

CIA Historical Records Policy Board which acts as the senior corporate board for the Agency. The record compiled (the request, the memoranda filed by the originator and interested parties, and the previous decision(s)) as well as any memorandum of law or policy the referent desires to be considered, shall be certified by the Executive Secretary of the Agency Release Panel and shall constitute the official record of the proceedings and must be included in any subsequent filings. In such cases, the factors to be determined as specified in 32 CFR 1909.14(a) will be considered by the Board de novo and that decision shall be final.

#### § 1909.17 Notification of decision.

The Coordinator shall inform the requester of the decision of the Agency Release Panel or the Historical Records Policy Board within ten (10) days of the decision and, if favorable, shall manage the access for such period as deemed required but in no event for more than two (2) years unless renewed by the Panel or Board in accordance with the requirements of 32 CFR 1909.14(a).

#### § 1909.18 Termination of access.

The Coordinator shall cancel any authorization whenever the Director of Personnel Security cancels the security clearance of a requester (or research associate, if any) or whenever the Agency Release Panel determines that continued access would not be in compliance with one or more of the requirements of 32 CFR 1909.14(a).

[FR Doc. 97-14883 Filed 6-13-97; 8:45 am]

BILLING CODE 6310-02-M

## ENVIRONMENTAL PROTECTION AGENCY

### 40 CFR Part 51

[FRL-5836-1]

RIN 2060-AF02

### Preparation, Adoption, and Submittal of State Implementation Plans; Appendix M, Test Methods 204, 204A-204F

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule.

**SUMMARY:** This rule adds seven methods to Appendix M of 40 CFR Part 51 for capture efficiency (CE) testing to assist States in adopting enforceable CE measurement protocols into their State implementation plans (SIP's) for ozone. These final methods, in conjunction with the protocols, would also improve

EPA's ability to enforce State regulations to reduce volatile organic compounds (VOC) emissions in ozone nonattainment areas.

**EFFECTIVE DATE:** These methods are effective June 16, 1997.

**ADDRESSES:** *Docket.* A Docket A-91-70, containing materials relevant to this rulemaking, is available for public inspection and copying between 8:00 a.m.-5:30 p.m., Monday through Friday, at the EPA's Air Docket Section Mail Code: 6102, Room M-1500, Waterside Mall (ground floor), 401 M Street, S.W., Washington D.C. 20460. A reasonable fee may be charged for copying.

#### FOR FURTHER INFORMATION CONTACT:

Candace Sorrell, Source Characterization Group A (MD-19), Emissions, Monitoring, and Analysis Division, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, telephone (919) 541-1064.

#### SUPPLEMENTARY INFORMATION:

##### I. The Rulemaking

This rulemaking adds seven methods for measuring CE to Appendix M of 40 CFR Part 51 to provide methods that States can use in their SIP's.

##### II. Public Participation

The proposed rulemaking was published in the **Federal Register** (FR) on August 2, 1995 (60 FR 39297).

The opportunity to hold a public hearing on August 30, 1995 at 10 a.m. was presented in the proposal notice, but no one desired to make an oral presentation. The public comment period was from August 2, 1995 to October 2, 1995.

##### III. Electronic Access

The background information document for the promulgated test methods is available on the Technology Transfer Network (TTN) on the EPA's electronic bulletin boards. The document is entitled "Summary of Comments and Responses for Methods 204, 204A-F." If necessary, a limited number of copies are available from Candace Sorrell, MD-19, U.S. EPA, Research Triangle Park, North Carolina 27711, telephone number (919) 541-1064.

##### IV. Significant Comments and Changes to the Proposed Rulemaking

Six comment letters were received from the proposal rulemaking. A detailed discussion of these comments is contained in the background document entitled "Summary of Comments and Responses for Methods 204, 204A-F," which is referred to in

the **SUPPLEMENTARY INFORMATION** section of this preamble. The major comments raised in these letters and the Agency's responses follow.

One commenter points out that even though Methods 204B and 204C measure the same parameter, captured VOC stream, the applicability sections of the methods were not consistent with respect to what type of material balance is permissible.

The EPA reviewed the applicability section for both methods and determined that there was an error in Method 204B. Method 204B is intended to be used only in a gas/gas protocol, not in a liquid/gas protocol. The method has been revised to correct this error.

One commenter suggests for Method 204D, section 8.2.4, and Method 204E, section 8.4, that EPA make it explicit that if on site gas chromatography (GC) is used as an alternative to flame ionization analyzers (FIA) than GC must also be used to measure the VOC concentration of the other gas or liquid streams.

The Agency agrees that further explanation is needed to explain that if a facility is conducting a gas/gas test and chooses to use the alternative GC procedure, it must use the GC procedure for both the captured and fugitive stream. If a facility wishes to conduct a liquid/gas test using GC, the facility must use Method 204F for the liquid stream. A GC is not an acceptable alternative to the FIA in Method 204A.

Another commenter suggests that Figure 204-1 of Method 204 be expanded to address capture efficiencies less than 80 percent since lower values are allowed in the current Reasonably Available Control Technology (RACT) rules.

The EPA agrees that further guidance is needed and has added an equation to section 7.2 to help in estimating the ventilation rate at different capture efficiencies.

Three commenters mention that Method 204A, section 11, the estimated uncertainty of 12 percent for the VOC fraction seemed too high.

The EPA went back and reviewed the method evaluation report and discovered that the 12 percent is an error. The estimated uncertainty for this method is 4.0 percent. The method has been revised to correct this error.

Two commenters note that several references in Method 204, sections 5.5 and 6.1, were incorrect.

The EPA agrees that several references in those sections are incorrect. The method has been revised to correct these errors.

A commenter suggests that section 8.4 of Method 204 be revised to be consistent with the Aerospace NESHAP concerning the verification of air flow direction.

The EPA agrees with the comment and the method has been revised to reflect these changes.

One commenter feels that dilutions systems calibrated using Method 205 should be allowed without approval of the Administrator in Methods 204A–E, section 5.1 and Method 204F, section 5.3.

The EPA agrees that calibration gas can be prepared using dilution systems calibrated using Method 205 without approval of the Administrator and the methods have been revised.

A commenter requested that Methods 204A–204F be revised to not automatically invalidate the CE results if the drift check is in excess of the proposed 3 percent calibration drift requirement. In such situations the method should allow the FIA to be recalibrated and whichever calibration results in the “worst case” results be reported.

The EPA agrees with the comment and the methods have been revised.

One commenter suggests that Methods 204A–E, section 5.1.1 and Method 204F, section 5.3.1, be revised to allow for the use of hydrogen in air if appropriate adjustments are made to eliminate the oxygen synergism effect.

The Agency agrees that alternative mixtures should be allowed if the user can demonstrate to the Administrator that there is no oxygen synergism effect. The method has been revised to allow alternative mixtures.

One commenter notes that in Methods 204, 204A–F the term “fugitive emissions” is used in a manner inconsistent with the definition contained in 40 CFR 51.165(a)(1)(ix). The commenter suggests the word “fugitive” should be changed to “uncaptured.”

The Agency agrees and the methods have been revised to change “fugitive” to “uncaptured.”

A commenter feels that in Method 204A and 204F the required accuracy of the input weight determinations should be changed to allow the balance/digital scales to weigh within 2 lbs instead of the proposed 0.2 lb.

The Agency believes that it is very important to get an accurate measurement of the amount of coating used during a test and that scales that read to within 2 lbs are not accurate enough in most test situations. However, after reviewing this issue, the Agency also feels that the 0.2 lb limit may be too restrictive in some

situations. Therefore, the method has been revised to read “within 0.2 lb or 1.0 percent of the total weight of VOC liquid used.”

The EPA has recently discovered that the pressure drop specified in section 8.3 of Method 204, which is suppose to correspond to the minimum required face velocity of 3,600 m/hr (200 fpm), is too low. According to the twenty first edition of the “Industrial Ventilation” handbook dated 1992 the required pressure drop is 0.013 mm Hg (0.007 in. H<sub>2</sub>O). Therefore, Method 204 has been revised to reflect this finding.

#### IV. Administrative Requirements

##### A. Docket

The docket is an organized and complete file for all information submitted or otherwise considered by EPA in the development of this promulgated rulemaking. The principal purposes of the docket are: (1) To allow interested parties to identify and locate documents so that they can effectively participate in the rulemaking process, and

(2) To serve as the record in case of judicial review (except for interagency review materials) [Clean Air Act Section 307(d)(7)(A)].

##### B. Office of Management and Budget Review

Under Executive Order 12866 (58 FR 51735 October 4, 1993), the EPA is required to judge whether a regulation is “significant” and therefore subject to Office of Management and Budget (OMB) review and the requirements of this Executive Order to prepare a regulatory impact analysis (RIA). The Order defines “significant regulatory action” as one that is likely to result in a rule that may: (1) Have an annual effect on the economy of \$100 million or more or adversely affect in a material way the economy, a sector of the economy, productivity, competition, jobs, the environment, public health or safety, or State, local, or tribal governments or communities; (2) create a serious inconsistency or otherwise interfere with an action taken or planned by another agency; (3) materially alter the budgetary impact of entitlements, grants, user fees, or loan programs, or the rights and obligation of recipients thereof; or (4) raise novel legal or policy issues arising out of legal mandates, the President’s priorities, or the principles set forth in the Executive Order. Pursuant to the terms of the Executive Order, this action has been determined to be “not significant.”

##### C. Regulatory Flexibility Act Compliance

The EPA has determined that it is not necessary to prepare a regulatory flexibility analysis in connection with this final rule. The EPA has also determined that this rule will not have a significant adverse impact on a substantial number of small businesses. This rulemaking does not impose emission measurement requirements beyond those specified in the current regulations, nor does it change any emission standard. As such, it will not present a significant economic impact on a substantial number of small businesses.

##### D. Paperwork Reduction Act

The rule does not change any information collection requirements subject of Office of Management and Budget review under the Paperwork Reduction Act of 1980, 44 U.S.C. 3501 *et seq.*

##### E. Unfunded Mandates

Under Section 202 of the Unfunded Mandates Reform Act of 1995 (“Unfunded Mandates Act”), signed into law on March 22, 1995, EPA must prepare a budgetary impact statement to accompany any proposed or final rule that includes a Federal mandate that may result in estimated costs to State, local, or tribal governments in the aggregate; or to the private sector, of \$100 million or more. Under Section 205, EPA must select the most cost-effective and least burdensome alternative that achieves the objectives of the rule and is consistent with statutory requirements. Section 203 requires EPA to establish a plan for significantly or uniquely impacted by the rule.

EPA has determined that this final action does not include a Federal mandate that may result in estimated costs of \$100 million or more to either State, local, or tribal governments in the aggregate, or to the private sector, nor does this action significantly or uniquely impact small governments, because this action contains no requirements that apply to such governments or impose obligations upon them. Therefore, the requirements of the Unfunded Mandates Act do not apply to this action.

##### F. Submission to Congress and the General Accounting Office

Under 5 U.S.C. 801(a)(1)(A) of the Administrative Procedures Act (APA), as added by the Small Business Regulatory Enforcement Fairness Act of 1996, the EPA submitted a report containing this rule and other required

information to the U.S. Senate, the U.S. House of Representatives and the Comptroller General of the General Accounting Office prior to publication of the rule in today's **Federal Register**. This rule is not a "major rule" as defined by 5 U.S.C. 804(2).

#### List of Subjects in 40 CFR Part 51

Environmental protection, Administrative practice and procedure, Air pollution control, Capture efficiency, Carbon monoxide, Intergovernmental relations, Lead, Nitrogen dioxide, Ozone, Particulate matter, Printing operations, Reporting and recordkeeping requirements, Surface coating operations, Sulfur oxides, Volatile organic compounds.

Dated: May 30, 1997.

**Carol M. Browner,**  
Administrator.

For the reasons set out in the preamble, Appendix M of 40 CFR Part 51 is amended as follows:

1. The authority citation for part 51 continues to read as follows:

**Authority:** 42 U.S.C. 7410.

2. Appendix M, Table of Contents is amended by adding seven entries to read as follows:

#### Appendix M to Part 51—Recommended Test Methods for State Implementation Plans

\* \* \* \* \*

Method 204—Criteria for and Verification of a Permanent or Temporary Total Enclosure.

Method 204A—Volatile Organic Compounds Content in Liquid Input Stream.

Method 204B—Volatile Organic Compounds Emissions in Captured Stream.

Method 204C—Volatile Organic Compounds Emissions in Captured Stream (Dilution Technique).

Method 204D—Volatile Organic Compounds Emissions in Uncaptured Stream from Temporary Total Enclosure.

Method 204E—Volatile Organic Compounds Emissions in Uncaptured Stream from Building Enclosure.

Method 204F—Volatile Organic Compounds Content in Liquid Input Stream (Distillation Approach).

\* \* \* \* \*

3. By adding Method 204 to read as follows:

#### Method 204—Criteria for and Verification of a Permanent or Temporary Total Enclosure

##### 1. Scope and Application

This procedure is used to determine whether a permanent or temporary enclosure meets the criteria for a total enclosure. An existing building may be used as a temporary or permanent enclosure as long as it meets the

appropriate criteria described in this method.

##### 2. Summary of Method

An enclosure is evaluated against a set of criteria. If the criteria are met and if all the exhaust gases from the enclosure are ducted to a control device, then the volatile organic compounds (VOC) capture efficiency (CE) is assumed to be 100 percent, and CE need not be measured. However, if part of the exhaust gas stream is not ducted to a control device, CE must be determined.

##### 3. Definitions

3.1 Natural Draft Opening (NDO). Any permanent opening in the enclosure that remains open during operation of the facility and is not connected to a duct in which a fan is installed.

3.2 Permanent Total Enclosure (PE). A permanently installed enclosure that completely surrounds a source of emissions such that all VOC emissions are captured and contained for discharge to a control device.

3.3 Temporary Total Enclosure (TTE). A temporarily installed enclosure that completely surrounds a source of emissions such that all VOC emissions that are not directed through the control device (i.e. uncaptured) are captured by the enclosure and contained for discharge through ducts that allow for the accurate measurement of the uncaptured VOC emissions.

3.4 Building Enclosure (BE). An existing building that is used as a TTE.

##### 4. Safety

An evaluation of the proposed building materials and the design for the enclosure is recommended to minimize any potential hazards.

##### 5. Criteria for Temporary Total Enclosure

5.1 Any NDO shall be at least four equivalent opening diameters from each VOC emitting point unless otherwise specified by the Administrator.

5.2 Any exhaust point from the enclosure shall be at least four equivalent duct or hood diameters from each NDO.

5.3 The total area of all NDO's shall not exceed 5 percent of the surface area of the enclosure's four walls, floor, and ceiling.

5.4 The average facial velocity (FV) of air through all NDO's shall be at least 3,600 m/hr (200 fpm). The direction of air flow through all NDO's shall be into the enclosure.

5.5 All access doors and windows whose areas are not included in section 5.3 and are not included in the

calculation in section 5.4 shall be closed during routine operation of the process.

##### 6. Criteria for a Permanent Total Enclosure

6.1 Same as sections 5.1 and 5.3 through 5.5.

6.2 All VOC emissions must be captured and contained for discharge through a control device.

##### 7. Quality Control

7.1 The success of this method lies in designing the TTE to simulate the conditions that exist without the TTE (i.e., the effect of the TTE on the normal flow patterns around the affected facility or the amount of uncaptured VOC emissions should be minimal). The TTE must enclose the application stations, coating reservoirs, and all areas from the application station to the oven. The oven does not have to be enclosed if it is under negative pressure. The NDO's of the temporary enclosure and an exhaust fan must be properly sized and placed.

7.2 Estimate the ventilation rate of the TTE that best simulates the conditions that exist without the TTE (i.e., the effect of the TTE on the normal flow patterns around the affected facility or the amount of uncaptured VOC emissions should be minimal). Figure 204-1 or the following equation may be used as an aid.

$$CE = \frac{Q_G C_G}{Q_G C_G + Q_F C_F} \quad \text{Eq. 204-1}$$

Measure the concentration ( $C_G$ ) and flow rate ( $Q_G$ ) of the captured gas stream, specify a safe concentration ( $C_F$ ) for the uncaptured gas stream, estimate the CE, and then use the plot in Figure 204-1 or Equation 204-1 to determine the volumetric flow rate of the uncaptured gas stream ( $Q_F$ ). An exhaust fan that has a variable flow control is desirable.

7.3 Monitor the VOC concentration of the captured gas stream in the duct before the capture device without the TTE. To minimize the effect of temporal variation on the captured emissions, the baseline measurement should be made over as long a time period as practical. However, the process conditions must be the same for the measurement in section 7.5 as they are for this baseline measurement. This may require short measuring times for this quality control check before and after the construction of the TTE.

7.4 After the TTE is constructed, monitor the VOC concentration inside the TTE. This concentration should not continue to increase, and must not exceed the safe level according to

Occupational Safety and Health Administration requirements for permissible exposure limits. An increase in VOC concentration indicates poor TTE design.

7.5 Monitor the VOC concentration of the captured gas stream in the duct before the capture device with the TTE. To limit the effect of the TTE on the process, the VOC concentration with and without the TTE must be within 10 percent. If the measurements do not agree, adjust the ventilation rate from the TTE until they agree within 10 percent.

#### 8. Procedure

8.1 Determine the equivalent diameters of the NDO's and determine the distances from each VOC emitting point to all NDO's. Determine the equivalent diameter of each exhaust duct or hood and its distance to all NDO's. Calculate the distances in terms of equivalent diameters. The number of equivalent diameters shall be at least four.

8.2 Measure the total surface area ( $A_T$ ) of the enclosure and the total area

( $A_N$ ) of all NDO's in the enclosure. Calculate the NDO to enclosure area ratio (NEAR) as follows:

$$\text{NEAR} = \frac{A_N}{A_T} \quad \text{Eq. 204-2}$$

The NEAR must be  $\leq 10.05$ .

8.3 Measure the volumetric flow rate, corrected to standard conditions, of each gas stream exiting the enclosure through an exhaust duct or hood using EPA Method 2. In some cases (e.g., when the building is the enclosure), it may be necessary to measure the volumetric flow rate, corrected to standard conditions, of each gas stream entering the enclosure through a forced makeup air duct using Method 2. Calculate FV using the following equation:

$$\text{FV} = \frac{Q_O - Q_I}{A_N} \quad \text{Eq. 204-3}$$

where:

$Q_O$  = the sum of the volumetric flow from all gas streams exiting the enclosure through an exhaust duct or hood.

$Q_I$  = the sum of the volumetric flow from all gas streams into the enclosure through a forced makeup air duct; zero, if there is no forced makeup air into the enclosure.

$A_N$  = total area of all NDO's in enclosure.

The FV shall be at least 3,600 m/hr (200 fpm). Alternatively, measure the pressure differential across the enclosure. A pressure drop of 0.013 mm Hg (0.007 in.  $H_2O$ ) corresponds to an FV of 3,600 m/hr (200 fpm).

