzer

5.2 Fuel. Hydrogen or a mixture of hydrogen and inert gas containing less than 1 ppm organics (methane or carbon equivalent).

5.3 Carrier Gas. Helium, nitrogen, air or hydrogen containing less than 1 ppm organics (methane or carbon equivalent).

5.4 Zero Gas. Air containing less than 1 ppm organics (methane or carbon equivalent).

5.5 Calibration Gases (2). Gas mixture standards with known propane (C_3H_8) concentrations corresponding to ranges of 5-10 ppm and 5-10 percent (methane or carbon equivalent) are prepared and certified by a gas manufacturer. The mixture shall consist of C_3H_8, CO, CO_2, and CH_4 in nitrogen. The gas manufacturer must recommend a maximum shelf life for each cylinder so that the C_3H_8 concentration does not change more than $\pm$ 5 percent from its certified value. The date of gas cylinder preparation, certified C_3H_8, CO, CO_2, and CH_4 concentratio and recommended maximum shelf life must be affixed to the cylinder before shipment from the gas manufacturer to the buyer. These gas mixture standards are to be used to prepare a chromatograph calibration curve as described in Section 7.2.

5.6 Span Gas. The calibration gas corresponding to 5 to 10 percen (methane or carbon equivalent) is used to span the analyzer.

6. Analyzer Performance Specifications

6.1 Linearity: $\pm$ 5 percent of the expected value for full scale settings up to the maximum percent absolute (methane or carbon equivalent) calibration point. The analyzer shall be demonstrated prio

to initial use to meet this specification through a 5-point (minimum) calibration. There shall be at least one calibration point in each of the following ranges: 5-10, 50-100, 500-1,000, 5,000-10,000, and 50,000-100,000 ppm (methane or carbon equivalent). Certification of such demonstration by the manufacturer is acceptable. An additional linearity performance check (see Section 7.2.1) must be made before each use.

6.2 Zero Drift. One percent full scale per test period.

6.3 Span Drift. One percent full scale per test period.

7. Procedure

7.1 Sampling

7.1.1 Assemble the system as shown in Figure 1. Locate the analyzer in a suitable environment. Take particular care that sample will be introduced to the system under the same conditions of pressure and flow rates as are used in calibration. For specific operating instructions for the TGNMO analyzer, refer to the operation manual.

7.1.2 Adjust the sampling system and analyzer heating system to provide a minimum temperature of 120°C and allow the system to warm up.

7.1.3 Perform a leak check as follows before sampling: Recheck to confirm that all fittings are tight. With the sample probe plugged, open the flow control valve and the excess sample bleed valve. Use leak detection fluid or immerse the tubing leading from the bleed valve in a jar of water to check that sample flow has ceased. At the conclusion of the sampling tests, recheck for leaks.

7.1.4 Begin Actual Sampling. Set the signal attenuation to yield a minimum response of 10 percent of full scale, unless the stack concentration is less than 1 ppm. Adjust the flow and bleed valves to minimize sample line residence time. Perform the analysis a minimum of four times. Report the average of the final four readings. The analyzer cycle time is normally 10 to 15 minutes.

7.1.5 At the conclusion of the sampling tests, but at least once every day, introduce zero and span gas to the analyzer to determine zero and span drifts. If the analyzer has drifted beyond the allowable performance specification, the tests shall be considered invalid.

7.2 Calibration

7.2.1 Calibration Curve. Maintain a record of performance of each item. Determine the linearity of the analyzer for TGNMO as follows: With the signal attenuation at the most sensitive setting, introduce zero gas and adjust the respectivezeroing controls to indicate a reading of less than 1 percent of full scale. With the signal attenuation at the least sensitive setting, introduce the span gas and adjust the span control to indicate the proper value on the analyzer readout. Repeat these two steps until adjustments are no longer necessary. Calculate a predicted response for the 5-10 ppm calibration gas. Introduce that calibration gas and note the value obtained. If this value is not within ± 5 percent of its predicted value, then the analyzer may need repairs, or one or both of the calibration gases may need replacement. In any event, this linearity performance specification shall be met before the analyzer is placed in actual use.

7.3 Catalyst Performance Check. These checks should be performed on a frequency established by the amount of use of the analyzer, and the nature of the organic emissions to which it is exposed. To confirm that the oxidation catalyst is functioning in the correct manner, the operator must turn off or bypass the reduction catalyst while operating the analyzer in an otherwise normal fashion. If oxidation is adequate, the only gas that will then reach the detector will be CO_2, to which the FID has no response. If responses are noted, then the oxidation catalyst must be replaced. To confirm the operation of the reduction catalyst, reverse the above procedure. If CO_2 in the calibration gases is not reduced to CH_4 as it should be, then the reduction catalyst must be replaced.

8. Calculations

8.1 Determine concentrations of TGNMO (propane equivalent) directly from the calibration curves. Multiply this number by 3 to obtain ppm TGNMO (methane or carbon equivalent).

8.2 Conversion to mass concentration values for TGNMO as carbon is made as follows:

$$\text{mg TGNMO/m}^3 \text{ as carbon} = \text{ppm TGNMO (methane or carbon equivalent)} \times 0.499$$

where:

$$1 \text{ ppm TGNMO (methane or carbon equivalent)} = \frac{1}{10^6} \times \frac{41.57 \text{ g-mole}}{\text{m}^3} \times \frac{12000 \text{ mg}}{\text{g-mole}} = 0.499 \text{ mg/m}^3 \text{ as carbon.}$$

where:

Molecular weight of carbon = 12

Standard conditions: 20°C, 1 atm.

9. References

9.1 Albert E. Salo, Samuel Whitz, and Robert D. MacPhee. "Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared With Flame Ionization Detectors." Presented at the 68th Annual Meeting of the Air Pollution Control Association, Boston, Ma. Paper No. 75-33.2. June 15-20, 1975.

9.2 Instruction Manual, Byron Model 401 Total Emission Analyzer, Byron Instruments, Inc., 520 1/2 S. Harrington Street, Raleigh, N.C. 27601.

ATTACHMENT 2. DETERMINATION OF TOTAL GASEOUS NONMETHANE ORGANIC EMISSIONS AS CARBON: MANUAL SAMPLING AND ANALYSIS PROCEDURE

1. Principle and Applicability

1.1 Principle. An emission sample is anisokinetically drawn from the stack through a heated filter and a chilled condensate trap by means of an evacuated gas collection tank. Total gaseous non-methane organics (TGNMO) are determined by combining the analytical results obtained from independent analyses of the condensate trap and evacuated tank fractions. After sampling is completed, the organic contents of the condensate trap are oxidized to carbon dioxide which is quantitatively collected in an evacuated vessel; a portion of the carbon dioxide is reduced to methane and measured by a flame ionization detector (FID). A portion of the sample collected in the gas sampling tank is injected into a gas chromatographic (GC) column to achieve separation of the nonmethane organics from carbon monoxide, carbon dioxide and methane; the nonmethane organics are oxidized to carbon dioxide, reduced to methane, and measured by a FID.

1.2 Applicability. This method is applicable to the measurement of total gaseous nonmethane organics in source emissions.

2. Apparatus

2.1 General. TGNMO sampling equipment can be constructed by a laboratory from commercially available components and

components fabricated in a machine shop. The primary components of the sampling system are a heated filter, condensate trap, flow control system, and gas sampling tank. (Figure 1). The primary components of the analytical system are an oxidation system for recovery of the sample from the condensate trap and a TGNMO analyzer. The TGNMO analyzer is a FID preceded by an oxidation catalyst, a reduction catalyst, and a GC column with backflush capability (Figure 2). The system for the removal and conditioning of the organics captured in the condensate trap consists of a heat source, oxidation catalyst, Non-Dispersive Infrared (NDIR) analyzer and an intermediate gas collection tank (Figure 3).

2.2 Sampling.

2.2.1 Probe. 1/8" stainless steel tubing heated to approximately 120°C.

2.2.2 Filter Holder. Stainless steel with a stainless steel or glass frit filter support and a Teflon gasket. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached at the outlet of the probe.

2.2.3 Filter Heating System. Any heating system capable of maintaining a temperature around the filter holder during sampling of 120 $\pm$ 14°C (248 $\pm$ 25° F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. A temperature gauge capable of measuring temperature to within

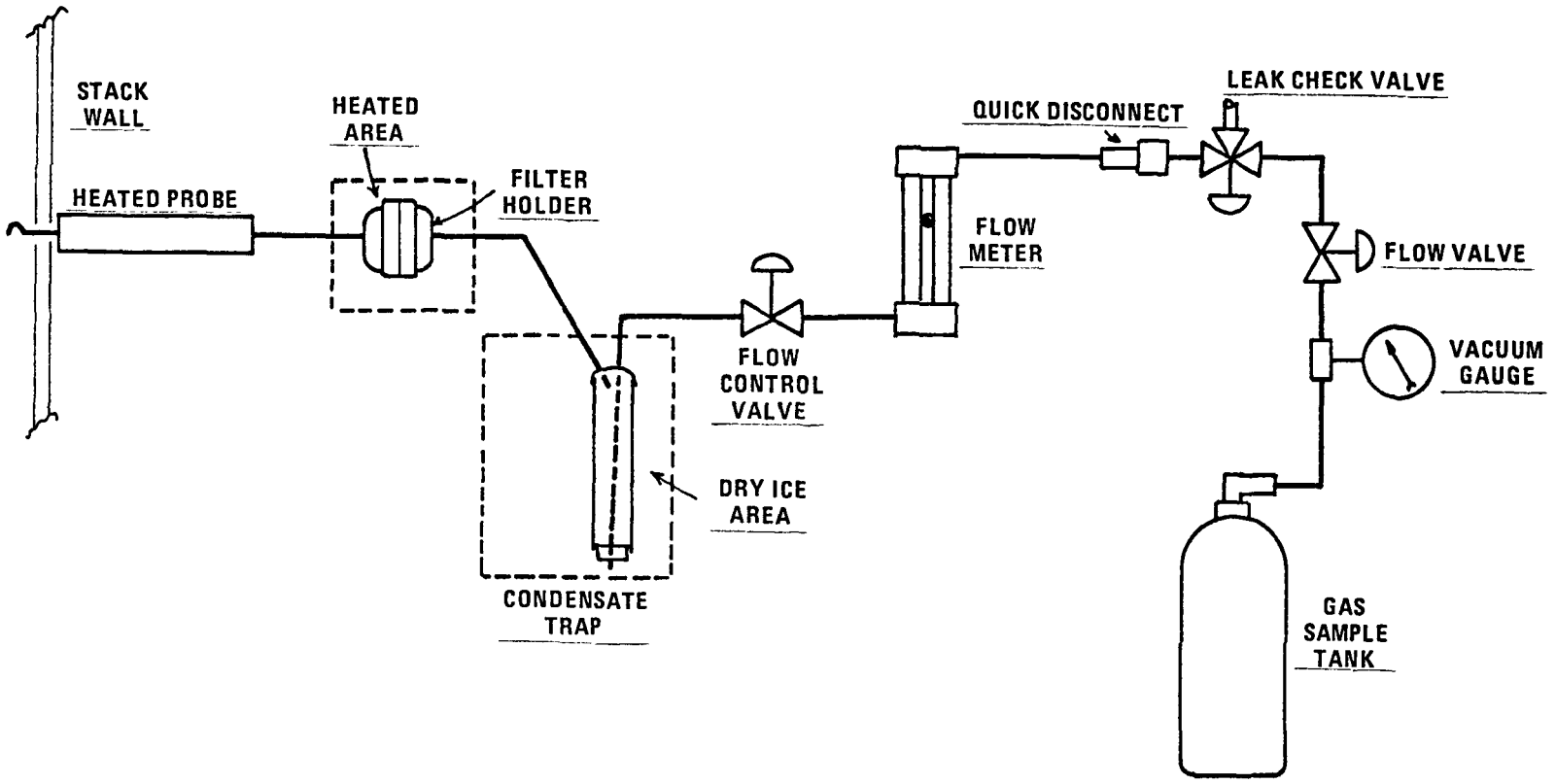


Figure 1. SAMPLING APPARATUS

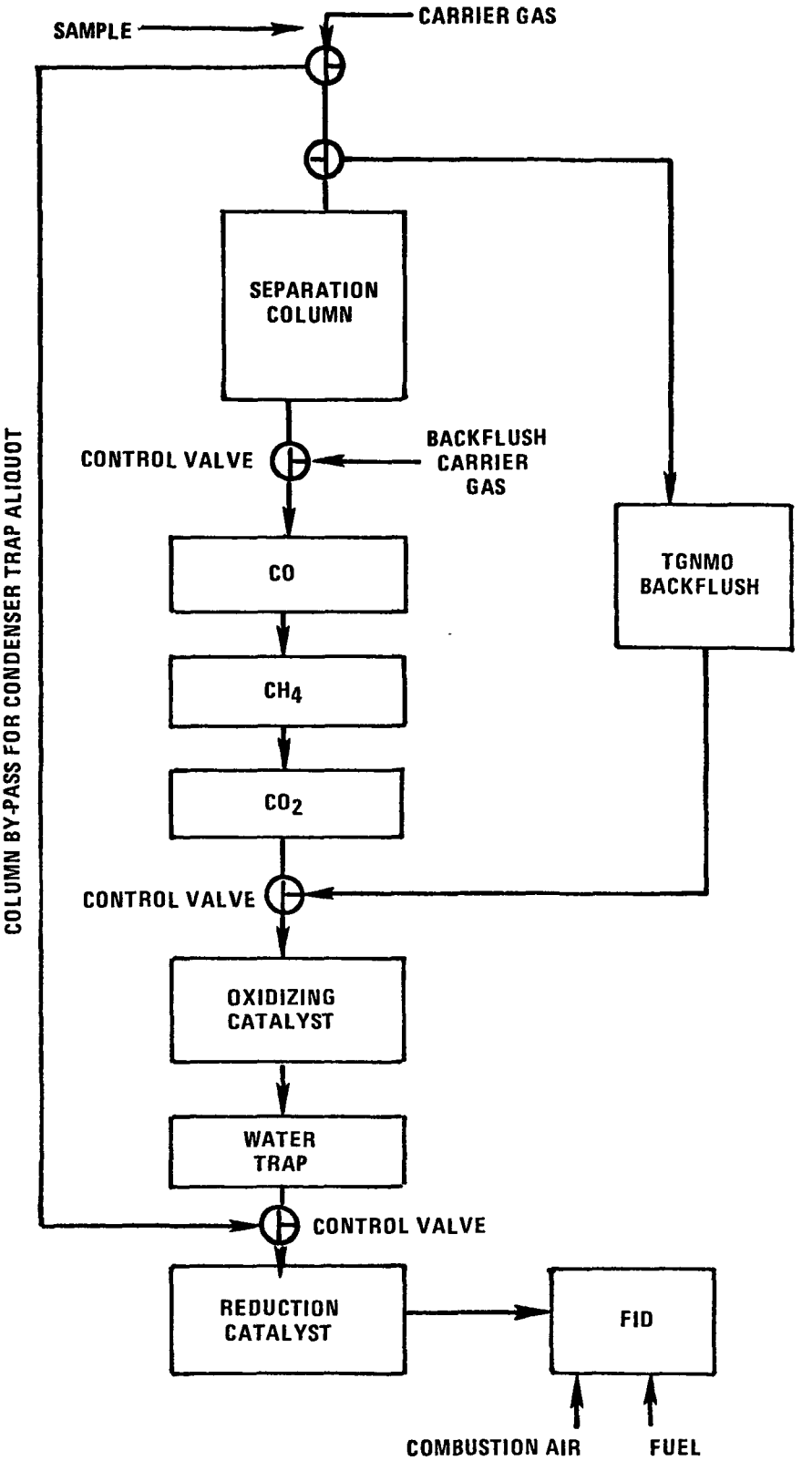
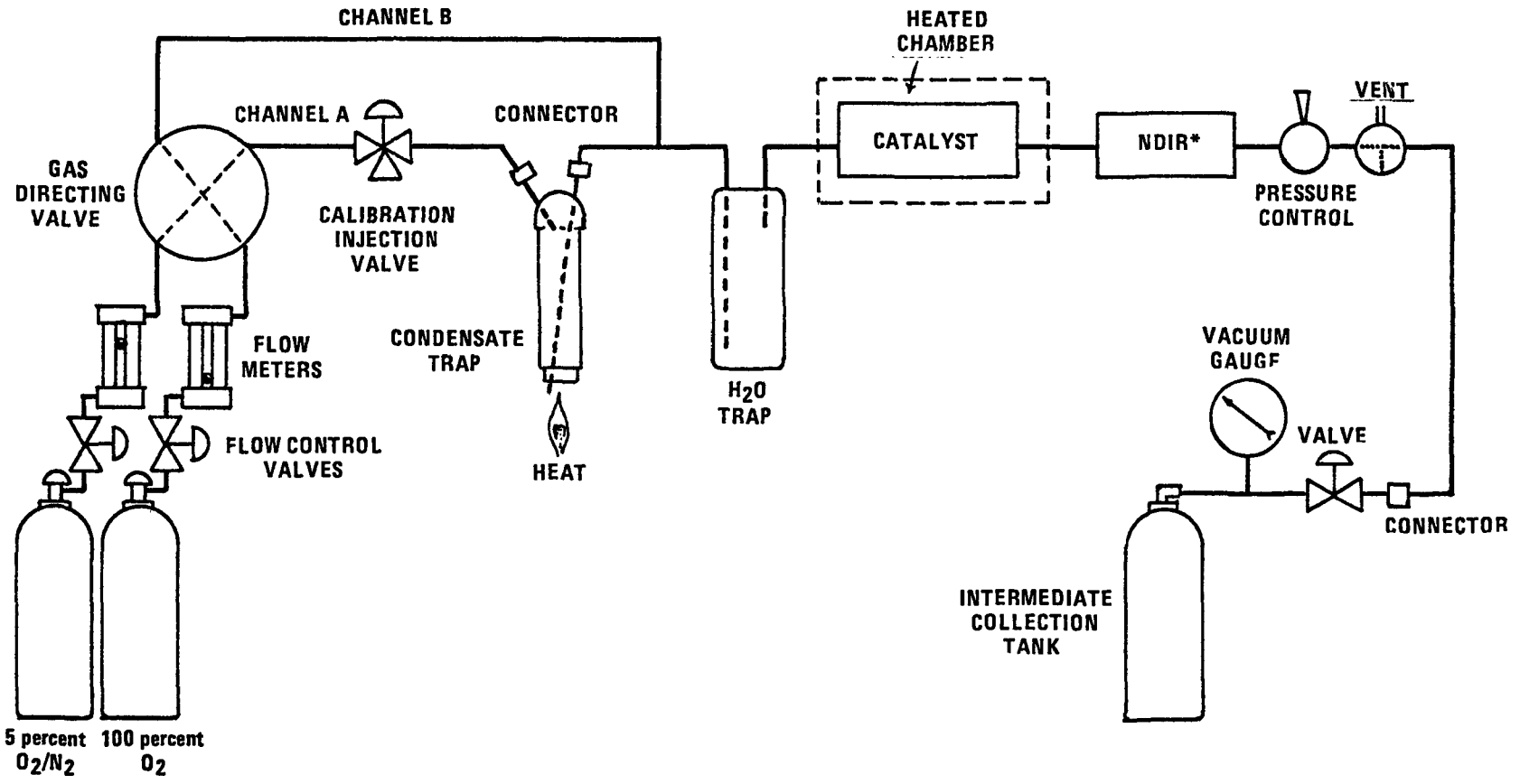


Figure 2. TOTAL GASEOUS NONMETHANE ORGANIC (TGNMO) ANALYZER SCHEMATIC



*FOR MONITORING PROGRESS OF COMBUSTION ONLY

Figure 3. CONDENSATE RECOVERY AND CONDITIONING APPARATUS

3° C (5.4° F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling.

2.2.4 Condensate Trap. The condensate trap shall be constructed of 316 stainless steel; construction details of a suitable trap are shown in Figure 4.

2.2.5 Flow Control System.

2.2.5.1 Needle Valve. To regulate sample gas flow rate.

2.2.5.2 Rate Meter. Rotameter, or equivalent capable of measuring flow rate to within ± 10 percent of the selected flow rate of about 80 cc/min. Other flow control systems capable of maintaining a constant sample rate of 80 cc/min ± 10 percent may be used subject to the approval of the Administrator.

2.2.6 Gas Collection Tank. Stainless steel or aluminum tank with a minimum volume of 6 liters. The tank is fitted with a vacuum gauge, a leakless valve, and a t-connector for conducting leak checks.

2.3 Analysis. For analysis, the following equipment is needed.

2.3.1 Condensate Recovery and Conditioning Apparatus (Figure 3).

2.3.1.1 Heat Source. A heat source sufficient to heat the condensate trap to a "cherry red" color. An electric muffle-type furnace or bunsen burner may be used.