8.4 Verify that the direction of air flow through all NDO's is inward. If FV is less than 9,000 m/hr (500 fpm), the continuous inward flow of air shall be verified using streamers, smoke tubes, or tracer gases. Monitor the direction of air flow for at least 1 hour, with checks made no more than 10 minutes apart. If FV is greater than 9,000 m/hr (500 fpm), the direction of air flow through the NDOs shall be presumed to be inward at all times without verification.

#### 9. Diagrams

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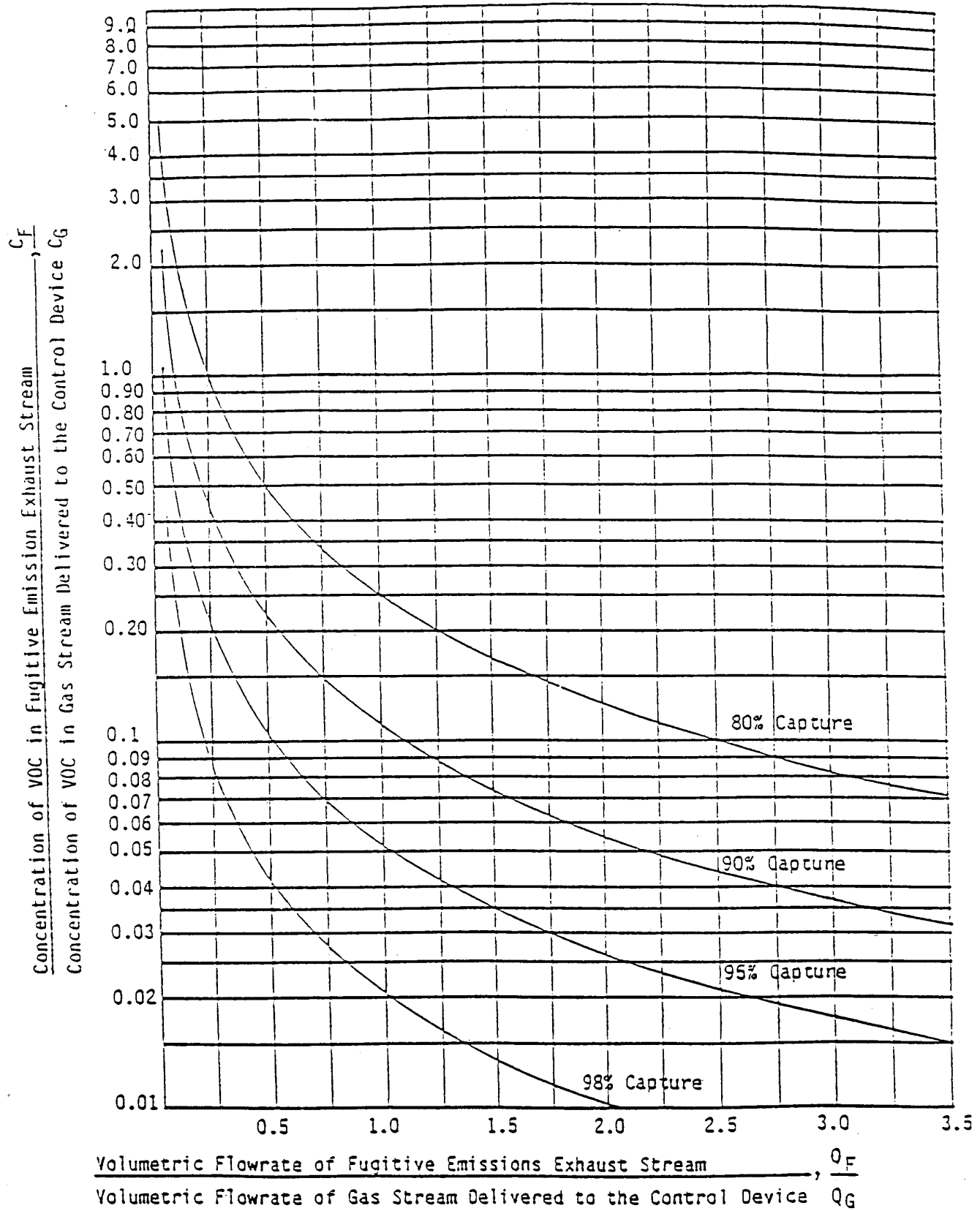


Figure 204-1. The crumpler chart.

## Method 204A—Volatile Organic Compounds Content in Liquid Input Stream

### 1. Scope and Application

1.1 Applicability. This procedure is applicable for determining the input of volatile organic compounds (VOC). It is intended to be used in the development of liquid/gas protocols for determining VOC capture efficiency (CE) for surface coating and printing operations.

1.2 Principle. The amount of VOC introduced to the process (L) is the sum of the products of the weight (W) of each VOC containing liquid (ink, paint, solvent, etc.) used and its VOC content (V).

1.3 Sampling Requirements. A CE test shall consist of at least three sampling runs. Each run shall cover at least one complete production cycle, but shall be at least 3 hours long. The sampling time for each run need not exceed 8 hours, even if the production cycle has not been completed. Alternative sampling times may be used with the approval of the Administrator.

### 2. Summary of Method

The amount of VOC containing liquid introduced to the process is determined as the weight difference of the feed material before and after each sampling run. The VOC content of the liquid input material is determined by volatilizing a small aliquot of the material and analyzing the volatile material using a flame ionization analyzer (FIA). A sample of each VOC containing liquid is analyzed with an FIA to determine V.

### 3. Safety

Because this procedure is often applied in highly explosive areas, caution and care should be exercised in choosing, installing, and using the appropriate equipment.

### 4. Equipment and Supplies

Mention of trade names or company products does not constitute endorsement. All gas concentrations (percent, ppm) are by volume, unless otherwise noted.

#### 4.1 Liquid Weight.

4.1.1 Balances/Digital Scales. To weigh drums of VOC containing liquids to within 0.2 lb or 1.0 percent of the total weight of VOC liquid used.

4.1.2 Volume Measurement Apparatus (Alternative). Volume meters, flow meters, density measurement equipment, etc., as needed to achieve the same accuracy as direct weight measurements.

4.2 VOC Content (FIA Technique). The liquid sample analysis system is

shown in Figures 204A-1 and 204A-2. The following equipment is required:

4.2.1 Sample Collection Can. An appropriately-sized metal can to be used to collect VOC containing materials. The can must be constructed in such a way that it can be grounded to the coating container.

4.2.2 Needle Valves. To control gas flow.

4.2.3 Regulators. For carrier gas and calibration gas cylinders.

4.2.4 Tubing. Teflon or stainless steel tubing with diameters and lengths determined by connection requirements of equipment. The tubing between the sample oven outlet and the FIA shall be heated to maintain a temperature of  $120\pm5$  °C.

4.2.5 Atmospheric Vent. A tee and 0- to 0.5-liter/min rotameter placed in the sampling line between the carrier gas cylinder and the VOC sample vessel to release the excess carrier gas. A toggle valve placed between the tee and the rotameter facilitates leak tests of the analysis system.

4.2.6 Thermometer. Capable of measuring the temperature of the hot water bath to within 1 °C.

4.2.7 Sample Oven. Heated enclosure, containing calibration gas coil heaters, critical orifice, aspirator, and other liquid sample analysis components, capable of maintaining a temperature of  $120\pm5$  °C.

4.2.8 Gas Coil Heaters. Sufficient lengths of stainless steel or Teflon tubing to allow zero and calibration gases to be heated to the sample oven temperature before entering the critical orifice or aspirator.

4.2.9 Water Bath. Capable of heating and maintaining a sample vessel temperature of  $100\pm5$  °C.

4.2.10 Analytical Balance. To measure  $\pm 0.001$  g.

4.2.11 Disposable Syringes. 2-cc or 5-cc.

4.2.12 Sample Vessel. Glass, 40-ml septum vial. A separate vessel is needed for each sample.

4.2.13 Rubber Stopper. Two-hole stopper to accommodate 3.2-mm (1/8-in.) Teflon tubing, appropriately sized to fit the opening of the sample vessel. The rubber stopper should be wrapped in Teflon tape to provide a tighter seal and to prevent any reaction of the sample with the rubber stopper. Alternatively, any leak-free closure fabricated of nonreactive materials and accommodating the necessary tubing fittings may be used.

4.2.14 Critical Orifices. Calibrated critical orifices capable of providing constant flow rates from 50 to 250 ml/min at known pressure drops. Sapphire orifice assemblies (available from

O'Keefe Controls Company) and glass capillary tubing have been found to be adequate for this application.

4.2.15 Vacuum Gauge. Zero to 760-mm (0- to 30-in.) Hg U-Tube manometer or vacuum gauge.

4.2.16 Pressure Gauge. Bourdon gauge capable of measuring the maximum air pressure at the aspirator inlet (e.g., 100 psig).

4.2.17 Aspirator. A device capable of generating sufficient vacuum at the sample vessel to create critical flow through the calibrated orifice when sufficient air pressure is present at the aspirator inlet. The aspirator must also provide sufficient sample pressure to operate the FIA. The sample is also mixed with the dilution gas within the aspirator.

4.2.18 Soap Bubble Meter. Of an appropriate size to calibrate the critical orifices in the system.

4.2.19 Organic Concentration Analyzer. An FIA with a span value of 1.5 times the expected concentration as propane; however, other span values may be used if it can be demonstrated that they would provide more accurate measurements. The FIA instrument should be the same instrument used in the gaseous analyses adjusted with the same fuel, combustion air, and sample back-pressure (flow rate) settings. The system shall be capable of meeting or exceeding the following specifications:

4.2.19.1 Zero Drift. Less than  $\pm 3.0$  percent of the span value.

4.2.19.2 Calibration Drift. Less than  $\pm 3.0$  percent of the span value.

4.2.19.3 Calibration Error. Less than  $\pm 5.0$  percent of the calibration gas value.

4.2.20 Integrator/Data Acquisition System. An analog or digital device or computerized data acquisition system used to integrate the FIA response or compute the average response and record measurement data. The minimum data sampling frequency for computing average or integrated values is one measurement value every 5 seconds. The device shall be capable of recording average values at least once per minute.

4.2.21 Chart Recorder (Optional). A chart recorder or similar device is recommended to provide a continuous analog display of the measurement results during the liquid sample analysis.

### 5. Reagents and Standards

5.1 Calibration and Other Gases. Gases used for calibration, fuel, and combustion air (if required) are contained in compressed gas cylinders. All calibration gases shall be traceable to National Institute of Standards and Technology standards and shall be

certified by the manufacturer to  $\pm 1$  percent of the tag value. 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  $\pm 2$  percent from the certified value. For calibration gas values not generally available, dilution systems calibrated using Method 205 may be used.

Alternative methods for preparing calibration gas mixtures may be used with the approval of the Administrator.

5.1.1 **Fuel.** The FIA manufacturer's recommended fuel should be used. A 40 percent H<sub>2</sub>/60 percent He or 40 percent H<sub>2</sub>/60 percent N<sub>2</sub> gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value. Other mixtures may be used provided the tester can demonstrate to the Administrator that there is no oxygen synergism effect.

5.1.2 **Carrier Gas.** High purity air with less than 1 ppm of organic material (as propane) or less than 0.1 percent of the span value, whichever is greater.

5.1.3 **FIA Linearity Calibration Gases.** Low-, mid-, and high-range gas mixture standards with nominal propane concentrations of 20–30, 45–55, and 70–80 percent of the span value in air, respectively. Other calibration values and other span values may be used if it can be shown to the Administrator's satisfaction that equally accurate measurements would be achieved.

5.1.4 **System Calibration Gas.** Gas mixture standard containing propane in air, approximating the undiluted VOC concentration expected for the liquid samples.

## 6. Sample Collection, Preservation and Storage

6.1 Samples must be collected in a manner that prevents or minimizes loss of volatile components and that does not contaminate the coating reservoir.

6.2 Collect a 100-ml or larger sample of the VOC containing liquid mixture at each application location at the beginning and end of each test run. A separate sample should be taken of each VOC containing liquid added to the application mixture during the test run. If a fresh drum is needed during the sampling run, then obtain a sample from the fresh drum.

6.3 When collecting the sample, ground the sample container to the coating drum. Fill the sample container as close to the rim as possible to minimize the amount of headspace.

6.4 After the sample is collected, seal the container so the sample cannot leak out or evaporate.

6.5 Label the container to clearly identify the contents.

## 7. Quality Control

7.1 Required instrument quality control parameters are found in the following sections:

7.1.1 The FIA system must be calibrated as specified in section 8.1.

7.1.2 The system drift check must be performed as specified in section 8.2.

### 7.2 Audits.

#### 7.2.1 Audit Procedure.

Concurrently, analyze the audit sample and a set of compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation. The same analyst, analytical reagents, and analytical system shall be used both for compliance samples and the EPA audit sample. If this condition is met, auditing of subsequent compliance analyses for the same enforcement agency within 30 days is not required. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of different enforcement agencies, unless prior arrangements are made with both enforcement agencies.

7.2.2 **Audit Samples and Audit Sample Availability.** Audit samples will be supplied only to enforcement agencies for compliance tests. The availability of audit samples may be obtained by writing: Source Test Audit Coordinator (STAC) (MD-77B), Quality Assurance Division, Atmospheric Research and Exposure Assessment Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711 or by calling the STAC at (919) 541-7834. The request for the audit sample must be made at least 30 days prior to the scheduled compliance sample analysis.

7.2.3 **Audit Results.** Calculate the audit sample concentration according to the calculation procedure described in the audit instructions included with the audit sample. Fill in the audit sample concentration and the analyst's name on the audit response form included with the audit instructions. Send one copy to the EPA Regional Office or the appropriate enforcement agency, and a second copy to the STAC. The EPA Regional Office or the appropriate enforcement agency will report the results of the audit to the laboratory being audited. Include this response with the results of the compliance samples in relevant reports to the EPA Regional Office or the appropriate enforcement agency.

## 8. Calibration and Standardization

8.1 **FIA Calibration and Linearity Check.** Make necessary adjustments to the air and fuel supplies for the FIA and ignite the burner. Allow the FIA to warm up for the period recommended by the manufacturer. Inject a calibration gas into the measurement system and adjust the back-pressure regulator to the value required to achieve the flow rates specified by the manufacturer. Inject the zero- and the high-range calibration gases and adjust the analyzer calibration to provide the proper responses. Inject the low- and mid-range gases and record the responses of the measurement system. The calibration and linearity of the system are acceptable if the responses for all four gases are within 5 percent of the respective gas values. If the performance of the system is not acceptable, repair or adjust the system and repeat the linearity check. Conduct a calibration and linearity check after assembling the analysis system and after a major change is made to the system.

8.2 **Systems Drift Checks.** After each sample, repeat the system calibration checks in section 9.2.7 before any adjustments to the FIA or measurement system are made. If the zero or calibration drift exceeds  $\pm 3$  percent of the span value, discard the result and repeat the analysis.

Alternatively, recalibrate the FIA as in section 8.1 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). The data that results in the lowest CE value shall be reported as the results for the test run.

### 8.3 Critical Orifice Calibration.

8.3.1 Each critical orifice must be calibrated at the specific operating conditions under which it will be used. Therefore, assemble all components of the liquid sample analysis system as shown in Figure 204A-3. A stopwatch is also required.

8.3.2 Turn on the sample oven, sample line, and water bath heaters, and allow the system to reach the proper operating temperature. Adjust the aspirator to a vacuum of 380 mm (15 in.) Hg vacuum. Measure the time required for one soap bubble to move a known distance and record barometric pressure.

8.3.3 Repeat the calibration procedure at a vacuum of 406 mm (16 in.) Hg and at 25-mm (1-in.) Hg intervals until three consecutive determinations provide the same flow rate. Calculate the critical flow rate for the orifice in ml/min at standard conditions. Record the vacuum necessary to achieve critical flow.

## 9. Procedure

### 9.1 Determination of Liquid Input Weight.

9.1.1 Weight Difference. Determine the amount of material introduced to the process as the weight difference of the feed material before and after each sampling run. In determining the total VOC containing liquid usage, account for:

- (a) The initial (beginning) VOC containing liquid mixture.
- (b) Any solvent added during the test run.
- (c) Any coating added during the test run.
- (d) Any residual VOC containing liquid mixture remaining at the end of the sample run.

9.1.1.1 Identify all points where VOC containing liquids are introduced to the process. To obtain an accurate measurement of VOC containing liquids, start with an empty fountain (if applicable). After completing the run, drain the liquid in the fountain back into the liquid drum (if possible) and weigh the drum again. Weigh the VOC containing liquids to  $\pm 0.5$  percent of the total weight (full) or  $\pm 1.0$  percent of the total weight of VOC containing liquid used during the sample run, whichever is less. If the residual liquid cannot be returned to the drum, drain the fountain into a preweighed empty drum to determine the final weight of the liquid.

9.1.1.2 If it is not possible to measure a single representative mixture, then weigh the various components separately (e.g., if solvent is added during the sampling run, weigh the solvent before it is added to the mixture). If a fresh drum of VOC containing liquid is needed during the run, then weigh both the empty drum and fresh drum.

9.1.2 Volume Measurement (Alternative). If direct weight measurements are not feasible, the tester may use volume meters or flow rate meters and density measurements to determine the weight of liquids used if it can be demonstrated that the technique produces results equivalent to the direct weight measurements. If a single representative mixture cannot be measured, measure the components separately.

### 9.2 Determination of VOC Content in Input Liquids

9.2.1 Assemble the liquid VOC content analysis system as shown in Figure 204A-1.

9.2.2 Permanently identify all of the critical orifices that may be used. Calibrate each critical orifice under the expected operating conditions (i.e., sample vacuum and temperature)

against a volume meter as described in section 8.3.

9.2.3 Label and tare the sample vessels (including the stoppers and caps) and the syringes.

9.2.4 Install an empty sample vessel and perform a leak test of the system. Close the carrier gas valve and atmospheric vent and evacuate the sample vessel to 250 mm (10 in.) Hg absolute or less using the aspirator. Close the toggle valve at the inlet to the aspirator and observe the vacuum for at least 1 minute. If there is any change in the sample pressure, release the vacuum, adjust or repair the apparatus as necessary, and repeat the leak test.

9.2.5 Perform the analyzer calibration and linearity checks according to the procedure in section 5.1. Record the responses to each of the calibration gases and the back-pressure setting of the FIA.

9.2.6 Establish the appropriate dilution ratio by adjusting the aspirator air supply or substituting critical orifices. Operate the aspirator at a vacuum of at least 25 mm (1 in.) Hg greater than the vacuum necessary to achieve critical flow. Select the dilution ratio so that the maximum response of the FIA to the sample does not exceed the high-range calibration gas.