2.3.1.2 Oxidizing Catalyst. A platinum and quartz catalyst constructed from a 44-inch length of 1/4" tubing of

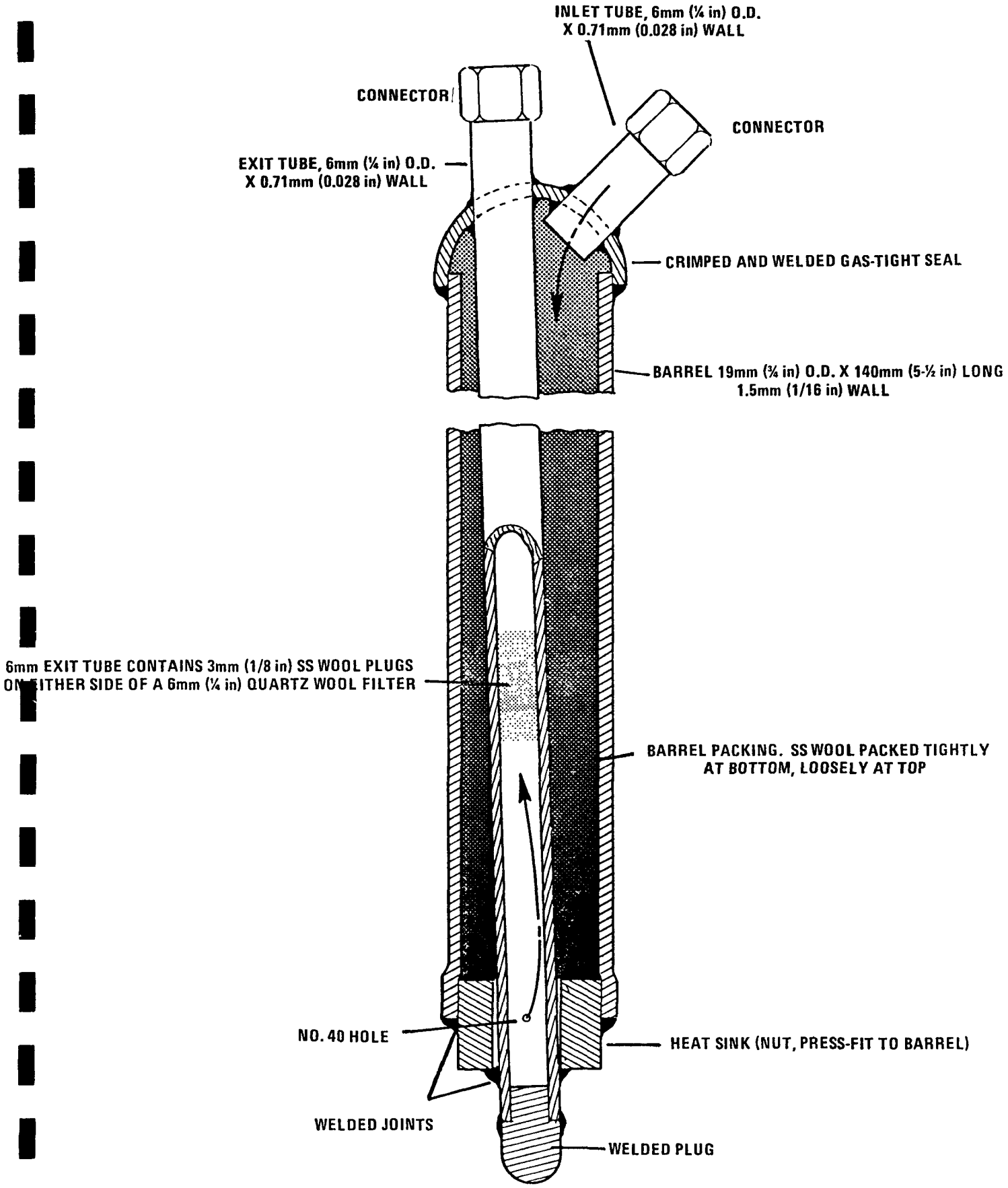


Figure 4. CONDENSATE TRAP[2]

70 percent Ni-30 percent Cr alloy packed as follows:

First 4 inches--empty.

Next 4 inches--8-10 mesh alumina coated with 0.5 percent finely divided platinum.

Next 28 inches--8 mesh quartz chips.

Last 8 inches--8-10 mesh alumina 0.5 percent platinum coated.

Other catalyst systems capable of meeting the catalyst efficiency criteria of this method (Section 4.4.2) may be used subject to the approval of the Administrator.

2.3.1.3 Water Trap. Any leak proof moisture trap capable of removing moisture from the gas stream may be used. A condensate trap designed according to the specifications of Figure 4 without packing in the exit tube will suffice.

2.3.1.4 NDIR Detector. Detector capable of indicating the CO_2 level in the zero to five percent range; required to monitor the combustion progress of the organic matter in the condensate trap.

2.3.1.5 Pressure Regulator. Stainless steel needle valve required to maintain the NDIR detector at a constant pressure.

2.3.1.6 Intermediate Collection Tank. Stainless steel or aluminum collection vessel. Tanks with nominal volumes of 2 and 6 liters are recommended. The end of the tank is fitted with a t-connector, vacuum gauge, and leakless valve.

2.3.1.7 Calibration Injection Port. Injection port valve and sample loop for injection of calibration standards required

to check the combustion efficiency of the condensate recovery system.

2.3.2 Total Gaseous Nonmethane Organic (TGNMO) Analyzer. Semicontinuous GC/FID analyzer capable of: (1) separating CO, CO_2, CH_4, and gaseous nonmethane organics, (2) oxidizing the nonmethane organic fraction to CO_2, reducing the CO_2 to methane, and quantifying the methane. The analyzer shall be demonstrated prior to initial use to be capable of proper separation, oxidation, reduction, and measurement. As a minimum, this demonstration shall include measurement of a known TGNMO concentration present in a mixture that also contains CH_4, CO, and CO_2. (see paragraph 4.4.1) In addition, the analyzer shall meet the following performance specifications:

2.3.2.1 Linearity. $\pm$ 5 percent of the expected value for each full scale setting up to the maximum percent absolute (methane or carbon equivalent) calibration point. The analyzer shall be demonstrated prior to initial use to meet this specification through a 5-point (minimum) calibration. There shall be at least one calibration point in each of the following ranges: 5-10, 50-100, 500-1,000, 5,000-10,000, and 40,000-100,000 ppm (methane or carbon equivalent). Certification of such demonstration by the manufacturer is acceptable. An additional linearity performance check (see Section 4.4.1.1) must be made before each use.

2.3.2.2 Zero Drift. One percent full scale per analysis of an emission test series.

2.3.2.3 Span Drift. One percent full scale per analysis of an emission test series.

2.3.2.4 The following components have been found to be acceptable for use in the TGNMO System:

2.3.2.4.1 Oxidation Catalyst. Type 316 stainless steel 0.25 inch OD tubing x 14 inches long packed with Hopcalite[1] 25 - 30 mesh; operated at 850° C.

2.3.2.4.2 Reduction Catalyst. Type 316 stainless steel 0.25 inch OD tubing x 7 inches long packed with 10 percent nickel on chromasorb W, 60-80 mesh; operated at 400° C. Method of preparation: 100 grams chromasorb W, 10 grams nickelous nitrate, 75 ml water, evaporated to dryness then heated in air for 4 hours to convert to nickel oxide. After packing the tubing, reduce overnight at 450° C and 30 ml/min H_2 to nickel metal.

2.3.2.5.3 Separation Column. Type 316 Stainless steel 0.125 inch OD tubing x 18 feet long packed with Porapak Q 60/80 mesh; operated isothermally at 80° F.

2.3.3 Mercury Manometer. U-tube mercury manometer capable of measuring pressure to within 1.0 mm Hg in the 0 - 900 mm range.

2.3.4 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 inch Hg).

3. Reagents

3.1 Sampling.

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[1]Mention of trade names or specific products does not constitute endorsement by the EPA.

3.1.1 Filter. Glass fiber filter without organic binder, exhibiting at least 99.95 percent efficiency ($\leq$ 0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D 2986-71. Test data from suppliers quality control program are sufficient for this purpose.

3.1.2 Crushed Dry Ice.

3.2 Analysis.

3.2.1 (TGNMO) Analyzer.

3.2.1.1 Carrier Gas. 5 percent O_2 in N_2 containing less than 1 ppm organics.

3.2.1.2 Fuel Gas. 40 percent hydrogen in nitrogen containing less than 1 ppm organics.

3.2.2 Condensate Recovery and Conditioning Apparatus.

3.2.2.1 Carrier Gas. 5 percent O_2 in N_2 containing less than 1 ppm organics.

3.2.2.2 Oxygen. Oxygen containing less than 1 ppm organics.

3.3 Calibration.

3.3.1 (TGNMO) Analyzer.

3.3.1.1 Calibration Gases (3). Gas mixture standards with known propane (C_3H_8) concentrations corresponding to ranges of 5-10 ppm, 50-10 percent and 20-25 percent methane or carbon equivalent are prepared and certified by a gas manufacturer. The mixture shall consist of C_3H_8, CO, CO_2, and CH_4 in nitrogen. The gas manufacturer must recommend a maximum shelf life for each cylinder so that the C_3H_8 concentration does not change

more than ± 5 percent from its certified value. The date of gas cylinder preparation, certified C_3H_8, CO, CO_2, and CH_4 concentrations and recommended maximum shelf life must be affixed to the cylinder before shipment from the gas manufacturer to the buyer. These gas mixture standards are to be used to prepare a chromatograph calibration curve as described in Section 4.4.1.1.

3.3.1.2 Span Gas. The calibration gas (Section 3.3.1.1) corresponding to 20 to 25 percent is used to span the analyzer.

3.3.1.3 Oxidation Catalyst Check. The calibration gas (Section 3.3.1.1) corresponding to 20 to 25 percent is used to check the oxidation catalyst.

3.3.1.4 Reduction Catalyst Check. A gas standard with a known concentration of 5 percent (nominal) CO_2 in nitrogen is used to check the reduction catalyst.

3.3.2 Condensate Recovery and Conditioning Apparatus. Gas mixture standards (2) with known propane (C_3H_8) concentrations in nitrogen corresponding to ranges of 5-10 ppm and 5-10 percent (methane or carbon equivalent) are prepared and certified by a gas manufacturer. These gas mixture standards are to be used to check the operation of the condensate trap oxidation system as described in Section 4.4.2.

4. Procedure

4.1 Sampling

4.1.1 Pretest Preparation. The sample tank shall be calibrated according to the procedure described in paragraph 4.4.3. Check filters visually against the light for irregularities,

flaws, or pinhole leaks. Either in the laboratory or in the field evacuate the sample tank to a vacuum of 755 mm mercury (measured by a mercury U-tube manometer). Record the temperature, barametric pressure, tank vacuum measured with the manometer, and the vacuum indicated on the tank gauge.

4.1.2 Assemble the system as shown in Figure 1. Immerse the condensate trap in dry ice and start the filter and probe heaters.

4.1.3 Leak check procedures.

4.1.3.1 Gas Sampling Tank Leak Check. Leak check the gas sampling tank immediately after the tank is evacuated. Once the tank is evacuated, allow the tank to sit for 30 minutes. The tank is acceptable if no change in tank vacuum (measured by the mercury manometer) is noted.

4.1.3.2 Pretest Leak Check. A pretest leak check is recommended, but not required. If the tester opts to conduct the pretest leak check, the following procedure is used. After the sampling train has been assembled (including cooling of condensate trap and heating of filter) plug the probe tip. Attach the vacuum line of the leak check apparatus (Figure 5) to the T-connector of the evacuated tank; open the valve on this connector (not the sample flow control valve to the evacuated tank) and evacuate the sample train to a vacuum of 625 mm Hg. Shut the valve on the pump side of the manometer and allow the sampling train to sit for 10 minutes. A leak rate in excess of 0.5 mm Hg for this 10 minute period is unacceptable. When the

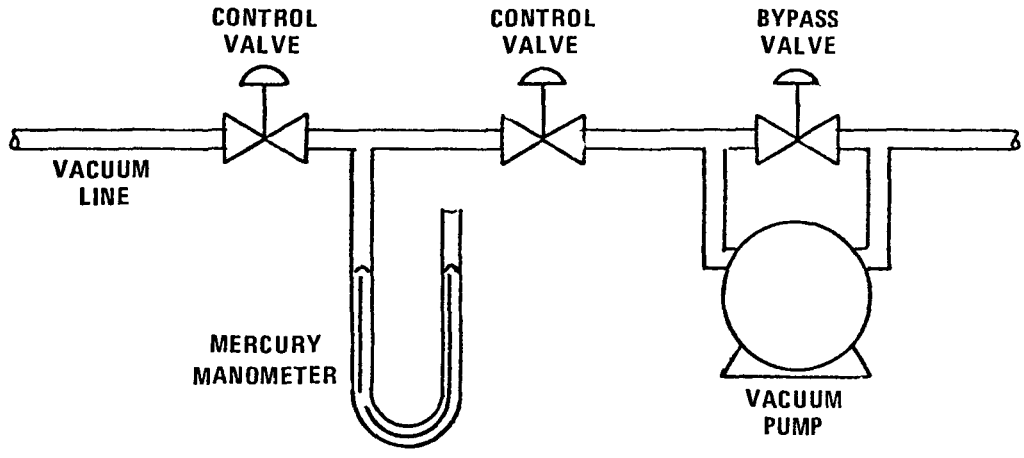


Figure 5. LEAK CHECK APPARATUS

leak check is completed, slowly release the vacuum in the train by unpluging the probe, close the T-connector valve, and plug this connector to assure a leak free system.

4.1.3.3 Post Test Leak Check. A leak check is mandatory at the conclusion of each test run. After sampling is completed, plug the end of the sampling probe and attach the vacuum line of the leak-check apparatus (Figure 5) to the evacuated tank t-connector. Assure that the flow valve to the evacuation pump (valve between manometer and pump) is closed. First open the t-connector valve to the manometer and then open the flow control valve to the evacuated tank. Record the clock time and tank vacuum. After 10 minutes note the tank vacuum. A leak rate in excess of 0.5 mm Hg for this ten minute period is unacceptable and the sampling run shall be voided. After completing the leak check, close the evacuated tank flow control valve and the t-connector flow control valve. Disconnect the leak check apparatus and plug the t-connector to assure a leakproof seal during shipping. Unplug the probe tip.

4.1.4 Sample Train Operation. Place the probe into the stack such that the probe tip is located at a pre-selected location. For stacks under negative pressure, assure that the sample port is sufficiently sealed to prevent leakage of ambient air around the probe. Record the clock time, sample tank gauge vacuum, and barometric pressure. Assure that the flow control needle valve is closed. Begin sampling by opening the evacuated tank flow valve all the way. Open the flow control needle valve until

the rotameter indicates the desired setting; maintain a constant flow rate (± 10 percent) throughout the duration of the sampling period. Record the gauge vacuum, rotameter setting, and filter temperature at 5 minute intervals. Select a total sample time greater than or equal to the minimum sampling time specified in the applicable subpart of the standard; end the sampling when this time period is reached or when a constant flow rate can no longer be maintained. When the sampling is completed, close the evacuated tank valve and remove the probe from the stack. Record the final readings. Conduct the post test leak check according to the procedures of paragraph 4.1.3.3.

If the sampling must be stopped before obtaining the minimum sampling time specified in the applicable subpart because a constant flow rate cannot be maintained, proceed as follows: After removing the probe from the stack, conduct the post test leak check. After the leak check is completed, remove the evacuated tank from the sampling train (without disconnecting other portions of the sampling train) and connect another evacuated tank to the sampling train. Proceed with the sampling; after the minimum total sampling time is exceeded, end the test.

4.2 Sample Recovery.

Disconnect the condensate trap at the filter and at the flow metering system. Tightly seal the ends of the condensate trap; keep the trap packed in dry ice until analysis is conducted. Seal the connection at the evacuated tank to assure a leak proof seal during shipping. After the evacuated tank has cooled to ambient

conditions, attach the U-tube manometer to the t-connector, open the valve, and record the tank vacuum, ambient temperature, barometric pressure, and indicated gauge vacuum. Close the flow valve and reseal the t-connector to assure a leak proof seal during shipping. Assure that the test run number is properly indentified on the condensate trap and evacuated tank(s).

4.3 Analysis

4.3.1 TGNMO Analyzer. Heat the catalysts to their operating temperatures and set the carrier gas and fuel flow rates. Conduct the calibration check required in paragraph 4.4.1.1 and the catalyst performance checks required in paragraph 4.4.1.2 prior to analyzing the test samples.

4.3.2 Condensate Trap. Return the condensate trap to the laboratory and hook it into the recovery and conditioning system (Figure 3). Set the oven for the oxidizing catalyst at 850° C and the trap heating furnace at 600° C. Set the gas directing valve to permit flow of 5 percent O_2/N_2 through channel A to the condensate trap at a rate of 80 cc/min; at the same time set the oxygen flow through channel B at 20 cc/min (1:4 ratio). After two minutes, switch the gas directing valve to permit the oxygen to flow via channel A directly through the condensate trap and the 5 percent O_2/N_2 carrier gas to flow through channel B. When the NDIR indicates that CO_2 is no longer being emitted from the combustion system, shut off the collection flask from the system and cease combustion. Record the collection flask pressure after combustion is completed (P_i) and then pressurize the flask to 860 mm Hg (nominal) with nitrogen and record the final pressure

(P_f). Remove a syringe sample from the flask and inject this into the TGNMO analyzer. Record the analyzer response (ppm C) for triplicate samples.

4.3.3 Gas Sampling Tank. Using a U-tube mercury manometer, record the tank vacuum (P_t). Pressurize the tank with nitrogen and record the final tank pressure (P_{t_f}), temperature and barometric pressure. Remove a syringe sample from the tank and inject this into the TGNMO analyzer. Record the analyzer response (ppm C) for the non-methane organic fraction for triplicate samples.