9.2.7 Perform system calibration checks at two levels by introducing compressed gases at the inlet to the sample vessel while the aspirator and dilution devices are operating. Perform these checks using the carrier gas (zero concentration) and the system calibration gas. If the response to the carrier gas exceeds  $\pm 0.5$  percent of span, clean or repair the apparatus and repeat the check. Adjust the dilution ratio as necessary to achieve the correct response to the upscale check, but do not adjust the analyzer calibration. Record the identification of the orifice, aspirator air supply pressure, FIA back-pressure, and the responses of the FIA to the carrier and system calibration gases.

9.2.8 After completing the above checks, inject the system calibration gas for approximately 10 minutes. Time the exact duration of the gas injection using a stopwatch. Determine the area under the FIA response curve and calculate the system response factor based on the sample gas flow rate, gas concentration, and the duration of the injection as compared to the integrated response using Equations 204A-2 and 204A-3.

9.2.9 Verify that the sample oven and sample line temperatures are  $120 \pm 5^\circ\text{C}$  and that the water bath temperature is  $100 \pm 5^\circ\text{C}$ .

9.2.10 Fill a tared syringe with approximately 1 g of the VOC

containing liquid and weigh it. Transfer the liquid to a tared sample vessel. Plug the sample vessel to minimize sample loss. Weigh the sample vessel containing the liquid to determine the amount of sample actually received. Also, as a quality control check, weigh the empty syringe to determine the amount of material delivered. The two coating sample weights should agree within 0.02 g. If not, repeat the procedure until an acceptable sample is obtained.

9.2.11 Connect the vessel to the analysis system. Adjust the aspirator supply pressure to the correct value. Open the valve on the carrier gas supply to the sample vessel and adjust it to provide a slight excess flow to the atmospheric vent. As soon as the initial response of the FIA begins to decrease, immerse the sample vessel in the water bath. (Applying heat to the sample vessel too soon may cause the FIA response to exceed the calibrated range of the instrument and, thus, invalidate the analysis.)

9.2.12 Continuously measure and record the response of the FIA until all of the volatile material has been evaporated from the sample and the instrument response has returned to the baseline (i.e., response less than 0.5 percent of the span value). Observe the aspirator supply pressure, FIA back-pressure, atmospheric vent, and other system operating parameters during the run; repeat the analysis procedure if any of these parameters deviate from the values established during the system calibration checks in section 9.2.7. After each sample, perform the drift check described in section 8.2. If the drift check results are acceptable, calculate the VOC content of the sample using the equations in section 11.2. Alternatively, recalibrate the FIA as in section 8.1 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). The data that results in the lowest CE value shall be reported as the results for the test run. Integrate the area under the FIA response curve, or determine the average concentration response and the duration of sample analysis.

## 10. Data Analysis and Calculations

### 10.1 Nomenclature.

$A_L$ =area under the response curve of the liquid sample, area count.

$A_S$ =area under the response curve of the calibration gas, area count.

$C_S$ =actual concentration of system calibration gas, ppm propane.

$K=1.830 \times 10^{-9}$  g/(ml-ppm).

$L$ =total VOC content of liquid input, kg.



M <sub>L</sub> =mass of liquid sample delivered to the sample vessel, g.	V <sub>Fj</sub> =final VOC fraction of VOC containing liquid j.	W <sub>Ij</sub> =weight of VOC containing liquid j at beginning of the run, kg.
q = flow rate through critical orifice, ml/min.	V <sub>Ij</sub> =initial VOC fraction of VOC containing liquid j.	W <sub>Aj</sub> =weight of VOC containing liquid j added during the run, kg.
RF=liquid analysis system response factor, g/area count.	V <sub>Aj</sub> =VOC fraction of VOC containing liquid j added during the run.	10.2 Calculations
θ <sub>s</sub> =total gas injection time for system calibration gas during integrator calibration, min.	V=VOC fraction of liquid sample.	10.2.1 Total VOC Content of the Input VOC Containing Liquid.
	W <sub>Fj</sub> =weight of VOC containing liquid j remaining at end of the run, kg.	

$$L = \sum_{j=1}^n V_{Ij} W_{Ij} - \sum_{j=1}^n V_{Fj} W_{Fj} + \sum_{j=1}^n V_{Aj} W_{Aj} \quad \text{Eq. 204A-1}$$

10.2.2 Liquid Sample Analysis System Response Factor for Systems Using Integrators, Grams/Area Count.

$$RF = \frac{C_s q \theta_s K}{A_s} \quad \text{Eq. 204A-2}$$

10.2.3 VOC Content of the Liquid Sample.

$$V = \frac{A_L RF}{M_L} \quad \text{Eq. 204A-3}$$

11. Method Performance

The measurement uncertainties are estimated for each VOC containing liquid as follows: W = ±2.0 percent and

V = ±4.0 percent. Based on these numbers, the probable uncertainty for L is estimated at about ±4.5 percent for each VOC containing liquid.

12. Diagrams

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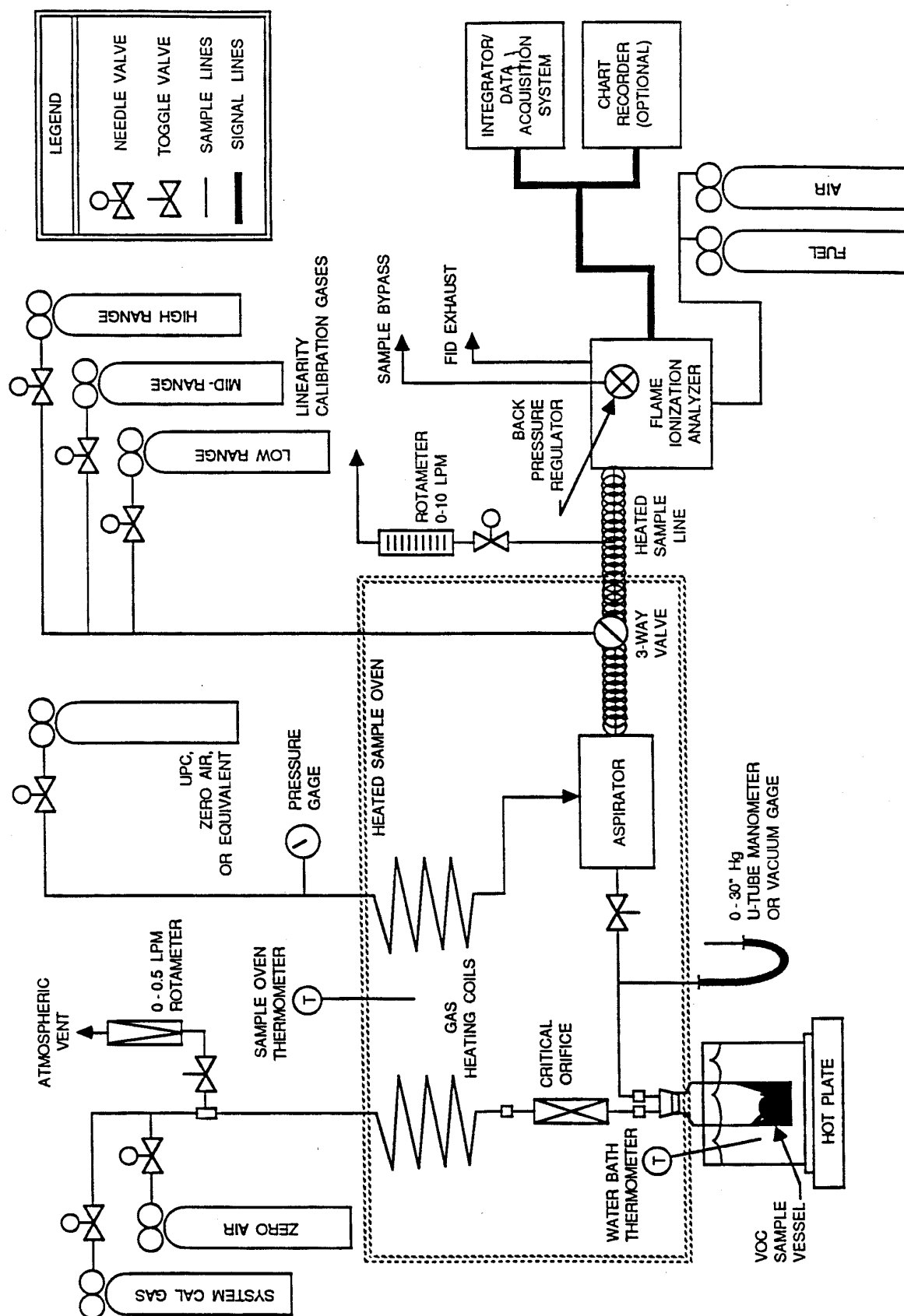


Figure 204A-1. Liquid analysis sample system.

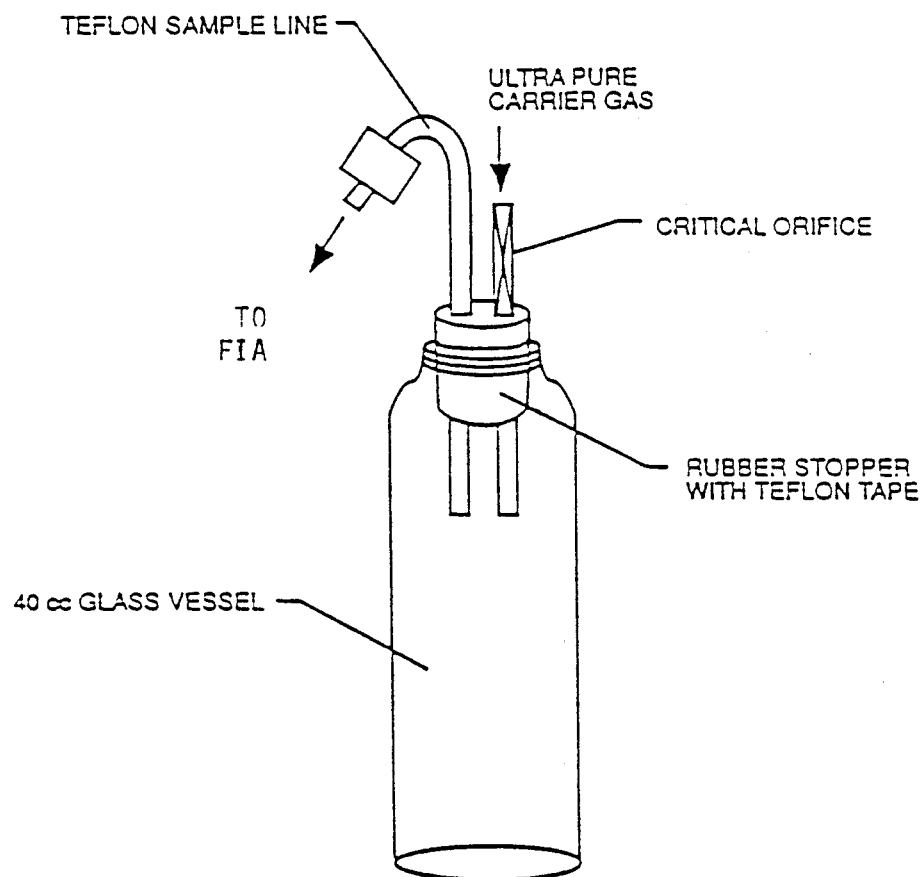


Figure 204A-2. VOC sampling vessel.

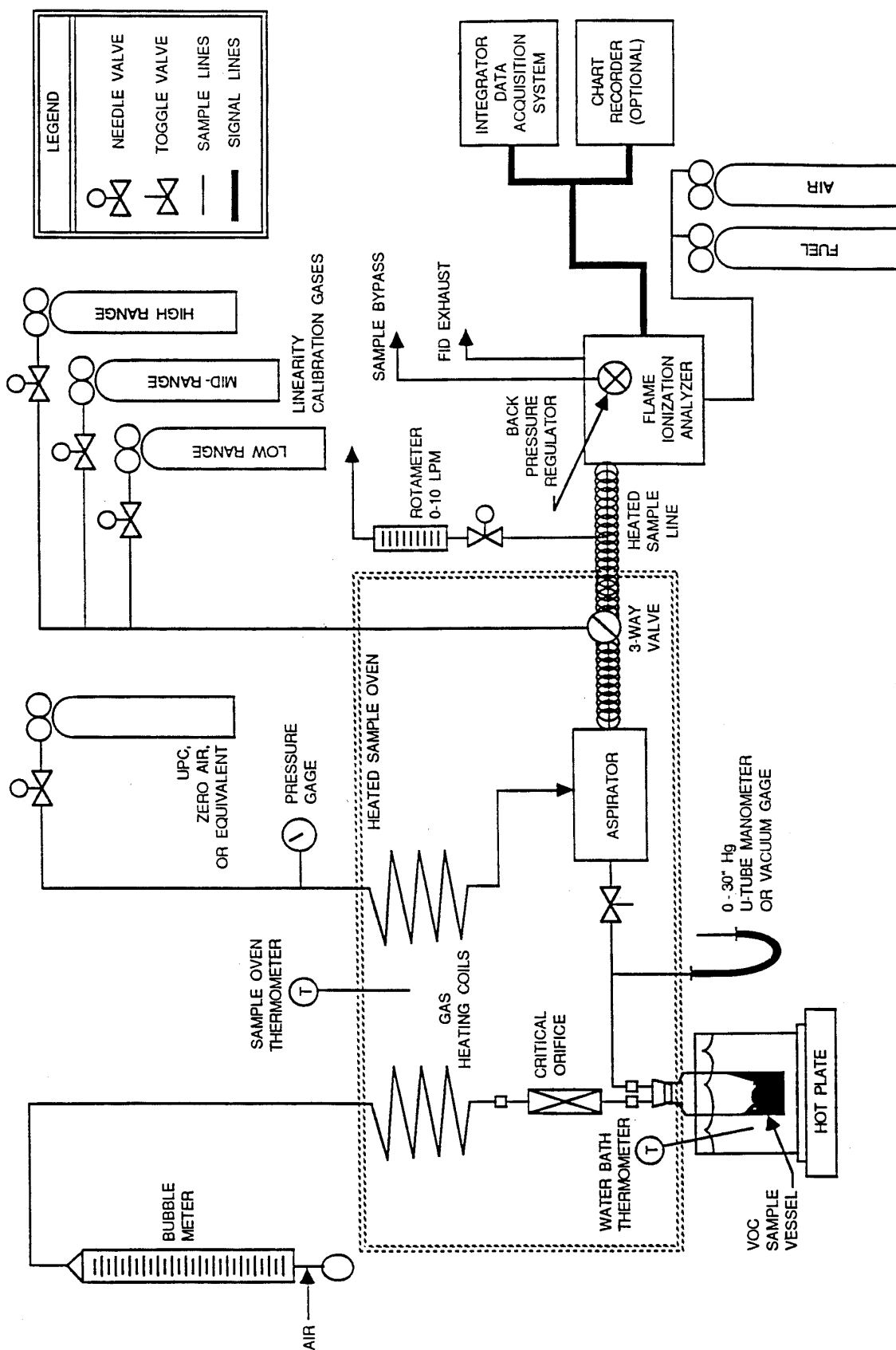


Figure 204A-3. Critical orifice calibration apparatus.

## Method 204B—Volatile Organic Compounds Emissions in Captured Stream

### 1. Scope and Application

1.1 Applicability. This procedure is applicable for determining the volatile organic compounds (VOC) content of captured gas streams. It is intended to be used in the development of a gas/gas protocol for determining VOC capture efficiency (CE) for surface coating and printing operations. The procedure may not be acceptable in certain site-specific situations [e.g., when: (1) direct-fired heaters or other circumstances affect the quantity of VOC at the control device inlet; and (2) particulate organic aerosols are formed in the process and are present in the captured emissions].

1.2 Principle. The amount of VOC captured (G) is calculated as the sum of the products of the VOC content ( $C_{Gj}$ ), the flow rate ( $Q_{Gj}$ ), and the sample time ( $\Theta_C$ ) from each captured emissions point.

1.3 Sampling Requirements. A CE test shall consist of at least three sampling runs. Each run shall cover at least one complete production cycle, but shall be at least 3 hours long. The sampling time for each run need not exceed 8 hours, even if the production cycle has not been completed. Alternative sampling times may be used with the approval of the Administrator.

### 2. Summary of Method

A gas sample is extracted from the source through a heated sample line and, if necessary, a glass fiber filter to a flame ionization analyzer (FIA).

### 3. Safety

Because this procedure is often applied in highly explosive areas, caution and care should be exercised in choosing, installing, and using the appropriate equipment.

### 4. Equipment and Supplies

Mention of trade names or company products does not constitute endorsement. All gas concentrations (percent, ppm) are by volume, unless otherwise noted.

4.1 Gas VOC Concentration. A schematic of the measurement system is shown in Figure 204B-1. The main components are as follows:

4.1.1 Sample Probe. Stainless steel or equivalent. The probe shall be heated to prevent VOC condensation.

4.1.2 Calibration Valve Assembly. Three-way valve assembly at the outlet of the sample probe to direct the zero and calibration gases to the analyzer. Other methods, such as quick-connect lines, to route calibration gases to the

outlet of the sample probe are acceptable.

4.1.3 Sample Line. Stainless steel or Teflon tubing to transport the sample gas to the analyzer. The sample line must be heated to prevent condensation.

4.1.4 Sample Pump. A leak-free pump, to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. The components of the pump that contact the gas stream shall be constructed of stainless steel or Teflon. The sample pump must be heated to prevent condensation.

4.1.5 Sample Flow Rate Control. A sample flow rate control valve and rotameter, or equivalent, to maintain a constant sampling rate within 10 percent. The flow rate control valve and rotameter must be heated to prevent condensation. A control valve may also be located on the sample pump bypass loop to assist in controlling the sample pressure and flow rate.

4.1.6 Organic Concentration Analyzer. An FIA with a span value of 1.5 times the expected concentration as propane; however, other span values may be used if it can be demonstrated to the Administrator's satisfaction that they would provide equally accurate measurements. The system shall be capable of meeting or exceeding the following specifications:

4.1.6.1 Zero Drift. Less than  $\pm 3.0$  percent of the span value.

4.1.6.2 Calibration Drift. Less than  $\pm 3.0$  percent of the span value.

4.1.6.3 Calibration Error. Less than  $\pm 5.0$  percent of the calibration gas value.

4.1.6.4 Response Time. Less than 30 seconds.

4.1.7 Integrator/Data Acquisition System. An analog or digital device, or computerized data acquisition system used to integrate the FIA response or compute the average response and record measurement data. The minimum data sampling frequency for computing average or integrated values is one measurement value every 5 seconds. The device shall be capable of recording average values at least once per minute.

4.2 Captured Emissions Volumetric Flow Rate.

4.2.1 Method 2 or 2A Apparatus. For determining volumetric flow rate.

4.2.2 Method 3 Apparatus and Reagents. For determining molecular weight of the gas stream. An estimate of the molecular weight of the gas stream may be used if approved by the Administrator.