4.4 Calibration. Maintain a record of performance of each item.

4.4.1 TGNMO Analyzer.

4.4.1.1 Calibration Curve. Determine the linearity of the analyzer for TGNMO as follows: With the signal attenuation at the most sensitive setting, introduce zero gas and adjust the respective zeroing controls to indicate a reading of less than 1 percent of full scale. With the signal attenuation at the least sensitive setting, introduce the span gas and adjust the span control to indicate the proper value on the analyzer readout. Repeat these two steps until adjustments are no longer necessary. Calculate a predicted response for the 5-10 ppm calibration gas. Introduce that calibration gas and note the value obtained. If this value is not within $\pm$ 5 percent of its predicted value, then the analyzer may need repairs, or one or both of the calibration gases may need replacement. In any

event, this linearity performance specification shall be met before the analyzer is placed in actual use.

4.4.1.2 Catalyst Performance Check. These checks should be performed on a frequency established by the amount of use of the analyzer and the nature of the organic emissions to which it is exposed. To confirm that the oxidation catalyst is functioning in the correct manner, the operator must turn off or bypass the reduction catalyst while operating the analyzer in an otherwise normal fashion. Inject the calibration gas (paragraph 3.3.1.3) into the system. If oxidation is adequate, the only gas that will then reach the detector will be CO_2, to which the FID has no response. If a response is noted, the oxidation catalyst must be replaced. To confirm the proper operation of the reduction catalyst, inject a sample of the CO_2 calibration gas (Section 3.3.1.4) into the system. If the CO_2 is not reduced to CH_4 as it should be, then the reduction catalyst must be replaced or regenerated.

4.4.2 Condensate Trap Oxidation Catalyst. Inject syringe samples of the calibration gases listed in Section 3.3.2 into the sample port of the condensate trap combustion system (Figure 3). Proceed with a normal analysis (i.e., collection of the CO_2 in the flask followed by analysis of triplicate aliquots using the TGNMO analyzer) and compare results to the actual concentration. Repair the system if the results (average of triplicate aliquots) deviate by greater than $\pm$ 5 percent from the calibration gas value.

4.4.3 Gas Sampling Tank. The volume of the gas sampling tanks used must be determined. Prior to putting each tank in

service, determine the tank volume by weighing the tanks empty and then filled with water; weigh to the nearest 0.5 gm and record the results.

4.4.4 Intermediate Collection Flask. The volume of the intermediate collection flasks used to collect CO_2 during the analysis of the condensate traps must be determined. Prior to putting each flask in service, determine the volume by weighing the flasks empty and then filled with water; weigh to the nearest 0.5 gm and record the results.

4.4.5 Condensate Trap Leak Check. Prior to each use, check each condensate trap for leaks by pressurizing with N_2 to approximately 50 psig and immersing in water.

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

5. Calculations

5.1 Sample Volume. For each test run calculate the gas volume sampled:

$$V_s = 0.36\ V\left(\frac{P_t}{T_t} - \frac{P_{t_i}}{T_{t_i}}\right)$$

5.2 Noncondensible TGNMO. For each collection tank, determine the concentration of TGNMO (ppm C):

$$C = 3 \times \frac{P_{t_f}}{P_t} \times \frac{T_t}{T_{t_f}} \times \sum_{j=1}^{m} C_{p_j}$$

5.3 Condensible TGNMO. For each condensate trap determine the concentration of TGNMO (ppm C):

$$C_c = \frac{3 \times V_f \times P_f}{V_s \times P_i} \times \sum_{k=1}^{n} C_{cp_k}$$

5.4 Total Gaseous Nonmethane Organics (TGNMO). To determine the TGNMO concentration for each test run, use the following equation:

$$C_t = C + C_c$$

5.5 Control Device Efficiency. To determine the TGNMO control device efficiency for each test run, use the following equation:

$$E = \frac{C_{ti} - C_{to}}{C_{ti}} \times 100$$

where:

C = Noncondensible TGNMO calculated concentration, ppm carbon equivalent.

C_p = TGNMO analyzer measured concentration for gas collection tank, ppm propane.

C_c = Condensible TGNMO (condensate trap) calculated concentration, ppm carbon equivalent.

C_{cp} = TGNMO analyzer measured concentration for intermediate collection flask, ppm propane.

C_t = Total gaseous nonmethane organic (TGNMO), ppm carbon equivalent.

C_{to} = TGNMO at control device outlet, ppm carbon equivalent.

C_{ti} = TGNMO at control device inlet, ppm carbon equivalent.

E = Control device efficiency, percent.

P_f = Final pressure of intermediate collection flask (nominal 860 mm Hg.), mm Hg, absolute.

P_i = Pressure of intermediate collection flask at completion of combustion, mm Hg, absolute.

P_{t_i} = Gas sample tank pressure prior to sampling, mm Hg, absolute.

P_t = Gas sample tank pressure after sampling, but prior to pressurizing, mm Hg, absolute.

P_{t_f} = Final gas sample tank pressure after pressurizing, mm Hg, absolute.

T_{t_i} = Gas sample tank temperature prior to sampling, °K.

T_t = Gas sample tank temperature at completion of sampling, °K.

T_{t_f} = Gas sample tank temperature after pressurizing, °K.

V = Gas collection tank volume, M^3

V_f = Intermediate collection tank volume, M^3

V_s = Gas volume sampled, dscm

m = Total number of injections of non-condensible TGNMO during analysis (where j = injection number, 1 . . . m)

n = Total number of injections of condensible TGNMO during analysis (where k = injection number, 1 . . . n)

0.36 = 273°K/760 mm Hg

Standard Conditions = Dry, 760 mm Hg, 273°K.

6. Bibliography

6.1 Albert E. Salo, Samuel Witz, and Robert D. MacPhee. "Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A comparison of Infrared with Flame Ionization Detectors." Presented at the 68th Annual Meeting of the Air Pollution Control Association, Boston, Ma. Paper No. 75-33.2. June 15-20, 1975.

6.2 Albert E. Salo, William L. Oaks, Robert D. MacPhee. "Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control." Presented at the 67th Annual Meeting of the Air Pollution Control Association, Denver, Colorado. Paper No. 74-190 June 9-13, 1974.

ATTACHMENT 3. ALTERNATE TEST METHOD FOR DIRECT MEASUREMENT OF TOTAL GASEOUS ORGANIC COMPOUNDS USING A FLAME IONIZATION ANALYZER

INTRODUCTION

Performance of this method should not be attempted by persons unfamiliar with the performance characteristics of the flame ionization detector, nor by those who are unfamiliar with source sampling.

1. Principle and Applicability

1.1 Principle. The sample is drawn from the source, through a heated sample line and glass fiber filter to a flame ionization analyzer (FIA). Ions formed in the combustion of a specific hydrocarbon compound in a H_2 - O_2 flame establish a current that is proportional to the mass flow rate of that hydrocarbon to the flame. This current is collected at two polarized electrodes, and is read out on a potentiometric recorder and compared with a calibration curve based on propane (C_3H_8), or an organic solvent, as appropriate. The results are reported as equivalents of methane (CH_4) or carbon, or in terms of an organic solvent.

1.2 Applicability. This method is applicable for the determination of the true carbon mass concentration, and/or an indicated volume or mass concentration (expressed in terms of carbon or of an assumed organic compound, e.g., methane equivalent) of gaseous organic compounds present in an emission stream. It can also be used to measure the mass concentration of an organic solvent if stable mass standards of the solvent can be generated.

The measurement will not exclude methane, so a supplemental measurement of methane may be necessary.

2. Range and Sensitivity

2.1 Range. Signal attenuators shall be available so that a minimum signal response of 10 percent of full scale can be produced when analyzing calibration gas or sample.

2.2 Sensitivity. The detector sensitivity shall be equal to or better than 2.0 percent of the full scale setting, with a minimum full scale setting of 10 ppm (methane or carbon equivalent).

3. Interferences

3.1 Nonorganic Gases. There is no response to nitrogen, carbon monoxide, carbon dioxide, or water vapor. however, the analyzer response to organics will be affected by the composition of the background or carrier gas. It is, therefore, required that the calibration gases be contained in air, which is most likely to be the same carrier gas as that of the actual sample.