4.2.3 Method 4 Apparatus and Reagents. For determining moisture content, if necessary.

### 5. Reagents and Standards

5.1 Calibration and Other Gases. Gases used for calibration, fuel, and combustion air (if required) are contained in compressed gas cylinders. All calibration gases shall be traceable to National Institute of Standards and Technology standards and shall be certified by the manufacturer to  $\pm 1$  percent of the tag value. 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  $\pm 2$  percent from the certified value. For calibration gas values not generally available, dilution systems calibrated using Method 205 may be used. Alternative methods for preparing calibration gas mixtures may be used with the approval of the Administrator.

5.1.1 Fuel. The FIA manufacturer's recommended fuel should be used. A 40 percent  $H_2/60$  percent He or 40 percent  $H_2/60$  percent  $N_2$  gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value. Other mixtures may be used provided the tester can demonstrate to the Administrator that there is no oxygen synergism effect.

5.1.2 Carrier Gas. High purity air with less than 1 ppm of organic material (as propane or carbon equivalent) or less than 0.1 percent of the span value, whichever is greater.

5.1.3 FIA Linearity Calibration Gases. Low-, mid-, and high-range gas mixture standards with nominal propane concentrations of 20–30, 45–55, and 70–80 percent of the span value in air, respectively. Other calibration values and other span values may be used if it can be shown to the Administrator's satisfaction that equally accurate measurements would be achieved.

5.2 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 must be heated to prevent any condensation unless it can be demonstrated that no condensation occurs.

### 6. Quality Control

6.1 Required instrument quality control parameters are found in the following sections:

6.1.1 The FIA system must be calibrated as specified in section 7.1.

6.1.2 The system drift check must be performed as specified in section 7.2.

6.1.3 The system check must be conducted as specified in section 7.3.

## 6.2 Audits.

### 6.2.1 Analysis Audit Procedure.

Immediately before each test, analyze an audit cylinder as described in section 7.2. The analysis audit must agree with the audit cylinder concentration within 10 percent.

**6.2.2 Audit Samples and Audit Sample Availability.** Audit samples will be supplied only to enforcement agencies for compliance tests. The availability of audit samples may be obtained by writing: Source Test Audit Coordinator (STAC) (MD-77B), Quality Assurance Division, Atmospheric Research and Exposure Assessment Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711 or by calling the STAC at (919) 541-7834. The request for the audit sample must be made at least 30 days prior to the scheduled compliance sample analysis.

**6.2.3 Audit Results.** Calculate the audit sample concentration according to the calculation procedure described in the audit instructions included with the audit sample. Fill in the audit sample concentration and the analyst's name on the audit response form included with the audit instructions. Send one copy to the EPA Regional Office or the appropriate enforcement agency, and a second copy to the STAC. The EPA Regional Office or the appropriate enforcement agency will report the results of the audit to the laboratory being audited. Include this response with the results of the compliance samples in relevant reports to the EPA Regional Office or the appropriate enforcement agency.

## 7. Calibration and Standardization

**7.1 FIA Calibration and Linearity Check.** Make necessary adjustments to the air and fuel supplies for the FIA and ignite the burner. Allow the FIA to warm up for the period recommended by the manufacturer. Inject a calibration gas into the measurement system and adjust the back-pressure regulator to the value required to achieve the flow rates specified by the manufacturer. Inject the zero- and the high-range calibration gases and adjust the analyzer calibration to provide the proper responses. Inject the low- and mid-range gases and record the responses of the measurement system. The calibration and linearity of the system are acceptable if the responses for all four gases are within 5 percent of the respective gas values. If the performance of the system is not acceptable, repair or adjust the system and repeat the linearity check. Conduct a calibration and linearity check after assembling the analysis system and after a major change is made to the system.

**7.2 Systems Drift Checks.** Select the calibration gas that most closely approximates the concentration of the captured emissions for conducting the drift checks. Introduce the zero and calibration gases at the calibration valve assembly and verify that the appropriate gas flow rate and pressure are present at the FIA. Record the measurement system responses to the zero and calibration gases. The performance of the system is acceptable if the difference between the drift check measurement and the value obtained in section 7.1 is less than 3 percent of the span value. Alternatively, recalibrate the FIA as in section 7.1 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). The data that results in the lowest CE value shall be reported as the results for the test run. Conduct the system drift checks at the end of each run.

**7.3 System Check.** Inject the high-range calibration gas at the inlet of the sampling probe and record the response. The performance of the system is acceptable if the measurement system response is within 5 percent of the value obtained in section 7.1 for the high-range calibration gas. Conduct a system check before and after each test run.

## 8. Procedure

### 8.1. Determination of Volumetric Flow Rate of Captured Emissions.

**8.1.1** Locate all points where emissions are captured from the affected facility. Using Method 1, determine the sampling points. Be sure to check each site for cyclonic or swirling flow.

**8.1.2** Measure the velocity at each sampling site at least once every hour during each sampling run using Method 2 or 2A.

### 8.2 Determination of VOC Content of Captured Emissions.

**8.2.1 Analysis Duration.** Measure the VOC responses at each captured emissions point during the entire test run or, if applicable, while the process is operating. If there are multiple captured emission locations, design a sampling system to allow a single FIA to be used to determine the VOC responses at all sampling locations.

#### 8.2.2 Gas VOC Concentration.

**8.2.2.1** Assemble the sample train as shown in Figure 204B-1. Calibrate the FIA according to the procedure in section 7.1.

**8.2.2.2** Conduct a system check according to the procedure in section 7.3.

**8.2.2.3** 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.

**8.2.2.4** Inject zero gas at the calibration valve assembly. Allow the measurement system response to reach zero. Measure the system response time as the time required for the system to reach the effluent concentration after the calibration valve has been returned to the effluent sampling position.

**8.2.2.5** Conduct a system check before, and a system drift check after, each sampling run according to the procedures in sections 7.2 and 7.3. If the drift check following a run indicates unacceptable performance (see section 7.3), the run is not valid. Alternatively, recalibrate the FIA as in section 7.1 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). The data that results in the lowest CE value shall be reported as the results for the test run. The tester may elect to perform system drift checks during the run not to exceed one drift check per hour.

**8.2.2.6** Verify that the sample lines, filter, and pump temperatures are  $120 \pm 5$  °C.

**8.2.2.7** Begin sampling at the start of the test period and continue to sample during the entire run. Record the starting and ending times and any required process information as appropriate. If multiple captured emission locations are sampled using a single FIA, sample at each location for the same amount of time (e.g., 2 minutes) and continue to switch from one location to another for the entire test run. Be sure that total sampling time at each location is the same at the end of the test run. Collect at least four separate measurements from each sample point during each hour of testing. Disregard the measurements at each sampling location until two times the response time of the measurement system has elapsed. Continue sampling for at least 1 minute and record the concentration measurements.

#### 8.2.3 Background Concentration.

**Note:** Not applicable when the building is used as the temporary total enclosure (TTE).

**8.2.3.1** Locate all natural draft openings (NDO's) of the TTE. A sampling point shall be at the center of each NDO, unless otherwise specified by the Administrator. If there are more than six NDO's, choose six sampling points evenly spaced among the NDO's.

**8.2.3.2** Assemble the sample train as shown in Figure 204B-2. Calibrate the FIA and conduct a system check according to the procedures in sections 7.1 and 7.3.

**Note:** This sample train shall be separate from the sample train used to measure the captured emissions.

8.2.3.3 Position the probe at the sampling location.

8.2.3.4 Determine the response time, conduct the system check, and sample according to the procedures described in sections 8.2.2.4 through 8.2.2.7.

8.2.4 Alternative Procedure. The direct interface sampling and analysis procedure described in section 7.2 of Method 18 may be used to determine the gas VOC concentration. The system must be designed to collect and analyze at least one sample every 10 minutes. If the alternative procedure is used to determine the VOC concentration of the captured emissions, it must also be used to determine the VOC concentration of the uncaptured emissions.

## 9. Data Analysis and Calculations

### 9.1 Nomenclature.

$A_i$ =area of NDO i, ft<sup>2</sup>.

$A_N$ =total area of all NDO's in the enclosure, ft<sup>2</sup>.

$C_{Bi}$ =corrected average VOC concentration of background emissions at point i, ppm propane.

$C_B$ =average background concentration, ppm propane.

$C_{Gj}$ =corrected average VOC concentration of captured emissions at point j, ppm propane.

$C_{DH}$ =average measured concentration for the drift check calibration gas, ppm propane.

$C_{DO}$ =average system drift check concentration for zero concentration gas, ppm propane.

$C_H$ =actual concentration of the drift check calibration gas, ppm propane.

$C_i$ =uncorrected average background VOC concentration measured at point i, ppm propane.

$C_j$ =uncorrected average VOC concentration measured at point j, ppm propane.

$G$ =total VOC content of captured emissions, kg.

$K_1=1.830 \times 10^{-6}$  kg/(m<sup>3</sup>-ppm).

$n$ =number of measurement points.

$Q_{Gj}$ =average effluent volumetric flow rate corrected to standard conditions at captured emissions point j, m<sup>3</sup>/min.

$\Theta_C$ =total duration of captured emissions.

### 9.2 Calculations.

#### 9.2.1 Total VOC Captured Emissions.

$$G = \sum_{j=1}^n (C_{Gj} - C_B) Q_{Gj} \Theta_C K_1 \quad \text{Eq. 204B-1}$$

#### 9.2.2 VOC Concentration of the Captured Emissions at Point j.

$$C_{Gj} = (C_j - C_{DO}) \frac{C_H}{C_{DH} - C_{DO}} \quad \text{Eq. 204B-2}$$

#### 9.2.3 Background VOC Concentration at Point i.

$$C_{Bi} = (C_i - C_{DO}) \frac{C_H}{C_{DH} - C_{DO}} \quad \text{Eq. 204B-3}$$

#### 9.2.4 Average Background Concentration.

$$C_B = \frac{\sum_{i=1}^n C_{Bi} A_i}{A_N} \quad \text{Eq. 204B-4}$$

**Note:** If the concentration at each point is within 20 percent of the average concentration of all points, then use the arithmetic average.

## 10. Method Performance

The measurement uncertainties are estimated for each captured or uncaptured emissions point as follows:  $Q_{Gj}=\pm 5.5$  percent and  $C_{Gj}=\pm 5.0$  percent. Based on these numbers, the probable uncertainty for  $G$  is estimated at about  $\pm 7.4$  percent.

## 11. Diagrams

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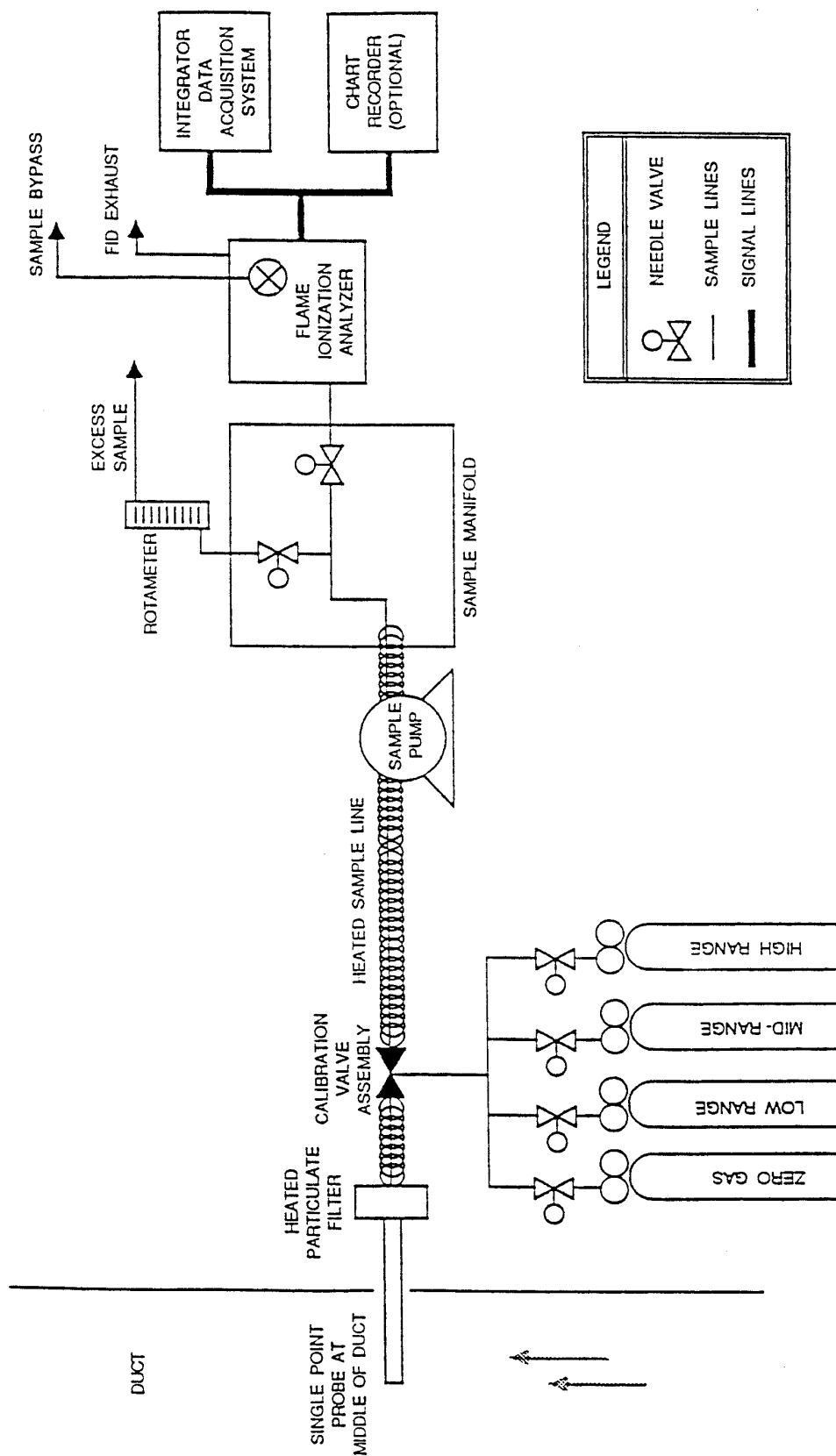


Figure 204B-1. Gas VOC concentration measurement system.



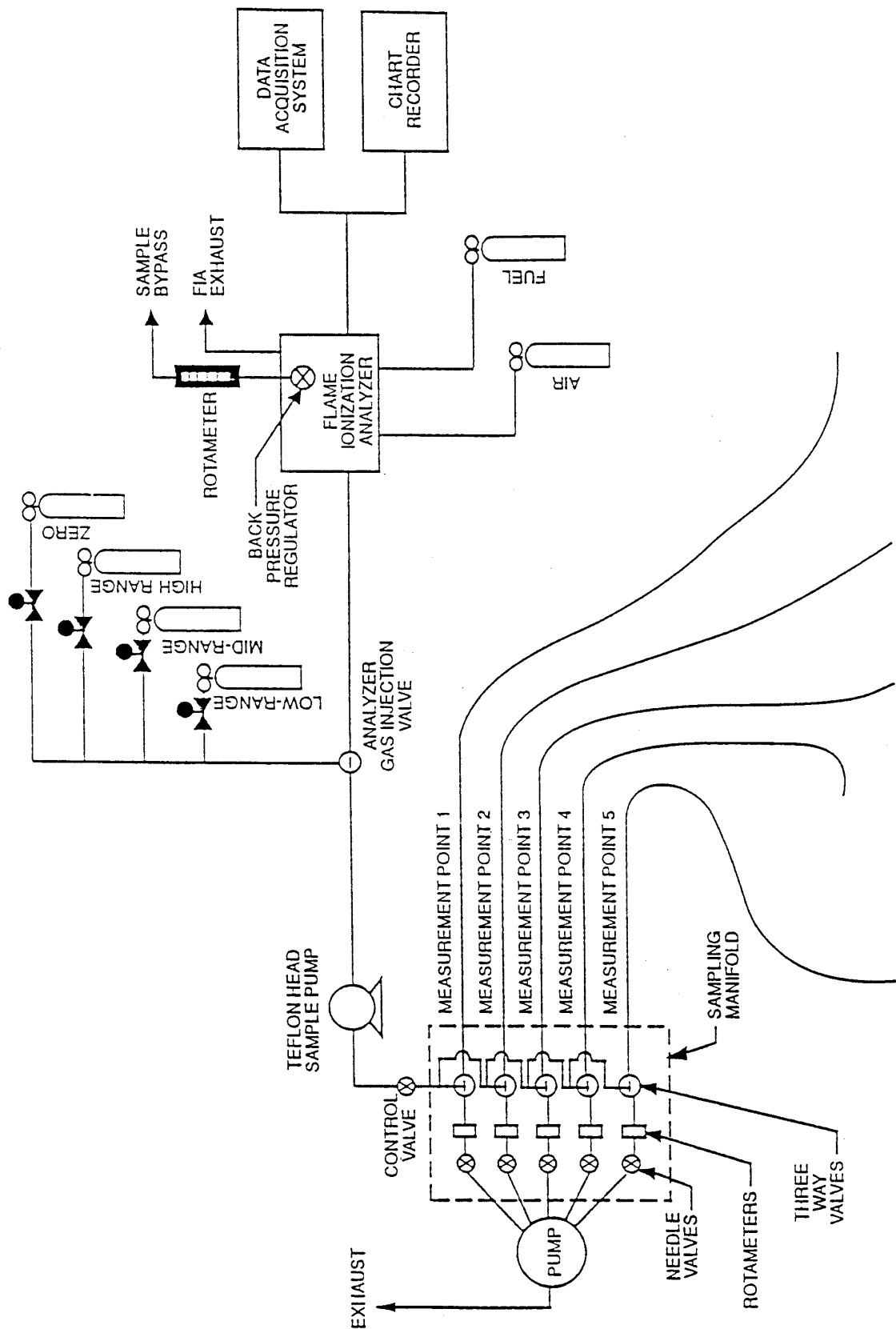


Figure 204B-2. Background measurement system.

## Method 204C—Volatile Organic Compounds Emissions in Captured Stream (Dilution Technique)

### 1. Scope and Application

1.1 Applicability. This procedure is applicable for determining the volatile organic compounds (VOC) content of captured gas streams. It is intended to be used in the development of a gas/gas protocol in which uncaptured emissions are also measured for determining VOC capture efficiency (CE) for surface coating and printing operations. A dilution system is used to reduce the VOC concentration of the captured emissions to about the same concentration as the uncaptured emissions. The procedure may not be acceptable in certain site-specific situations [e.g., when: (1) direct-fired heaters or other circumstances affect the quantity of VOC at the control device inlet; and (2) particulate organic aerosols are formed in the process and are present in the captured emissions].

1.2 Principle. The amount of VOC captured (G) is calculated as the sum of the products of the VOC content ( $C_{Gj}$ ), the flow rate ( $Q_{Gj}$ ), and the sampling time ( $\Theta_c$ ) from each captured emissions point.

1.3 Sampling Requirements. A CE test shall consist of at least three sampling runs. Each run shall cover at least one complete production cycle, but shall be at least 3 hours long. The sampling time for each run need not exceed 8 hours, even if the production cycle has not been completed. Alternative sampling times may be used with the approval of the Administrator.

### 2. Summary of Method

A gas sample is extracted from the source using an in-stack dilution probe through a heated sample line and, if necessary, a glass fiber filter to a flame ionization analyzer (FIA). The sample train contains a sample gas manifold which allows multiple points to be sampled using a single FIA.

### 3. Safety

Because this procedure is often applied in highly explosive areas, caution and care should be exercised in choosing, installing, and using the appropriate equipment.

### 4. Equipment and Supplies

Mention of trade names or company products does not constitute endorsement. All gas concentrations (percent, ppm) are by volume, unless otherwise noted.

4.1 Gas VOC Concentration. A schematic of the measurement system is

shown in Figure 204C-1. The main components are as follows:

4.1.1 Dilution System. A Kipp in-stack dilution probe and controller or similar device may be used. The dilution rate may be changed by substituting different critical orifices or adjustments of the aspirator supply pressure. The dilution system shall be heated to prevent VOC condensation. Note: An out-of-stack dilution device may be used.

4.1.2 Calibration Valve Assembly. Three-way valve assembly at the outlet of the sample probe to direct the zero and calibration gases to the analyzer. Other methods, such as quick-connect lines, to route calibration gases to the outlet of the sample probe are acceptable.

4.1.3 Sample Line. Stainless steel or Teflon tubing to transport the sample gas to the analyzer. The sample line must be heated to prevent condensation.

4.1.4 Sample Pump. A leak-free pump, to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. The components of the pump that contact the gas stream shall be constructed of stainless steel or Teflon. The sample pump must be heated to prevent condensation.

4.1.5 Sample Flow Rate Control. A sample flow rate control valve and rotameter, or equivalent, to maintain a constant sampling rate within 10 percent. The flow control valve and rotameter must be heated to prevent condensation. A control valve may also be located on the sample pump bypass loop to assist in controlling the sample pressure and flow rate.

4.1.6 Sample Gas Manifold. Capable of diverting a portion of the sample gas stream to the FIA, and the remainder to the bypass discharge vent. The manifold components shall be constructed of stainless steel or Teflon. If captured or uncaptured emissions are to be measured at multiple locations, the measurement system shall be designed to use separate sampling probes, lines, and pumps for each measurement location and a common sample gas manifold and FIA. The sample gas manifold and connecting lines to the FIA must be heated to prevent condensation.

**Note:** Depending on the number of sampling points and their location, it may not be possible to use only one FIA. However to reduce the effect of calibration error, the number of FIA's used during a test should be kept as small as possible.

4.1.7 Organic Concentration Analyzer. An FIA with a span value of 1.5 times the expected concentration as

propane; however, other span values may be used if it can be demonstrated to the Administrator's satisfaction that they would provide equally accurate measurements. The system shall be capable of meeting or exceeding the following specifications:

4.1.7.1 Zero Drift. Less than  $\pm 3.0$  percent of the span value.

4.1.7.2 Calibration Drift. Less than  $\pm 3.0$  percent of the span value.

4.1.7.3 Calibration Error. Less than  $\pm 5.0$  percent of the calibration gas value.

4.1.7.4 Response Time. Less than 30 seconds.

4.1.8 Integrator/Data Acquisition System. An analog or digital device or computerized data acquisition system used to integrate the FIA response or compute the average response and record measurement data. The minimum data sampling frequency for computing average or integrated values is one measurement value every 5 seconds. The device shall be capable of recording average values at least once per minute.

### 4.2 Captured Emissions Volumetric Flow Rate.

4.2.1 Method 2 or 2A Apparatus. For determining volumetric flow rate.

4.2.2 Method 3 Apparatus and Reagents. For determining molecular weight of the gas stream. An estimate of the molecular weight of the gas stream may be used if approved by the Administrator.

4.2.3 Method 4 Apparatus and Reagents. For determining moisture content, if necessary.

### 5. Reagents and Standards

5.1 Calibration and Other Gases. Gases used for calibration, fuel, and combustion air (if required) are contained in compressed gas cylinders. All calibration gases shall be traceable to National Institute of Standards and Technology standards and shall be certified by the manufacturer to  $\pm 1$  percent of the tag value. 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  $\pm 2$  percent from the certified value. For calibration gas values not generally available, dilution systems calibrated using Method 205 may be used. Alternative methods for preparing calibration gas mixtures may be used with the approval of the Administrator.

5.1.1 Fuel. The FIA manufacturer's recommended fuel should be used. A 40 percent  $H_2$ /60 percent He or 40 percent  $H_2$ /60 percent  $N_2$  gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies

significantly from a mean value. Other mixtures may be used provided the tester can demonstrate to the Administrator that there is no oxygen synergism effect.

**5.1.2 Carrier Gas and Dilution Air Supply.** High purity air with less than 1 ppm of organic material (as propane or carbon equivalent), or less than 0.1 percent of the span value, whichever is greater.

**5.1.3 FIA Linearity Calibration Gases.** Low-, mid-, and high-range gas mixture standards with nominal propane concentrations of 20–30, 45–55, and 70–80 percent of the span value in air, respectively. Other calibration values and other span values may be used if it can be shown to the Administrator's satisfaction that equally accurate measurements would be achieved.

**5.1.4 Dilution Check Gas.** Gas mixture standard containing propane in air, approximately half the span value after dilution.

**5.2 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 must be heated to prevent any condensation unless it can be demonstrated that no condensation occurs.

## 6. Quality Control

**6.1 Required instrument quality control parameters** are found in the following sections:

**6.1.1** The FIA system must be calibrated as specified in section 7.1.

**6.1.2** The system drift check must be performed as specified in section 7.2.

**6.1.3** The dilution factor must be determined as specified in section 7.3.

**6.1.4** The system check must be conducted as specified in section 7.4.

### 6.2 Audits.

**6.2.1 Analysis Audit Procedure.** Immediately before each test, analyze an audit cylinder as described in section 7.2. The analysis audit must agree with the audit cylinder concentration within 10 percent.

**6.2.2 Audit Samples and Audit Sample Availability.** Audit samples will be supplied only to enforcement agencies for compliance tests. The availability of audit samples may be obtained by writing: Source Test Audit Coordinator (STAC) (MD-77B), Quality Assurance Division, Atmospheric Research and Exposure Assessment Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711 or by calling the STAC at (919) 541-7834. The request for the audit sample must be made at least 30

days prior to the scheduled compliance sample analysis.

**6.2.3 Audit Results.** Calculate the audit sample concentration according to the calculation procedure described in the audit instructions included with the audit sample. Fill in the audit sample concentration and the analyst's name on the audit response form included with the audit instructions. Send one copy to the EPA Regional Office or the appropriate enforcement agency, and a second copy to the STAC. The EPA Regional Office or the appropriate enforcement agency will report the results of the audit to the laboratory being audited. Include this response with the results of the compliance samples in relevant reports to the EPA Regional Office or the appropriate enforcement agency.

## 7. Calibration and Standardization

**7.1 FIA Calibration and Linearity Check.** Make necessary adjustments to the air and fuel supplies for the FIA and ignite the burner. Allow the FIA to warm up for the period recommended by the manufacturer. Inject a calibration gas into the measurement system after the dilution system and adjust the back-pressure regulator to the value required to achieve the flow rates specified by the manufacturer. Inject the zero and the high-range calibration gases and adjust the analyzer calibration to provide the proper responses. Inject the low- and mid-range gases and record the responses of the measurement system. The calibration and linearity of the system are acceptable if the responses for all four gases are within 5 percent of the respective gas values. If the performance of the system is not acceptable, repair or adjust the system and repeat the linearity check. Conduct a calibration and linearity check after assembling the analysis system and after a major change is made to the system.

**7.2 Systems Drift Checks.** Select the calibration gas that most closely approximates the concentration of the diluted captured emissions for conducting the drift checks. Introduce the zero and calibration gases at the calibration valve assembly, and verify that the appropriate gas flow rate and pressure are present at the FIA. Record the measurement system responses to the zero and calibration gases. The performance of the system is acceptable if the difference between the drift check measurement and the value obtained in section 7.1 is less than 3 percent of the span value. Alternatively, recalibrate the FIA as in section 7.1 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). The data that results in the lowest CE value shall be reported as the results for the test run. Conduct the system drift check at the end of each run.

**7.3 Determination of Dilution Factor.** Inject the dilution check gas into the measurement system before the dilution system and record the response. Calculate the dilution factor using Equation 204C-3.

**7.4 System Check.** Inject the high-range calibration gas at the inlet to the sampling probe while the dilution air is turned off. Record the response. The performance of the system is acceptable if the measurement system response is within 5 percent of the value obtained in section 7.1 for the high-range calibration gas. Conduct a system check before and after each test run.

## 8. Procedure

### 8.1 Determination of Volumetric Flow Rate of Captured Emissions

**8.1.1** Locate all points where emissions are captured from the affected facility. Using Method 1, determine the sampling points. Be sure to check each site for cyclonic or swirling flow.

**8.2.2** Measure the velocity at each sampling site at least once every hour during each sampling run using Method 2 or 2A.

### 8.2 Determination of VOC Content of Captured Emissions

**8.2.1 Analysis Duration.** Measure the VOC responses at each captured emissions point during the entire test run or, if applicable, while the process is operating. If there are multiple captured emissions locations, design a sampling system to allow a single FIA to be used to determine the VOC responses at all sampling locations.

#### 8.2.2 Gas VOC Concentration.

**8.2.2.1** Assemble the sample train as shown in Figure 204C-1. Calibrate the FIA according to the procedure in section 7.1.

**8.2.2.2** Set the dilution ratio and determine the dilution factor according to the procedure in section 7.3.

**8.2.2.3** Conduct a system check according to the procedure in section 7.4.

**8.2.2.4** 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.

**8.2.2.5** Inject zero gas at the calibration valve assembly. Measure the system response time as the time required for the system to reach the effluent concentration after the calibration valve has been returned to the effluent sampling position.

**8.2.2.6** Conduct a system check before, and a system drift check after,

each sampling run according to the procedures in sections 7.2 and 7.4. If the drift check following a run indicates unacceptable performance (see section 7.4), the run is not valid. Alternatively, recalibrate the FIA as in section 7.1 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). The data that results in the lowest CE value shall be reported as the results for the test run. The tester may elect to perform system drift checks during the run not to exceed one drift check per hour.

8.2.2.7 Verify that the sample lines, filter, and pump temperatures are  $120 \pm 5$  °C.

8.2.2.8 Begin sampling at the start of the test period and continue to sample during the entire run. Record the starting and ending times and any required process information as appropriate. If multiple captured emission locations are sampled using a single FIA, sample at each location for the same amount of time (e.g., 2 min.) and continue to switch from one location to another for the entire test run. Be sure that total sampling time at each location is the same at the end of the test run. Collect at least four separate measurements from each sample point during each hour of testing. Disregard the measurements at each sampling location until two times the response time of the measurement system has elapsed. Continue sampling for at least 1 minute and record the concentration measurements.

#### 8.2.3 Background Concentration.

**Note:** Not applicable when the building is used as the temporary total enclosure (TTE).

8.2.3.1 Locate all natural draft openings (NDO's) of the TTE. A sampling point shall be at the center of each NDO, unless otherwise approved by the Administrator. If there are more than six NDO's, choose six sampling points evenly spaced among the NDO's.

8.2.3.2 Assemble the sample train as shown in Figure 204C-2. Calibrate the FIA and conduct a system check

according to the procedures in sections 7.1 and 7.4.

8.2.3.3 Position the probe at the sampling location.

8.2.3.4 Determine the response time, conduct the system check, and sample according to the procedures described in sections 8.2.2.4 through 8.2.2.8.

8.2.4 Alternative Procedure. The direct interface sampling and analysis procedure described in section 7.2 of Method 18 may be used to determine the gas VOC concentration. The system must be designed to collect and analyze at least one sample every 10 minutes. If the alternative procedure is used to determine the VOC concentration of the captured emissions, it must also be used to determine the VOC concentration of the uncaptured emissions.

### 9. Data Analysis and Calculations

#### 9.1 Nomenclature.

$A_i$ =area of NDO i, ft<sup>2</sup>.

$A_N$ =total area of all NDO's in the enclosure, ft<sup>2</sup>.

$C_A$  = actual concentration of the dilution check gas, ppm propane.

$C_{Bi}$ =corrected average VOC concentration of background emissions at point i, ppm propane.

$C_B$ =average background concentration, ppm propane.

$C_{DH}$ =average measured concentration for the drift check calibration gas, ppm propane.

$C_{D0}$ =average system drift check concentration for zero concentration gas, ppm propane.

$C_H$ =actual concentration of the drift check calibration gas, ppm propane.

$C_i$ =uncorrected average background VOC concentration measured at point i, ppm propane.

$C_j$ =uncorrected average VOC concentration measured at point j, ppm propane.

$C_M$ =measured concentration of the dilution check gas, ppm propane.

DF=dilution factor.

G=total VOC content of captured emissions, kg.

$K_1=1.830 \times 10^{-6}$  kg/(m<sup>3</sup> - ppm).

n=number of measurement points.

$Q_{Gj}$ =average effluent volumetric flow rate corrected to standard conditions at captured emissions point j, m<sup>3</sup>/min.

$\Theta_C$ =total duration of CE sampling run, min.

#### 9.2 Calculations.

##### 9.2.1 Total VOC Captured Emissions.

$$G = \sum_{j=1}^n (C_{Gj} - C_B) Q_{Gj} \Theta_C K_1 \quad \text{Eq. 204C-1}$$

##### 9.2.2 VOC Concentration of the Captured Emissions at Point j.

$$C_{Gj} = DF (C_j - C_{D0}) \frac{C_H}{C_{DH} - C_{D0}} \quad \text{Eq. 204C-2}$$

##### 9.2.3 Dilution Factor.

$$DF = \frac{C_A}{C_M} \quad \text{Eq. 204C-3}$$

##### 9.2.4 Background VOC Concentration at Point i.

$$C_{Bi} = (C_i - C_{D0}) \frac{C_H}{C_{DH} - C_{D0}} \quad \text{Eq. 204C-4}$$

##### 9.2.5 Average Background Concentration.

$$C_B = \frac{\sum_{i=1}^n C_{Bi} A_i}{A_N} \quad \text{Eq. 204C-5}$$

**Note:** If the concentration at each point is within 20 percent of the average concentration of all points, then use the arithmetic average.

### 10. Method Performance

The measurement uncertainties are estimated for each captured or uncaptured emissions point as follows:  $Q_{Gj} = \pm 5.5$  percent and  $C_{Gj} = \pm 5$  percent. Based on these numbers, the probable uncertainty for G is estimated at about  $\pm 7.4$  percent.

### 11. Diagrams

BILLING CODE 6560-SO-P

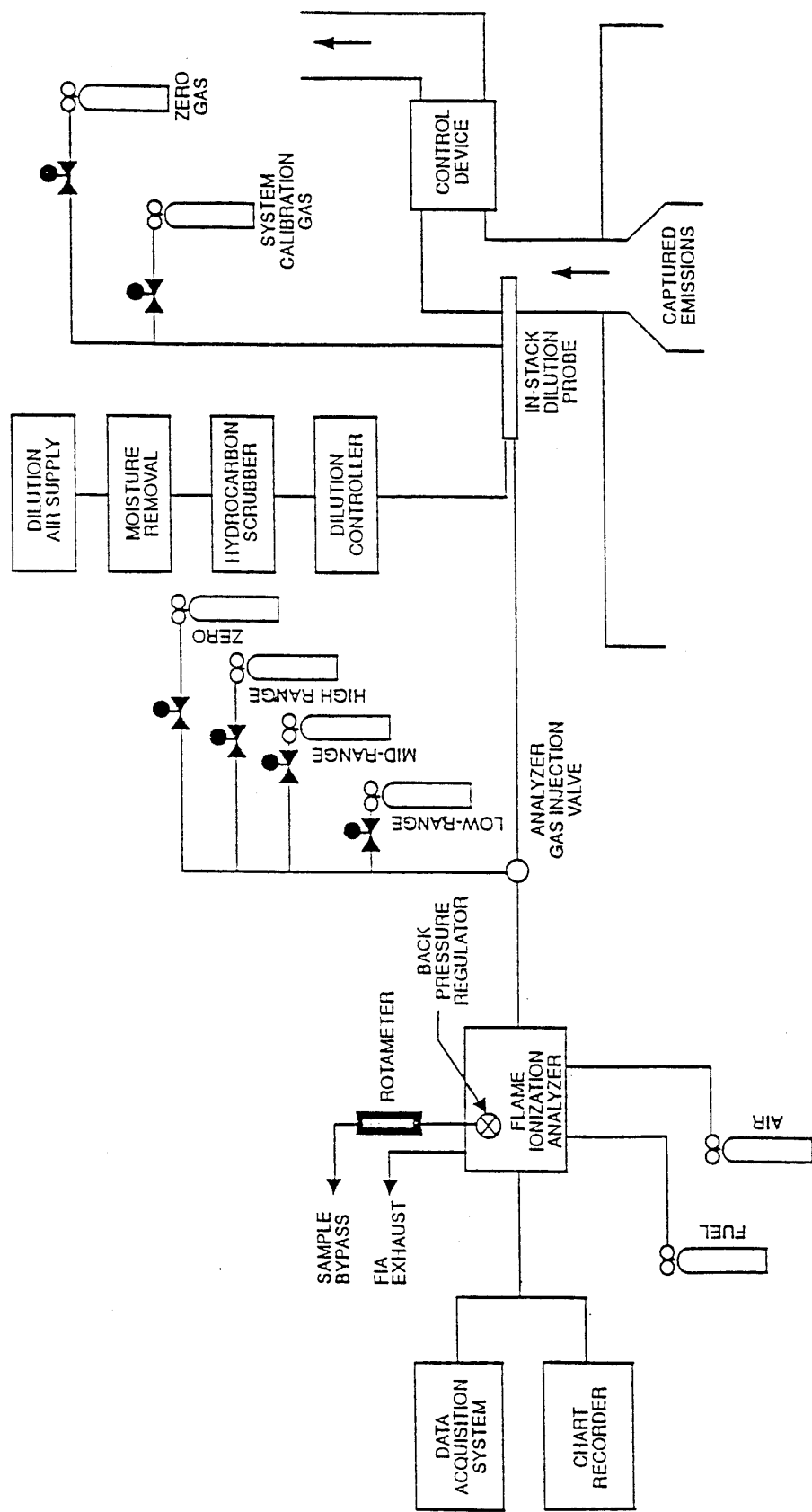
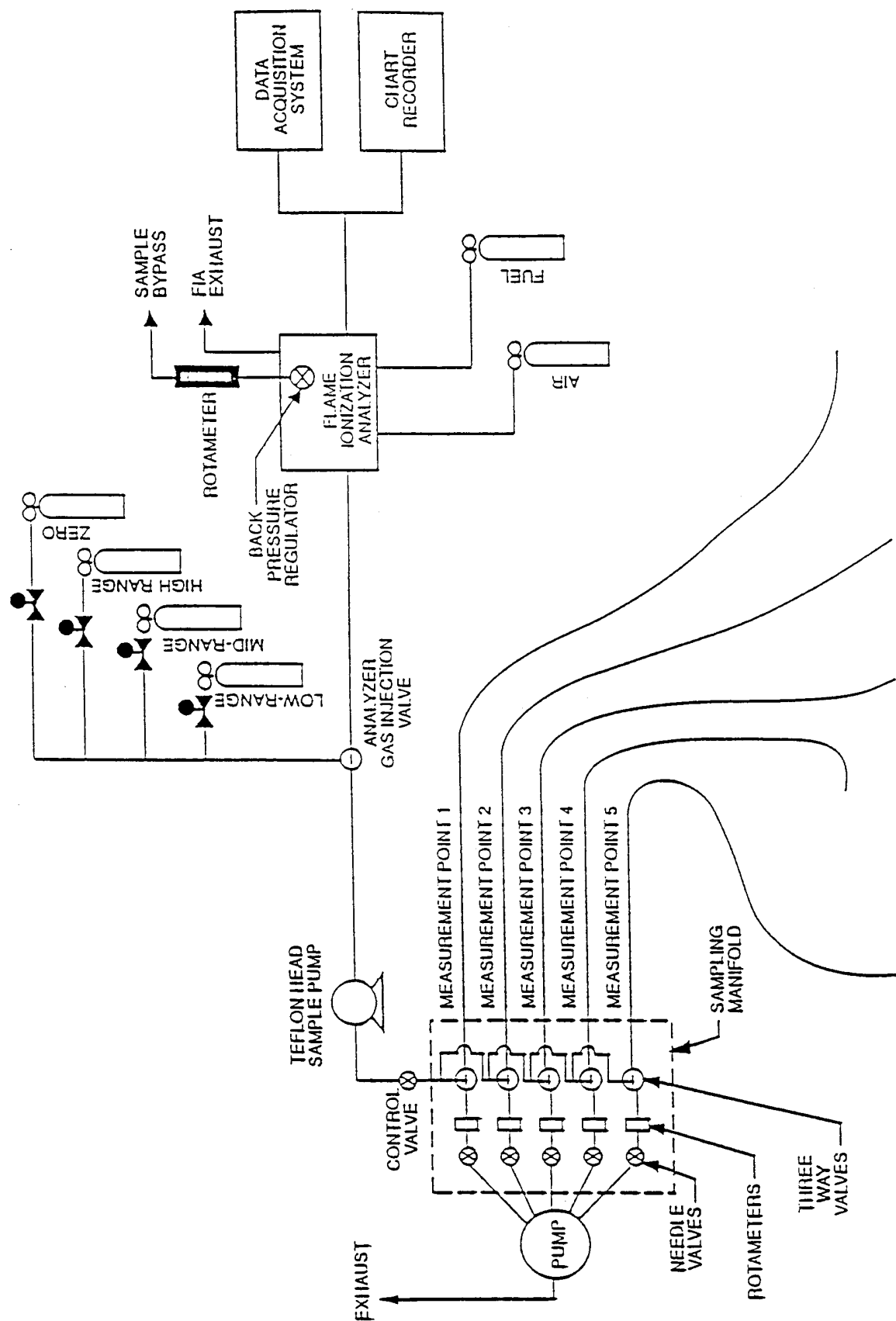