Investigation of a reported oxygen synergism[2] has shown that a 40/60 mixed fuel (40 percent H_2, 60 percent He) is required if the oxygen content of the emission stream varies more than a few percent from its mean value. Mixed fuel will also be required if the oxygen content of the emission stream varies more than a few percent from the oxygen content of the calibration gases.

3.2 Organic compounds. Acetylenic compounds give a slightly higher response than aliphatic compounds. Carbon atoms bound to oxygen, nitrogen, or halogens give a reduced or zero response.

Table 1[3] illustrates these effects in terms of the relative response of one FIA to various hydrocarbons. The response is shown as effective carbon number (ECN), as follows:

$$ECN = \frac{\text{Instrument response caused by atom of given type}}{\text{Instrument response caused by aliphatic carbon atom}}$$

These values are true for one mode of operation of a specific detector under specific conditions (e.g., mixed N_2, H_2 fuel). It has been reported that these numbers may vary widely for different operating conditions and for different detectors. Variations of as much as 25 percent have been observed in studies of the types of organics associated with automotive emissions. The variation was observed to decrease with decreasing sample flow rate, but with an accompanying decrease in sensitivity.[7]

TABLE 1. APPROXIMATE EFFECTIVE CARBON NUMBERS (FROM BECKMAN INSTRUMENTS)

Type of Atom	Occurrence	Effective Carbon Number
Carbon	In Aliphatic Compound	+1.0
Carbon	In Aromatic Compound	+1.0
Carbon	In Olefinic Compound	+0.95
Carbon	In Acetylenic Compound	+1.30
Carbon	In Carbonyl Radical	0.0
Carbon	In Nitrite	+0.3
Oxygen	In Ether	-1.0

TABLE 1. APPROXIMATE EFFECTIVE CARBON NUMBERS
(FROM BECKMAN INSTRUMENTS)
(Continued)

Type of Atom	Occurrence	Effective Carbon Number
Oxygen	In Primary Alcohol	-0.6
Oxygen	In Secondary Alcohol	-0.75
Oxygen	In Tertiary Alcohol, Ester	-0.25
Chlorine	As two or more chlorine atoms on single aliphatic carbon atom	-0.12 each
Chlorine	In Olefinic Carbon Atom	+0.05
Nitrogen	In Amine	Value similar to that for oxygen atom in corresponding alcohol

From this information it can be seen that the accuracy of this method for a given source will be largely dependent on the particular makeup of organic emissions from the source.

3.3 Other effects. Significant changes in viscosity of the emission gas from that of the calibration gas will affect the mass rate of organics to the detector. If this phenomena is expected to occur, a corrective technique must be devised.

If the instrument is calibrated with organic solvent standards, and then used to measure emissions of that solvent, their response variations have been calibrated out.

4. Apparatus

4.1 Commercially available heated FIA. The analyzer should

be demonstrated, preferably by the manufacturer, or his representative, to meet or exceed manufacturer's specifications and those described in this method. The entire sampling and analysis system as encountered by gaseous organics must be capable of being maintained in the temperature range of 350 to 440°F, or less, consistent with the emission regulation.

4.2 Sample conditioning or interface system. Probe with filter, Teflon* sample line, Teflon-coated diaphragm pump or stainless steel bellows pump and Teflon flow control valves, capable of being maintained in the temperature range of 350 to 400°F, or less, consistent with the emission regulation.

4.3 Potentiometric Recorder (optional). Strip chart recorder with a voltage output compatible with the FIA.

5. Reagents

5.1 Fuel. A hydrogen and helium mixture containing less than 2 ppm organics (methane or carbon equivalent).

5.2 Combustion Air. High purity air with less than 2 ppm organics (methane or carbon equivalent). Required only if the emission stream does not contain sufficient oxygen.

5.3 Zero Gas. Less than 0.1 ppm organics (methane or carbon equivalent).

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

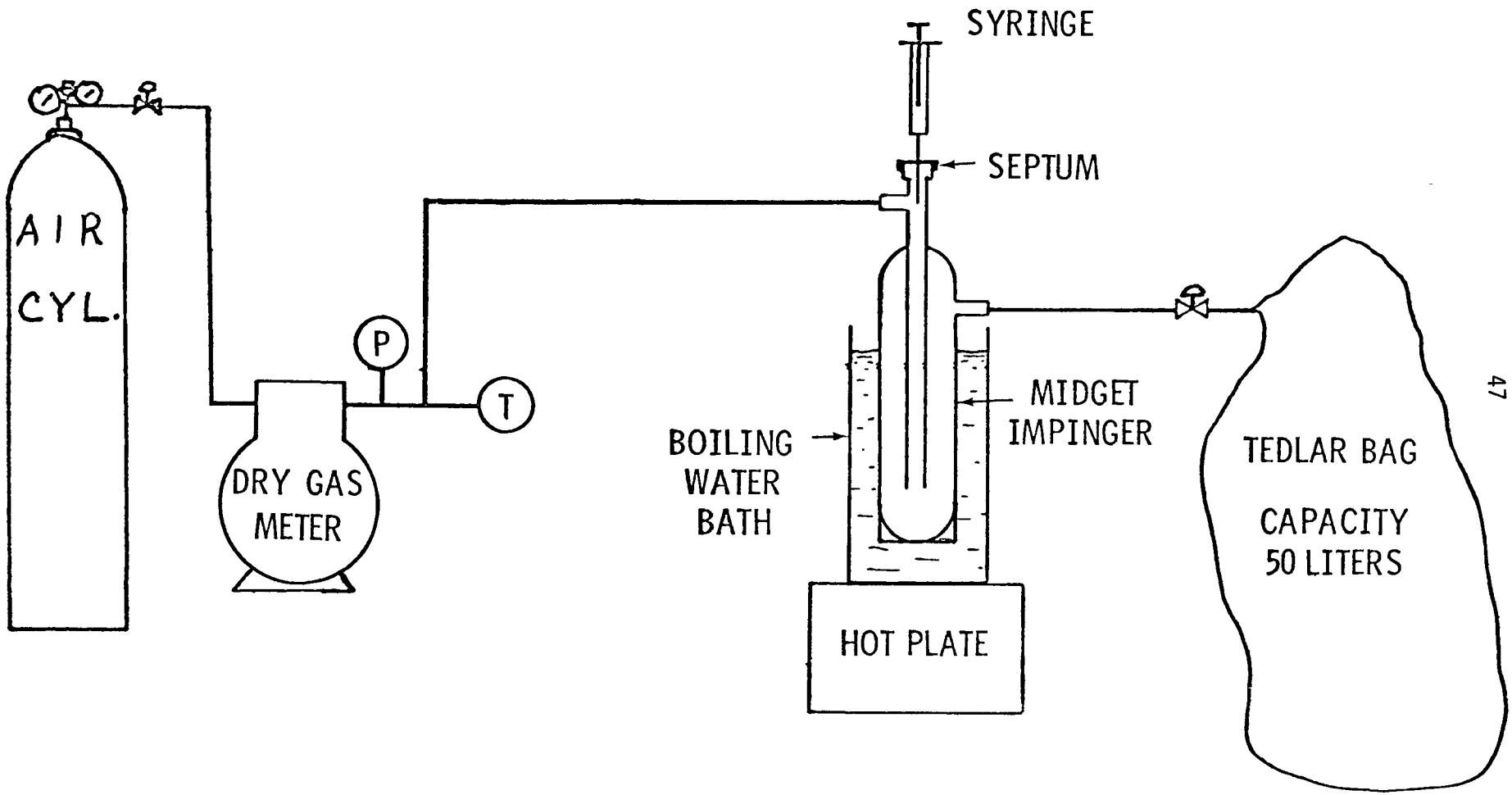


FIGURE 2. PREPARATION OF SOLVENT STANDARDS

5.4 Calibration Gases (2). Gas mixture standards with known concentrations corresponding to ranges of 5 to 10 ppm and 5 to 10 percent (methane or carbon equivalent) are prepared and certified by a gas manufacturer. The mixture will normally consist of C_3H_8 in air. Other organic(s) can be used, if appropriate. The gas manufacturer must recommend a maximum shelf life for each cylinder so that the concentration does not change more than $\pm$ 5 percent from the certified value. The date of gas cylinder preparation, certified propane concentration and recommended maximum shelf life must be affixed to the cylinder before shipment from the gas manufacturer to the buyer. These gas mixture standards are to be used to prepare a calibration curve as described in Section 7.2.