Figure 204C-1. Captured emissions measurement system.



## Method 204D—Volatile Organic Compounds Emissions in Uncaptured Stream From Temporary Total Enclosure

### 1. Scope and Application

1.1 Applicability. This procedure is applicable for determining the uncaptured volatile organic compounds (VOC) emissions from a temporary total enclosure (TTE). It is intended to be used as a segment in the development of liquid/gas or gas/gas protocols for determining VOC capture efficiency (CE) for surface coating and printing operations.

1.2 Principle. The amount of uncaptured VOC emissions (F) from the TTE is calculated as the sum of the products of the VOC content ( $C_{Fj}$ ), the flow rate ( $Q_{Fj}$ ) from each uncaptured emissions point, and the sampling time ( $\Theta_F$ ).

1.3 Sampling Requirements. A CE test shall consist of at least three sampling runs. Each run shall cover at least one complete production cycle, but shall be at least 3 hours long. The sampling time for each run need not exceed 8 hours, even if the production cycle has not been completed. Alternative sampling times may be used with the approval of the Administrator.

### 2. Summary of Method

A gas sample is extracted from the uncaptured exhaust duct of a TTE through a heated sample line and, if necessary, a glass fiber filter to a flame ionization analyzer (FIA).

### 3. Safety

Because this procedure is often applied in highly explosive areas, caution and care should be exercised in choosing, installing, and using the appropriate equipment.

### 4. Equipment and Supplies

Mention of trade names or company products does not constitute endorsement. All gas concentrations (percent, ppm) are by volume, unless otherwise noted.

4.1 Gas VOC Concentration. A schematic of the measurement system is shown in Figure 204D-1. The main components are as follows:

4.1.1 Sample Probe. Stainless steel or equivalent. The probe shall be heated to prevent VOC condensation.

4.1.2 Calibration Valve Assembly. Three-way valve assembly at the outlet of the sample probe to direct the zero and calibration gases to the analyzer. Other methods, such as quick-connect lines, to route calibration gases to the outlet of the sample probe are acceptable.

4.1.3 Sample Line. Stainless steel or Teflon tubing to transport the sample gas to the analyzer. The sample line must be heated to prevent condensation.

4.1.4 Sample Pump. A leak-free pump, to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. The components of the pump that contact the gas stream shall be constructed of stainless steel or Teflon. The sample pump must be heated to prevent condensation.

4.1.5 Sample Flow Rate Control. A sample flow rate control valve and rotameter, or equivalent, to maintain a constant sampling rate within 10 percent. The flow control valve and rotameter must be heated to prevent condensation. A control valve may also be located on the sample pump bypass loop to assist in controlling the sample pressure and flow rate.

4.1.6 Sample Gas Manifold. Capable of diverting a portion of the sample gas stream to the FIA, and the remainder to the bypass discharge vent. The manifold components shall be constructed of stainless steel or Teflon. If emissions are to be measured at multiple locations, the measurement system shall be designed to use separate sampling probes, lines, and pumps for each measurement location and a common sample gas manifold and FIA. The sample gas manifold and connecting lines to the FIA must be heated to prevent condensation.

4.1.7 Organic Concentration Analyzer. An FIA with a span value of 1.5 times the expected concentration as propane; however, other span values may be used if it can be demonstrated to the Administrator's satisfaction that they would provide more accurate measurements. The system shall be capable of meeting or exceeding the following specifications:

4.1.7.1 Zero Drift. Less than  $\pm 3.0$  percent of the span value.

4.1.7.2 Calibration Drift. Less than  $\pm 3.0$  percent of the span value.

4.1.7.3 Calibration Error. Less than  $\pm 5.0$  percent of the calibration gas value.

4.1.7.4 Response Time. Less than 30 seconds.

4.1.8 Integrator/Data Acquisition System. An analog or digital device or computerized data acquisition system used to integrate the FIA response or compute the average response and record measurement data. The minimum data sampling frequency for computing average or integrated values is one measurement value every 5 seconds. The device shall be capable of recording average values at least once per minute.

4.2 Uncaptured Emissions Volumetric Flow Rate.

4.2.1 Method 2 or 2A Apparatus. For determining volumetric flow rate.

4.2.2 Method 3 Apparatus and Reagents. For determining molecular weight of the gas stream. An estimate of the molecular weight of the gas stream may be used if approved by the Administrator.

4.2.3 Method 4 Apparatus and Reagents. For determining moisture content, if necessary.

4.3 Temporary Total Enclosure. The criteria for designing an acceptable TTE are specified in Method 204.

### 5. Reagents and Standards

5.1 Calibration and Other Gases. Gases used for calibration, fuel, and combustion air (if required) are contained in compressed gas cylinders. All calibration gases shall be traceable to National Institute of Standards and Technology standards and shall be certified by the manufacturer to  $\pm 1$  percent of the tag value. 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  $\pm 2$  percent from the certified value. For calibration gas values not generally available, dilution systems calibrated using Method 205 may be used. Alternative methods for preparing calibration gas mixtures may be used with the approval of the Administrator.

5.1.1 Fuel. The FIA manufacturer's recommended fuel should be used. A 40 percent  $H_2$ /60 percent He or 40 percent  $H_2$ /60 percent  $N_2$  gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value. Other mixtures may be used provided the tester can demonstrate to the Administrator that there is no oxygen synergism effect.

5.1.2 Carrier Gas. High purity air with less than 1 ppm of organic material (as propane or carbon equivalent) or less than 0.1 percent of the span value, whichever is greater.

5.1.3 FIA Linearity Calibration Gases. Low-, mid-, and high-range gas mixture standards with nominal propane concentrations of 20–30, 45–55, and 70–80 percent of the span value in air, respectively. Other calibration values and other span values may be used if it can be shown to the Administrator's satisfaction that equally accurate measurements would be achieved.

5.2 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 must be heated to prevent any condensation unless it can be demonstrated that no condensation occurs.

## 6. Quality Control

6.1 Required instrument quality control parameters are found in the following sections:

- 6.1.1 The FIA system must be calibrated as specified in section 7.1.
- 6.1.2 The system drift check must be performed as specified in section 7.2.
- 6.1.3 The system check must be conducted as specified in section 7.3.

### 6.2 Audits.

6.2.1 Analysis Audit Procedure. Immediately before each test, analyze an audit cylinder as described in section 7.2. The analysis audit must agree with the audit cylinder concentration within 10 percent.

6.2.2 Audit Samples and Audit Sample Availability. Audit samples will be supplied only to enforcement agencies for compliance tests. The availability of audit samples may be obtained by writing: Source Test Audit Coordinator (STAC) (MD-77B) Quality Assurance Division, Atmospheric Research and Exposure Assessment Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711 or by calling the STAC at (919) 541-7834. The request for the audit sample must be made at least 30 days prior to the scheduled compliance sample analysis.

6.2.3 Audit Results. Calculate the audit sample concentration according to the calculation procedure described in the audit instructions included with the audit sample. Fill in the audit sample concentration and the analyst's name on the audit response form included with the audit instructions. Send one copy to the EPA Regional Office or the appropriate enforcement agency, and a second copy to the STAC. The EPA Regional Office or the appropriate enforcement agency will report the results of the audit to the laboratory being audited. Include this response with the results of the compliance samples in relevant reports to the EPA Regional Office or the appropriate enforcement agency.

## 7. Calibration and Standardization

7.1 FIA Calibration and Linearity Check. Make necessary adjustments to the air and fuel supplies for the FIA and ignite the burner. Allow the FIA to warm up for the period recommended by the manufacturer. Inject a calibration gas into the measurement system and adjust the back-pressure regulator to the value required to achieve the flow rates

specified by the manufacturer. Inject the zero and the high-range calibration gases and adjust the analyzer calibration to provide the proper responses. Inject the low and mid-range gases and record the responses of the measurement system. The calibration and linearity of the system are acceptable if the responses for all four gases are within 5 percent of the respective gas values. If the performance of the system is not acceptable, repair or adjust the system and repeat the linearity check. Conduct a calibration and linearity check after assembling the analysis system and after a major change is made to the system.

7.2 Systems Drift Checks. Select the calibration gas concentration that most closely approximates that of the uncaptured gas emissions concentration to conduct the drift checks. Introduce the zero and calibration gases at the calibration valve assembly and verify that the appropriate gas flow rate and pressure are present at the FIA. Record the measurement system responses to the zero and calibration gases. The performance of the system is acceptable if the difference between the drift check measurement and the value obtained in section 7.1 is less than 3 percent of the span value. Alternatively, recalibrate the FIA as in section 7.1 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). The data that results in the lowest CE value shall be reported as the results for the test run. Conduct a system drift check at the end of each run.

7.3 System Check. Inject the high-range calibration gas at the inlet of the sampling probe and record the response. The performance of the system is acceptable if the measurement system response is within 5 percent of the value obtained in section 7.1 for the high-range calibration gas. Conduct a system check before each test run.

## 8. Procedure

### 8.1 Determination of Volumetric Flow Rate of Uncaptured Emissions

8.1.1 Locate all points where uncaptured emissions are exhausted from the TTE. Using Method 1, determine the sampling points. Be sure to check each site for cyclonic or swirling flow.

8.1.2 Measure the velocity at each sampling site at least once every hour during each sampling run using Method 2 or 2A.

### 8.2 Determination of VOC Content of Uncaptured Emissions.

8.2.1 Analysis Duration. Measure the VOC responses at each uncaptured emission point during the entire test run

or, if applicable, while the process is operating. If there are multiple emission locations, design a sampling system to allow a single FIA to be used to determine the VOC responses at all sampling locations.

### 8.2.2 Gas VOC Concentration.

8.2.2.1 Assemble the sample train as shown in Figure 204D-1. Calibrate the FIA and conduct a system check according to the procedures in sections 7.1 and 7.3, respectively.

8.2.2.2 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.

8.2.2.3 Inject zero gas at the calibration valve assembly. Allow the measurement system response to reach zero. Measure the system response time as the time required for the system to reach the effluent concentration after the calibration valve has been returned to the effluent sampling position.

8.2.2.4 Conduct a system check before, and a system drift check after, each sampling run according to the procedures in sections 7.2 and 7.3. If the drift check following a run indicates unacceptable performance (see section 7.3), the run is not valid. Alternatively, recalibrate the FIA as in section 7.1 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). The data that results in the lowest CE value shall be reported as the results for the test run. The tester may elect to perform system drift checks during the run not to exceed one drift check per hour.

8.2.2.5 Verify that the sample lines, filter, and pump temperatures are  $120 \pm 5$  °C.

8.2.2.6 Begin sampling at the start of the test period and continue to sample during the entire run. Record the starting and ending times and any required process information, as appropriate. If multiple emission locations are sampled using a single FIA, sample at each location for the same amount of time (e.g., 2 min.) and continue to switch from one location to another for the entire test run. Be sure that total sampling time at each location is the same at the end of the test run. Collect at least four separate measurements from each sample point during each hour of testing. Disregard the response measurements at each sampling location until 2 times the response time of the measurement system has elapsed. Continue sampling for at least 1 minute and record the concentration measurements.

### 8.2.3 Background Concentration.



8.2.3.1 Locate all natural draft openings (NDO's) of the TTE. A sampling point shall be at the center of each NDO, unless otherwise approved by the Administrator. If there are more than six NDO's, choose six sampling points evenly spaced among the NDO's.

8.2.3.2 Assemble the sample train as shown in Figure 204D-2. Calibrate the FIA and conduct a system check according to the procedures in sections 7.1 and 7.3.

8.2.3.3 Position the probe at the sampling location.

8.2.3.4 Determine the response time, conduct the system check, and sample according to the procedures described in sections 8.2.2.3 through 8.2.2.6.

8.2.4 Alternative Procedure. The direct interface sampling and analysis procedure described in section 7.2 of Method 18 may be used to determine the gas VOC concentration. The system must be designed to collect and analyze at least one sample every 10 minutes. If the alternative procedure is used to determine the VOC concentration of the uncaptured emissions in a gas/gas protocol, it must also be used to determine the VOC concentration of the captured emissions. If a tester wishes to conduct a liquid/gas protocol using a gas chromatograph, the tester must use Method 204F for the liquid stream. A gas chromatograph is not an acceptable alternative to the FIA in Method 204A.

## 9. Data Analysis and Calculations

### 9.1 Nomenclature.

$A_i$ =area of NDO  $i$ , ft<sup>2</sup>.

$A_N$ =total area of all NDO's in the enclosure, ft<sup>2</sup>.

$C_{Bi}$ =corrected average VOC concentration of background emissions at point  $i$ , ppm propane.

$C_B$ =average background concentration, ppm propane.

$C_{DH}$ =average measured concentration for the drift check calibration gas, ppm propane.

$C_{DO}$ =average system drift check concentration for zero concentration gas, ppm propane.

$C_{Fj}$ =corrected average VOC concentration of uncaptured emissions at point  $j$ , ppm propane.

$C_H$ =actual concentration of the drift check calibration gas, ppm propane.

$C_i$ =uncorrected average background VOC concentration at point  $i$ , ppm propane.

$C_j$ =uncorrected average VOC concentration measured at point  $j$ , ppm propane.

$F$ =total VOC content of uncaptured emissions, kg.

$K_1=1.830 \times 10^{-6}$  kg/(m<sup>3</sup>-ppm).

$n$ =number of measurement points.

$Q_{Fj}$ =average effluent volumetric flow rate corrected to standard conditions at uncaptured emissions point  $j$ , m<sup>3</sup>/min.

$\Theta_F$ =total duration of uncaptured emissions sampling run, min.

## 9.2 Calculations.

### 9.2.1 Total Uncaptured VOC Emissions.

$$F = \sum_{j=1}^n (C_{Fj} - C_B) Q_{Fj} \theta_F K_1 \quad \text{Eq. 204D-1}$$

### 9.2.2 VOC Concentration of the Uncaptured Emissions at Point $j$ .

$$C_{Fj} = (C_j - C_{DO}) \frac{C_H}{C_{DH} - C_{DO}} \quad \text{Eq. 204D-2}$$

### 9.2.3 Background VOC Concentration at Point $i$ .

$$C_{Bi} = (C_i - C_{DO}) \frac{C_H}{C_{DH} - C_{DO}} \quad \text{Eq. 204D-3}$$

### 9.2.4 Average Background Concentration.

$$C_B = \frac{\sum_{i=1}^n C_{Bi} A_i}{A_N} \quad \text{Eq. 204D-4}$$

**Note:** If the concentration at each point is within 20 percent of the average concentration of all points, use the arithmetic average.

## 10. Method Performance

The measurement uncertainties are estimated for each uncaptured emission point as follows:  $Q_{Fj}=\pm 5.5$  percent and  $C_{Fj}=\pm 5.0$  percent. Based on these numbers, the probable uncertainty for  $F$  is estimated at about  $\pm 7.4$  percent.

## 11. Diagrams

BILLING CODE 6560-50-P

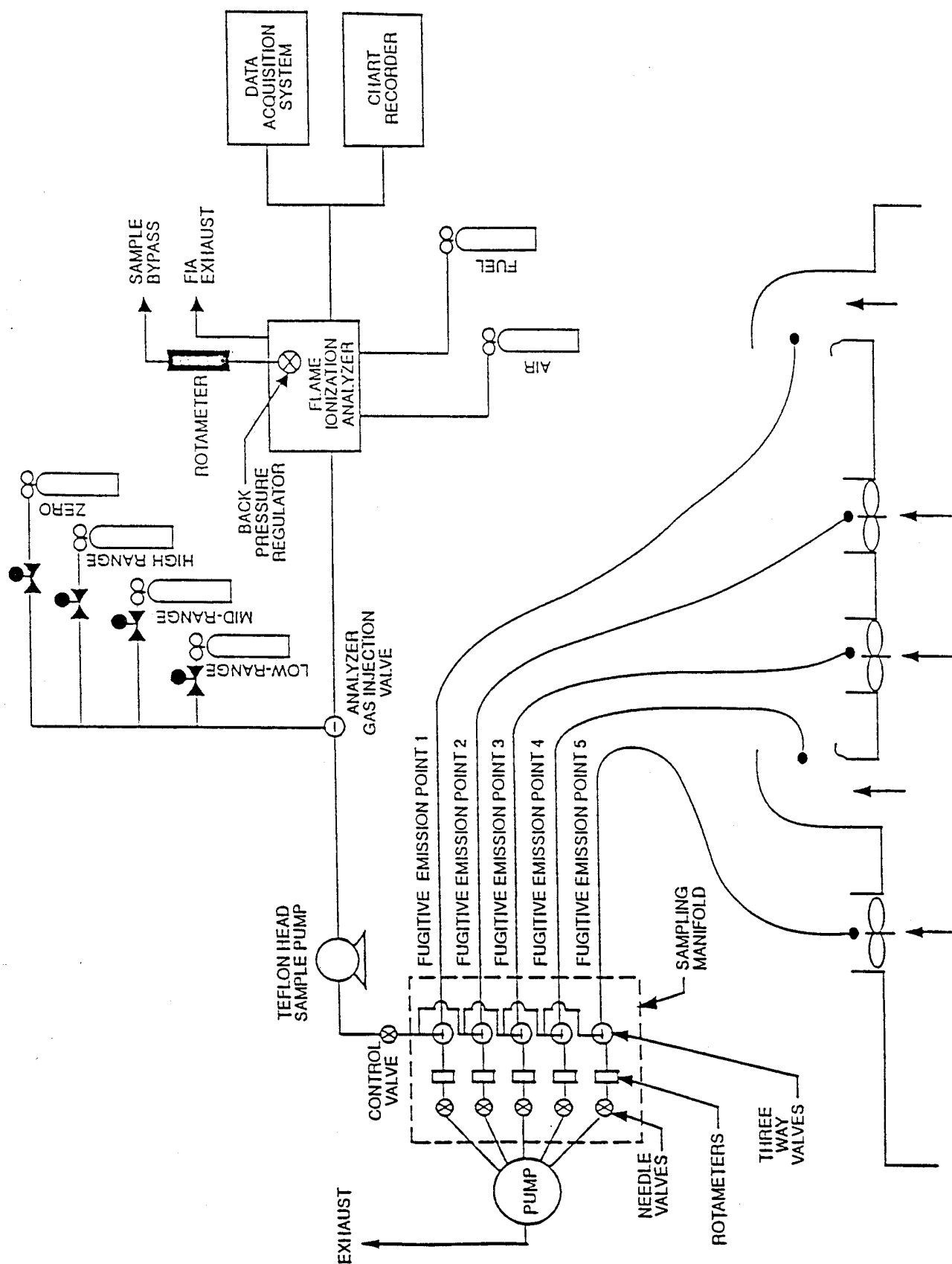


Figure 204D-1. Fugitive emissions measurement system.

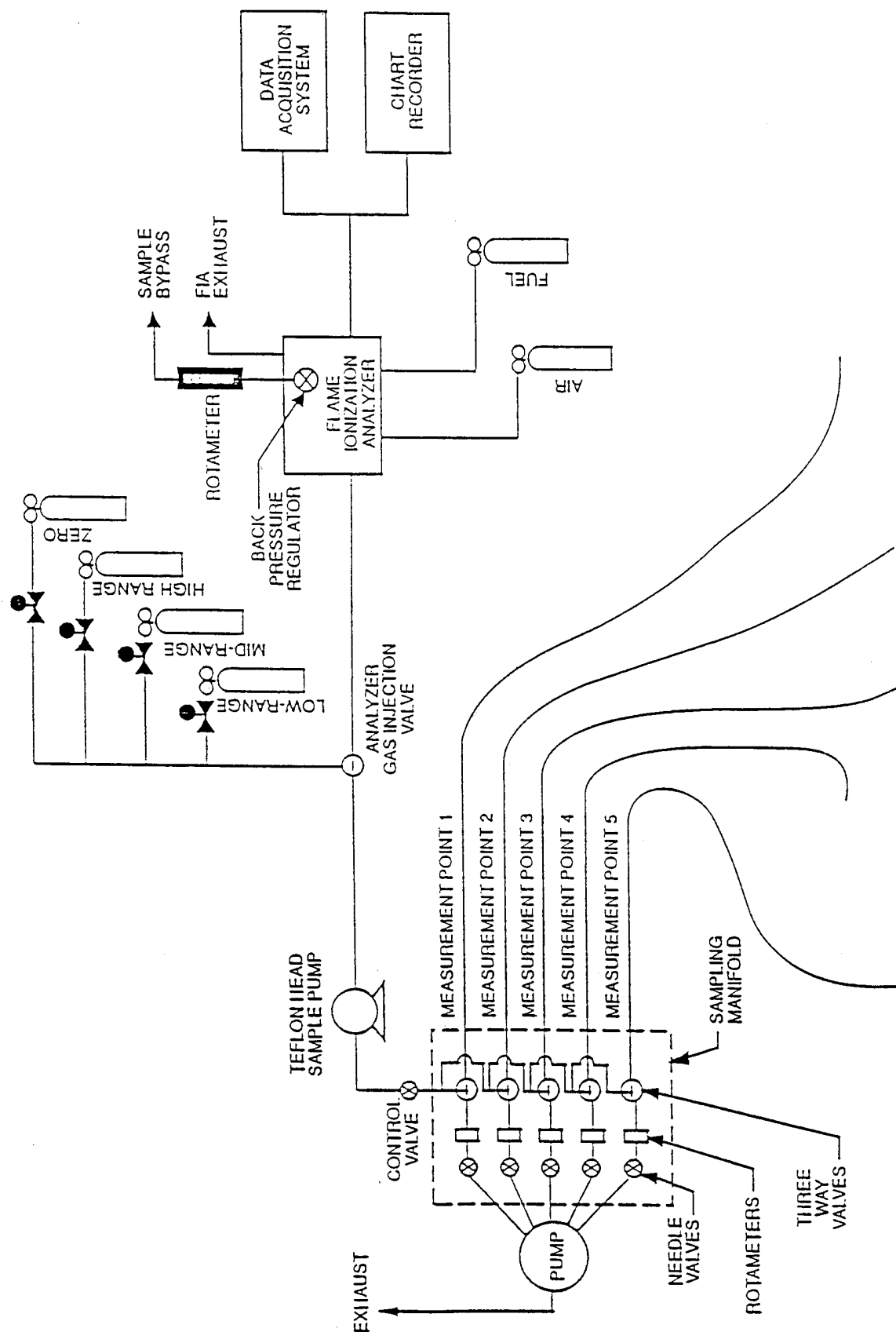


Figure 204D-2. Background measurement system.

## Method 204E—Volatile Organic Compounds Emissions in Uncaptured Stream From Building Enclosure

### 1. Scope and Application

1.1 Applicability. This procedure is applicable for determining the uncaptured volatile organic compounds (VOC) emissions from a building enclosure (BE). It is intended to be used in the development of liquid/gas or gas/gas protocols for determining VOC capture efficiency (CE) for surface coating and printing operations.

1.2 Principle. The total amount of uncaptured VOC emissions ( $F_B$ ) from the BE is calculated as the sum of the products of the VOC content ( $C_{Fj}$ ) of each uncaptured emissions point, the flow rate ( $Q_{Fj}$ ) at each uncaptured emissions point, and time ( $\Theta_F$ ).

1.3 Sampling Requirements. A CE test shall consist of at least three sampling runs. Each run shall cover at least one complete production cycle, but shall be at least 3 hours long. The sampling time for each run need not exceed 8 hours, even if the production cycle has not been completed. Alternative sampling times may be used with the approval of the Administrator.

### 2. Summary of Method

A gas sample is extracted from the uncaptured exhaust duct of a BE through a heated sample line and, if necessary, a glass fiber filter to a flame ionization analyzer (FIA).

### 3. Safety

Because this procedure is often applied in highly explosive areas, caution and care should be exercised in choosing, installing, and using the appropriate equipment.

### 4. Equipment and Supplies

Mention of trade names or company products does not constitute endorsement. All gas concentrations (percent, ppm) are by volume, unless otherwise noted.

4.1 Gas VOC Concentration. A schematic of the measurement system is shown in Figure 204E-1. The main components are as follows:

4.1.1 Sample Probe. Stainless steel or equivalent. The probe shall be heated to prevent VOC condensation.

4.1.2 Calibration Valve Assembly. Three-way valve assembly at the outlet of the sample probe to direct the zero and calibration gases to the analyzer. Other methods, such as quick-connect lines, to route calibration gases to the outlet of the sample probe are acceptable.

4.1.3 Sample Line. Stainless steel or Teflon tubing to transport the sample

gas to the analyzer. The sample line must be heated to prevent condensation.

4.1.4 Sample Pump. A leak-free pump, to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. The components of the pump that contact the gas stream shall be constructed of stainless steel or Teflon. The sample pump must be heated to prevent condensation.

4.1.5 Sample Flow Rate Control. A sample flow rate control valve and rotameter, or equivalent, to maintain a constant sampling rate within 10 percent. The flow rate control valve and rotameter must be heated to prevent condensation. A control valve may also be located on the sample pump bypass loop to assist in controlling the sample pressure and flow rate.

4.1.6 Sample Gas Manifold. Capable of diverting a portion of the sample gas stream to the FIA, and the remainder to the bypass discharge vent. The manifold components shall be constructed of stainless steel or Teflon. If emissions are to be measured at multiple locations, the measurement system shall be designed to use separate sampling probes, lines, and pumps for each measurement location, and a common sample gas manifold and FIA. The sample gas manifold must be heated to prevent condensation.

4.1.7 Organic Concentration Analyzer. An FIA with a span value of 1.5 times the expected concentration as propane; however, other span values may be used if it can be demonstrated to the Administrator's satisfaction that they would provide equally accurate measurements. The system shall be capable of meeting or exceeding the following specifications:

4.1.7.1 Zero Drift. Less than  $\pm 3.0$  percent of the span value.

4.1.7.2 Calibration Drift. Less than  $\pm 3.0$  percent of the span value.

4.1.7.3 Calibration Error. Less than  $\pm 5.0$  percent of the calibration gas value.

4.1.7.4 Response Time. Less than 30 seconds.

4.1.8 Integrator/Data Acquisition System. An analog or digital device or computerized data acquisition system used to integrate the FIA response or compute the average response and record measurement data. The minimum data sampling frequency for computing average or integrated values is one measurement value every 5 seconds. The device shall be capable of recording average values at least once per minute.

4.2 Uncaptured Emissions Volumetric Flow Rate.

4.2.1 Flow Direction Indicators. Any means of indicating inward or outward

flow, such as light plastic film or paper streamers, smoke tubes, filaments, and sensory perception.

4.2.2 Method 2 or 2A Apparatus. For determining volumetric flow rate. Anemometers or similar devices calibrated according to the manufacturer's instructions may be used when low velocities are present. Vane anemometers (Young-maximum response propeller), specialized pitots with electronic manometers (e.g., Shortridge Instruments Inc., Airdata Multimeter 860) are commercially available with measurement thresholds of 15 and 8 mpm (50 and 25 fpm), respectively.

4.2.3 Method 3 Apparatus and Reagents. For determining molecular weight of the gas stream. An estimate of the molecular weight of the gas stream may be used if approved by the Administrator.

4.2.4 Method 4 Apparatus and Reagents. For determining moisture content, if necessary.

4.3 Building Enclosure. The criteria for an acceptable BE are specified in Method 204.

### 5. Reagents and Standards

5.1 Calibration and Other Gases. Gases used for calibration, fuel, and combustion air (if required) are contained in compressed gas cylinders. All calibration gases shall be traceable to National Institute of Standards and Technology standards and shall be certified by the manufacturer to  $\pm 1$  percent of the tag value. 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  $\pm 2$  percent from the certified value. For calibration gas values not generally available, dilution systems calibrated using Method 205 may be used. Alternative methods for preparing calibration gas mixtures may be used with the approval of the Administrator.

5.1.1 Fuel. The FIA manufacturer's recommended fuel should be used. A 40 percent  $H_2$ /60 percent He or 40 percent  $H_2$ /60 percent  $N_2$  gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value. Other mixtures may be used provided the tester can demonstrate to the Administrator that there is no oxygen synergism effect.

5.1.2 Carrier Gas. High purity air with less than 1 ppm of organic material (propane or carbon equivalent) or less than 0.1 percent of the span value, whichever is greater.

5.1.3 FIA Linearity Calibration Gases. Low-, mid-, and high-range gas mixture standards with nominal propane concentrations of 20–30, 45–55, and 70–80 percent of the span value in air, respectively. Other calibration values and other span values may be used if it can be shown to the Administrator's satisfaction that equally accurate measurements would be achieved.

5.2 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 must be heated to prevent any condensation unless it can be demonstrated that no condensation occurs.

## 6. Quality Control

6.1 Required instrument quality control parameters are found in the following sections:

6.1.1 The FIA system must be calibrated as specified in section 7.1.

6.1.2 The system drift check must be performed as specified in section 7.2.

6.1.3 The system check must be conducted as specified in section 7.3.

### 6.2 Audits.

6.2.1 Analysis Audit Procedure. Immediately before each test, analyze an audit cylinder as described in section 7.2. The analysis audit must agree with the audit cylinder concentration within 10 percent.

6.2.2 Audit Samples and Audit Sample Availability. Audit samples will be supplied only to enforcement agencies for compliance tests. The availability of audit samples may be obtained by writing: Source Test Audit Coordinator (STAC) (MD-77B), Quality Assurance Division, Atmospheric Research and Exposure Assessment Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711 or by calling the STAC at (919) 541-7834. The request for the audit sample must be made at least 30 days prior to the scheduled compliance sample analysis.

6.2.3 Audit Results. Calculate the audit sample concentration according to the calculation procedure described in the audit instructions included with the audit sample. Fill in the audit sample concentration and the analyst's name on the audit response form included with the audit instructions. Send one copy to the EPA Regional Office or the appropriate enforcement agency, and a second copy to the STAC. The EPA Regional Office or the appropriate enforcement agency will report the results of the audit to the laboratory being audited. Include this response with the results of the compliance

samples in relevant reports to the EPA Regional Office or the appropriate enforcement agency.

## 7. Calibration and Standardization

7.1 FIA Calibration and Linearity Check. Make necessary adjustments to the air and fuel supplies for the FIA and ignite the burner. Allow the FIA to warm up for the period recommended by the manufacturer. Inject a calibration gas into the measurement system and adjust the back-pressure regulator to the value required to achieve the flow rates specified by the manufacturer. Inject the zero-and the high-range calibration gases, and adjust the analyzer calibration to provide the proper responses. Inject the low-and mid-range gases and record the responses of the measurement system. The calibration and linearity of the system are acceptable if the responses for all four gases are within 5 percent of the respective gas values. If the performance of the system is not acceptable, repair or adjust the system and repeat the linearity check. Conduct a calibration and linearity check after assembling the analysis system and after a major change is made to the system.

7.2 Systems Drift Checks. Select the calibration gas that most closely approximates the concentration of the captured emissions for conducting the drift checks. Introduce the zero and calibration gases at the calibration valve assembly and verify that the appropriate gas flow rate and pressure are present at the FIA. Record the measurement system responses to the zero and calibration gases. The performance of the system is acceptable if the difference between the drift check measurement and the value obtained in section 7.1 is less than 3 percent of the span value. Alternatively, recalibrate the FIA as in section 7.1 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). The data that results in the lowest CE value shall be reported as the results for the test run. Conduct a system drift check at the end of each run.

7.3 System Check. Inject the high-range calibration gas at the inlet of the sampling probe and record the response. The performance of the system is acceptable if the measurement system response is within 5 percent of the value obtained in section 7.1 for the high-range calibration gas. Conduct a system check before each test run.

## 8. Procedure

8.1 Preliminary Determinations. The following points are considered exhaust

points and should be measured for volumetric flow rates and VOC concentrations:

8.1.1 Forced Draft Openings. Any opening in the facility with an exhaust fan. Determine the volumetric flow rate according to Method 2.

8.1.2 Roof Openings. Any openings in the roof of a facility which does not contain fans are considered to be exhaust points. Determine volumetric flow rate from these openings. Use the appropriate velocity measurement devices (e.g., propeller anemometers).

8.2 Determination of Flow Rates. 8.2.1 Measure the volumetric flow rate at all locations identified as exhaust points in section 8.1. Divide each exhaust opening into nine equal areas for rectangular openings and into eight equal areas for circular openings.

8.2.2 Measure the velocity at each site at least once every hour during each sampling run using Method 2 or 2A, if applicable, or using the low velocity instruments in section 4.2.2.

8.3 Determination of VOC Content of Uncaptured Emissions.

8.3.1 Analysis Duration. Measure the VOC responses at each uncaptured emissions point during the entire test run or, if applicable, while the process is operating. If there are multiple emissions locations, design a sampling system to allow a single FIA to be used to determine the VOC responses at all sampling locations.

8.3.2 Gas VOC Concentration.

8.3.2.1 Assemble the sample train as shown in Figure 204E-1. Calibrate the FIA and conduct a system check according to the procedures in sections 7.1 and 7.3, respectively.

8.3.2.2 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.

8.3.2.3 Inject zero gas at the calibration valve assembly. Allow the measurement system response to reach zero. Measure the system response time as the time required for the system to reach the effluent concentration after the calibration valve has been returned to the effluent sampling position.

8.3.2.4 Conduct a system check before, and a system drift check after, each sampling run according to the procedures in sections 7.2 and 7.3. If the drift check following a run indicates unacceptable performance (see section 7.3), the run is not valid. Alternatively, recalibrate the FIA as in section 7.1 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). The data that results in the lowest CE value shall be reported as the results for

the test run. The tester may elect to perform drift checks during the run, not to exceed one drift check per hour.

8.3.2.5 Verify that the sample lines, filter, and pump temperatures are  $120 \pm 5$  °C.

8.3.2.6 Begin sampling at the start of the test period and continue to sample during the entire run. Record the starting and ending times, and any required process information, as appropriate. If multiple emission locations are sampled using a single FIA, sample at each location for the same amount of time (e.g., 2 minutes) and continue to switch from one location to another for the entire test run. Be sure that total sampling time at each location is the same at the end of the test run. Collect at least four separate measurements from each sample point during each hour of testing. Disregard the response measurements at each sampling location until 2 times the response time of the measurement system has elapsed. Continue sampling for at least 1 minute, and record the concentration measurements.