5.5 Span Gas. The calibration gas corresponding to 5 to 10 percent (methane or carbon equivalent) is used to span the analyzer.

5.6 Organic Solvent. Either a sample obtained from the solvent source, or a sample distilled from paint, ink, etc. in accordance with ASTM Procedure D3272-73T. Required only if unaltered solvent emissions are being measured, mass calculations in terms of the solvent are necessary, and the relative response factor of the FIA to the solvent is unknown.

6. System Performance Specifications

6.1 Linearity. $\pm$ 5 percent of the expected value for full scale settings up to the maximum percent absolute (methane or

carbon equivalent) calibration point. The analyzer shall be demonstrated prior to initial use to meet this specification through a 5-point (minimum) calibration. There shall be at least one calibration point in each of the following ranges: 5-10, 50-100, 500-1,000, 5,000-10,000, and 50,000-100,000 ppm (methane or carbon equivalent). Certification of such demonstration by the manufacturer is acceptable. An additional linearity performance check (see Section 7.2.1) must be made before each use.

6.2 Zero Drift. One percent full scale per test period.

6.3 Span Drift. One percent full scale per test period.

7. Procedure

7.1 Sampling.

7.1.1 Assemble the systems as shown in Figure 1. Locate the FIA in a suitably protected environment. Take particular care that sample will be introduced to the FIA under the same conditions of pressure and flow rates as are used in calibration. For specific operating instructions for the FID, refer to manufacturer's manual.

7.1.2 Adjust the sample conditioning and analyzer heating systems to provide a temperature of 350 to 400°F, or less, consistent with the emission regulation, and allow the systems to warm up.

7.1.3 Perform a leak check as follows before sampling. Recheck to confirm that all fittings are tight. With the sample

probe plugged, open the flow control valve and the excess sample bleed valve. Use leak detection fluid or immerse the tubing leading from the bleed valve in a jar of water to check that sample flow has ceased. At the conclusion of the sampling tests, recheck for leaks.

7.1.4 Begin Actual Sampling. Set the signal attenuation to yield a minimum response of 10 percent of full scale unless the stack concentration is less than 1 ppm. Adjust the flow and bleed valves to minimize sample line residence time. Compare instrument readings with the calibration curve to obtain emission concentrations based on the calibration gas.

7.1.5 At the conclusion of the sampling tests, but at least once every day, introduce zero and span gases to the analyzer to determine zero and span drifts. If the analyzer has drifted beyond the allowable performance specification, the tests shall be considered invalid.

7.2 Calibration and Solvent Standards.

7.2.1 Calibration Curve. Maintain a record of performance of each item. Determine the linearity of the analyzer as follows: With the signal attenuation at the most sensitive setting, introduce zero gas and adjust the respective zeroing controls to indiate a reading of less than 1 percent of full scale. With the signal attenuation at the least sensitive setting, introduce the span gas and adjust the span control to indicate the proper value on the analyzer readout. Repeat these

two steps until adjustments are no longer necessary. Calculate a predicted response for the 5 to 10 ppm calibration gas. Introduce that calibration gas and note the value obtained. If the value is not within ± 5 percent of its predicted value, then the analyzer may need repairs, or one or both of the calibration gases may need replacement. In any event, this linearity performance specification shall be met before the analyzer is placed in actual use.

7.2.2 Preparation of Solvent Standard Gas Mixtures. (Optional--see Sections 1.2 and 5.6). Assemble the apparatus shown in Figure 2. Evacuate a 50-liter Tedlar or aluminized Mylar bag that has passed a leak check (described in Section 7.2.2.1) and meter in about 50 liters of air. Measure the barometric pressure, the relative pressure at the dry gas meter, and the temperature at the dry gas meter. While the bag is filling use the 10 µl syringe to inject 10 µl of the solvent through the septum on top of the impinger. This gives a concentration of approximately 200 µg/liter. In a like manner, use the other syringe to prepare dilutions having approximately 40 and 20 µg/liter concentrations. To calculate the specific concentrations, refer to Section 8.1. These gas mixture standards may be used for a few days from the date of preparation, as determined by repetitive analysis for concentration degradation. (Caution: Contamination may be a problem when a bag is reused if the new gas mixture standard is a lower concentration than the previous gas mixture standard.)

7.2.2.1 Solvent Standards Bag Leak Checks. While performance of this section is required subsequent to bag use, it is also advised that it be performed prior to bag use. After each use, make sure a bag did not develop leaks as follows: to leak check, connect a water manometer and pressurize the bag to 5-10 cm H_2O (2-4 in. H_2O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. Also, check the rigid container for leaks in this manner. (Note: an alternative leak check method is to pressurize the bag to 5-10 cm H_2O or 2-4 in. H_2O and allow to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

8. Calculations

All measurements or calculations must be corrected for CH_4, if required by the emission regulation.

8.1 Carbon or Surrogate Organic Compound Concentration.

8.1.1 Volume concentration [ppm]. To determine emission concentrations of total gaseous organics (wet basis) on a CH_4 or carbon equivalent basis, multiply the recorded emission values by the number of carbon atoms in a molecule of calibration gas. In some instances it will be required to report emissions on the basis of the calibration gas, in which case no calculations are necessary.

8.1.2 Mass concentration [mg/m^3]. To convert volume concentration to mass concentration, proceed as follows:

8.1.2.1 Establish Standard Conditions. Find the volume occupied by 1 mg. mole of ideal gas at these conditions. Then find the number of mg. moles in 1 m^3 (at saturation).

8.1.2.2 Determine the molecular weight of the assumed organic compound in which the emission is to be expressed.

8.1.2.3 Use the values obtained in 8.1.2.1 and 8.1.2.2 to determine the mass concentration (mg/m^3) at saturation. Divide this number by 10^6 to find the mg/m^3 equivalent to 1 ppm.

8.1.2.4 Multiply the result obtained in 8.1.2.3 by the volume concentration obtained in 8.1.1. The result is the mass concentration expressed in terms of the compound whose molecular weight was determined in 8.1.2.2.

8.2 Organic Solvent Concentration

8.2.1 Solvent Standards Concentrations. Calculate each solvent standard concentration prepared in accordance with Section 7.2.1.2 as follows:

$$C_c = \frac{B(d.\ \frac{mg}{\mu l})\ \frac{10^3\ \mu g}{mg}}{V_m\ Y\ \frac{293}{T_m}\ \frac{P_m}{760}} \qquad \text{Equation 1}$$

where:

C_c = Solvent standard concentration, µg/l.

B = Number of µl of solvent injected.

V_m = Gas volume measured by dry gas meter in liters.

Y = Dry gas meter, calibration factor.

P_m = Absolute pressure of the dry gas meter, mm Hg.

T_m = Absolute temperature of the dry gas meter, °A.

d. = Density of the solvent at 293°A.

8.2.2 Solvent Emission Concentrations The emission values in µg/ml are taken from the solvent standards response curve. No further calculations are required.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

This document discusses the rationale of total volatile organics stationary source emission measurement through the determination of organic carbon mass concentration. A conceptual approach for writing emission regulations in terms of volatile organic carbon is recommended, and drafts of two specific test methods are presented for regulation implementation. The methods are the measurement of total gaseous nonmethane organics as carbon by the chromatographic oxidation/reduction procedure, and the relative organic measurement derived by direct application of the flame ionization analyzer.

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