8.4 Alternative Procedure. The direct interface sampling and analysis procedure described in section 7.2 of Method 18 may be used to determine

the gas VOC concentration. The system must be designed to collect and analyze at least one sample every 10 minutes. If the alternative procedure is used to determine the VOC concentration of the uncaptured emissions in a gas/gas protocol, it must also be used to determine the VOC concentration of the captured emissions. If a tester wishes to conduct a liquid/gas protocol using a gas chromatograph, the tester must use Method 204F for the liquid stream. A gas chromatograph is not an acceptable alternative to the FIA in Method 204A.

## 9. Data Analysis and Calculations

### 9.1 Nomenclature.

$C_{DH}$ =average measured concentration for the drift check calibration gas, ppm propane.

$C_{DO}$ =average system drift check concentration for zero concentration gas, ppm propane.

$C_{Fj}$ =corrected average VOC concentration of uncaptured emissions at point j, ppm propane.

$C_H$ =actual concentration of the drift check calibration gas, ppm propane.

$C_j$ =uncorrected average VOC concentration measured at point j, ppm propane.

$F_B$ =total VOC content of uncaptured emissions from the building, kg.

$K_1 = 1.830 \times 10^{-6}$  kg/(m<sup>3</sup>-ppm).

n=number of measurement points.

$Q_{Fj}$ =average effluent volumetric flow rate corrected to standard conditions at uncaptured emissions point j, m<sup>3</sup>/min.

$\Theta_F$ =total duration of CE sampling run, min.

## 9.2 Calculations

### 9.2.1 Total VOC Uncaptured Emissions from the Building.

$$F_B = \sum_{j=1}^n C_{Fj} Q_{Fj} \Theta_F K_1 \quad \text{Eq. 204E-1}$$

### 9.2.2 VOC Concentration of the Uncaptured Emissions at Point j.

$$C_{Fj} = (C_j - C_{DO}) \frac{C_H}{C_{DH} - C_{DO}} \quad \text{Eq. 204E-2}$$

## 10. Method Performance

The measurement uncertainties are estimated for each uncaptured emissions point as follows:  $Q_{Fj} = \pm 10.0$  percent and  $C_{Fj} = \pm 5.0$  percent. Based on these numbers, the probable uncertainty for  $F_B$  is estimated at about  $\pm 11.2$  percent.

## 11. Diagrams

BILLING CODE 6560-50-P

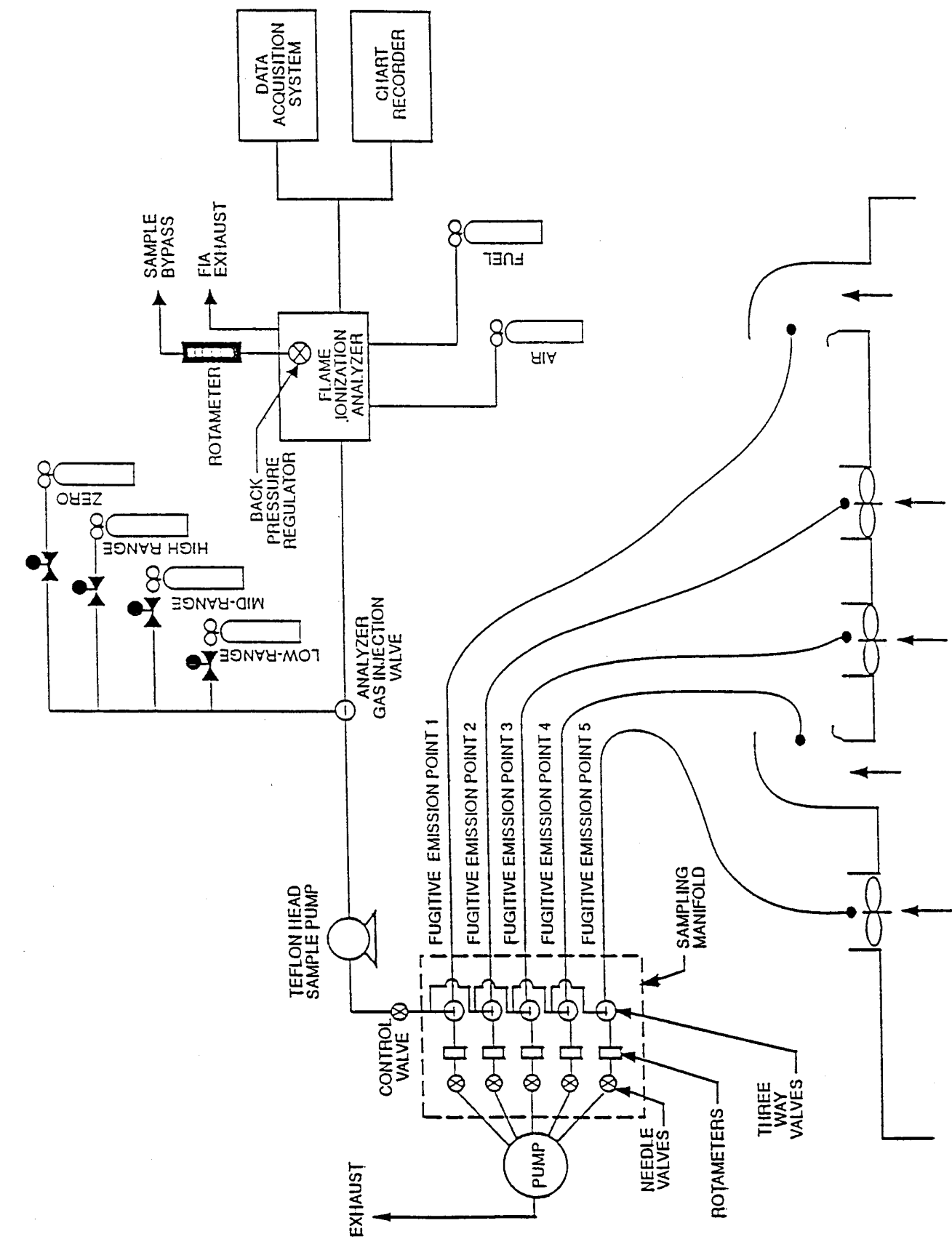


Figure 204E-1. Fugitive emissions measurement system.

## Method 204F—Volatile Organic Compounds Content in Liquid Input Stream (Distillation Approach)

### 1. Introduction

1.1 Applicability. This procedure is applicable for determining the input of volatile organic compounds (VOC). It is intended to be used as a segment in the development of liquid/gas protocols for determining VOC capture efficiency (CE) for surface coating and printing operations.

1.2 Principle. The amount of VOC introduced to the process (L) is the sum of the products of the weight (W) of each VOC containing liquid (ink, paint, solvent, etc.) used, and its VOC content (V), corrected for a response factor (RF).

1.3 Sampling Requirements. A CE test shall consist of at least three sampling runs. Each run shall cover at least one complete production cycle, but shall be at least 3 hours long. The sampling time for each run need not exceed 8 hours, even if the production cycle has not been completed. Alternative sampling times may be used with the approval of the Administrator.

### 2. Summary of Method

A sample of each coating used is distilled to separate the VOC fraction. The distillate is used to prepare a known standard for analysis by an flame ionization analyzer (FIA), calibrated against propane, to determine its RF.

### 3. Safety

Because this procedure is often applied in highly explosive areas, caution and care should be exercised in choosing, installing, and using the appropriate equipment.

### 4. Equipment and Supplies

Mention of trade names or company products does not constitute endorsement. All gas concentrations (percent, ppm) are by volume, unless otherwise noted.

#### 4.1 Liquid Weight.

4.1.1 Balances/Digital Scales. To weigh drums of VOC containing liquids to within 0.2 lb or 1.0 percent of the total weight of VOC liquid used.

4.1.2 Volume Measurement Apparatus (Alternative). Volume meters, flow meters, density measurement equipment, etc., as needed to achieve the same accuracy as direct weight measurements.

4.2 Response Factor Determination (FIA Technique). The VOC distillation system and Tedlar gas bag generation system apparatuses are shown in Figures 204F-1 and 204F-2, respectively. The following equipment is required:

4.2.1 Sample Collection Can. An appropriately-sized metal can to be used

to collect VOC containing materials. The can must be constructed in such a way that it can be grounded to the coating container.

4.2.2 Needle Valves. To control gas flow.

4.2.3 Regulators. For calibration, dilution, and sweep gas cylinders.

4.2.4 Tubing and Fittings. Teflon and stainless steel tubing and fittings with diameters, lengths, and sizes determined by the connection requirements of the equipment.

4.2.5 Thermometer. Capable of measuring the temperature of the hot water and oil baths to within 1 °C.

4.2.6 Analytical Balance. To measure  $\pm 0.01$  mg.

4.2.7 Microliter Syringe. 10- $\mu$ l size.

4.2.8 Vacuum Gauge or Manometer. 0- to 760-mm (0- to 30-in.) Hg U-Tube manometer or vacuum gauge.

4.2.9 Hot Oil Bath, With Stirring Hot Plate. Capable of heating and maintaining a distillation vessel at  $110 \pm 3$  °C.

4.2.10 Ice Water Bath. To cool the distillation flask.

4.2.11 Vacuum/Water Aspirator. A device capable of drawing a vacuum to within 20 mm Hg from absolute.

4.2.12 Rotary Evaporator System. Complete with folded inner coil, vertical style condenser, rotary speed control, and Teflon sweep gas delivery tube with valved inlet. Buchi Rotavapor or equivalent.

4.2.13 Ethylene Glycol Cooling/Circulating Bath. Capable of maintaining the condenser coil fluid at  $-10$  °C.

4.2.14 Dry Gas Meter (DGM). Capable of measuring the dilution gas volume within 2 percent, calibrated with a spirometer or bubble meter, and equipped with a temperature gauge capable of measuring temperature within 3 °C.

4.2.15 Activated Charcoal/Mole Sieve Trap. To remove any trace level of organics picked up from the DGM.

4.2.16 Gas Coil Heater. Sufficient length of 0.125-inch stainless steel tubing to allow heating of the dilution gas to near the water bath temperature before entering the volatilization vessel.

4.2.17 Water Bath, With Stirring Hot Plate. Capable of heating and maintaining a volatilization vessel and coil heater at a temperature of  $100 \pm 5$  °C.

4.2.18 Volatilization Vessel. 50-ml midget impinger fitted with a septum top and loosely filled with glass wool to increase the volatilization surface.

4.2.19 Tedlar Gas Bag. Capable of holding 30 liters of gas, flushed clean with zero air, leak tested, and evacuated.

4.2.20 Organic Concentration Analyzer. An FIA with a span value of 1.5 times the expected concentration as propane; however, other span values may be used if it can be demonstrated that they would provide equally accurate measurements. The FIA instrument should be the same instrument used in the gaseous analyses adjusted with the same fuel, combustion air, and sample back-pressure (flow rate) settings. The system shall be capable of meeting or exceeding the following specifications:

4.2.20.1 Zero Drift. Less than  $\pm 3.0$  percent of the span value.

4.2.20.2 Calibration Drift. Less than  $\pm 3.0$  percent of the span value.

4.2.20.3 Calibration Error. Less than  $\pm 3.0$  percent of the calibration gas value.

4.2.21 Integrator/Data Acquisition System. An analog or digital device or computerized data acquisition system used to integrate the FIA response or compute the average response and record measurement data. The minimum data sampling frequency for computing average or integrated value is one measurement value every 5 seconds. The device shall be capable of recording average values at least once per minute.

4.2.22 Chart Recorder (Optional). A chart recorder or similar device is recommended to provide a continuous analog display of the measurement results during the liquid sample analysis.

### 5. Reagents and Standards

5.1 Zero Air. High purity air with less than 1 ppm of organic material (as propane) or less than 0.1 percent of the span value, whichever is greater. Used to supply dilution air for making the Tedlar bag gas samples.

5.2 THC Free N<sub>2</sub>. High purity N<sub>2</sub> with less than 1 ppm THC. Used as sweep gas in the rotary evaporator system.

5.3 Calibration and Other Gases. Gases used for calibration, fuel, and combustion air (if required) are contained in compressed gas cylinders. All calibration gases shall be traceable to National Institute of Standards and Technology standards and shall be certified by the manufacturer to  $\pm 1$  percent of the tag value. 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  $\pm 2$  percent from the certified value. For calibration gas values not generally available, dilution systems calibrated using Method 205 may be used. Alternative methods for preparing



calibration gas mixtures may be used with the approval of the Administrator.

5.3.1 Fuel. The FIA manufacturer's recommended fuel should be used. A 40 percent H<sub>2</sub>/60 percent He, or 40 percent H<sub>2</sub>/60 percent N<sub>2</sub> mixture is recommended to avoid fuels with oxygen to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value. Other mixtures may be used provided the tester can demonstrate to the Administrator that there is no oxygen synergism effect.

5.3.2 Combustion Air. High purity air with less than 1 ppm of organic material (as propane) or less than 0.1 percent of the span value, whichever is greater.

5.3.3 FIA Linearity Calibration Gases. Low-, mid-, and high-range gas mixture standards with nominal propane concentration of 20–30, 45–55, and 70–80 percent of the span value in air, respectively. Other calibration values and other span values may be used if it can be shown that equally accurate measurements would be achieved.

5.3.4 System Calibration Gas. Gas mixture standard containing propane in air, approximating the VOC concentration expected for the Tedlar gas bag samples.

## 6. Quality Control

6.1 Required instrument quality control parameters are found in the following sections:

6.1.1 The FIA system must be calibrated as specified in section 7.1.

6.1.2 The system drift check must be performed as specified in section 7.2.

6.2 Precision Control. A minimum of one sample in each batch must be distilled and analyzed in duplicate as a precision control. If the results of the two analyses differ by more than  $\pm 10$  percent of the mean, then the system must be reevaluated and the entire batch must be redistilled and analyzed.

## 6.3 Audits.

6.3.1 Audit Procedure. Concurrently, analyze the audit sample and a set of compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation. The same analyst, analytical reagents, and analytical system shall be used both for compliance samples and the EPA audit sample. If this condition is met, auditing of subsequent compliance analyses for the same enforcement agency within 30 days is not required. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of different enforcement

agencies, unless prior arrangements are made with both enforcement agencies.

6.3.2 Audit Samples. Audit Sample Availability. Audit samples will be supplied only to enforcement agencies for compliance tests. The availability of audit samples may be obtained by writing: Source Test Audit Coordinator (STAC) (MD-77B), Quality Assurance Division, Atmospheric Research and Exposure Assessment Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711 or by calling the STAC at (919) 541-7834. The request for the audit sample must be made at least 30 days prior to the scheduled compliance sample analysis.

6.3.3 Audit Results. Calculate the audit sample concentration according to the calculation procedure described in the audit instructions included with the audit sample. Fill in the audit sample concentration and the analyst's name on the audit response form included with the audit instructions. Send one copy to the EPA Regional Office or the appropriate enforcement agency, and a second copy to the STAC. The EPA Regional Office or the appropriate enforcement agency will report the results of the audit to the laboratory being audited. Include this response with the results of the compliance samples in relevant reports to the EPA Regional Office or the appropriate enforcement agency.

## 7. Calibration and Standardization

7.1 FIA Calibration and Linearity Check. Make necessary adjustments to the air and fuel supplies for the FIA and ignite the burner. Allow the FIA to warm up for the period recommended by the manufacturer. Inject a calibration gas into the measurement system and adjust the back-pressure regulator to the value required to achieve the flow rates specified by the manufacturer. Inject the zero- and the high-range calibration gases and adjust the analyzer calibration to provide the proper responses. Inject the low- and mid-range gases and record the responses of the measurement system. The calibration and linearity of the system are acceptable if the responses for all four gases are within 5 percent of the respective gas values. If the performance of the system is not acceptable, repair or adjust the system and repeat the linearity check. Conduct a calibration and linearity check after assembling the analysis system and after a major change is made to the system. A calibration curve consisting of zero gas and two calibration levels must be performed at the beginning and end of each batch of samples.

7.2 Systems Drift Checks. After each sample, repeat the system calibration

checks in section 7.1 before any adjustments to the FIA or measurement system are made. If the zero or calibration drift exceeds  $\pm 3$  percent of the span value, discard the result and repeat the analysis. Alternatively, recalibrate the FIA as in section 7.1 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). The data that results in the lowest CE value shall be reported as the results for the test run.

## 8. Procedures

### 8.1 Determination of Liquid Input Weight

8.1.1 Weight Difference. Determine the amount of material introduced to the process as the weight difference of the feed material before and after each sampling run. In determining the total VOC containing liquid usage, account for: (a) The initial (beginning) VOC containing liquid mixture; (b) any solvent added during the test run; (c) any coating added during the test run; and (d) any residual VOC containing liquid mixture remaining at the end of the sample run.

8.1.1.1 Identify all points where VOC containing liquids are introduced to the process. To obtain an accurate measurement of VOC containing liquids, start with an empty fountain (if applicable). After completing the run, drain the liquid in the fountain back into the liquid drum (if possible), and weigh the drum again. Weigh the VOC containing liquids to  $\pm 0.5$  percent of the total weight (full) or  $\pm 1.0$  percent of the total weight of VOC containing liquid used during the sample run, whichever is less. If the residual liquid cannot be returned to the drum, drain the fountain into a preweighed empty drum to determine the final weight of the liquid.

8.1.1.2 If it is not possible to measure a single representative mixture, then weigh the various components separately (e.g., if solvent is added during the sampling run, weigh the solvent before it is added to the mixture). If a fresh drum of VOC containing liquid is needed during the run, then weigh both the empty drum and fresh drum.

8.1.2 Volume Measurement (Alternative). If direct weight measurements are not feasible, the tester may use volume meters and flow rate meters (and density measurements) to determine the weight of liquids used if it can be demonstrated that the technique produces results equivalent to the direct weight measurements. If a single representative mixture cannot be

measured, measure the components separately.

## 8.2 Determination of VOC Content in Input Liquids

### 8.2.1 Collection of Liquid Samples.

8.2.1.1 Collect a 1-pint or larger sample of the VOC containing liquid mixture at each application location at the beginning and end of each test run. A separate sample should be taken of each VOC containing liquid added to the application mixture during the test run. If a fresh drum is needed during the sampling run, then obtain a sample from the fresh drum.

8.2.1.2 When collecting the sample, ground the sample container to the coating drum. Fill the sample container as close to the rim as possible to minimize the amount of headspace.

8.2.1.3 After the sample is collected, seal the container so the sample cannot leak out or evaporate.

8.2.1.4 Label the container to identify clearly the contents.

### 8.2.2 Distillation of VOC.

8.2.2.1 Assemble the rotary evaporator as shown in Figure 204F-1.

8.2.2.2 Leak check the rotary evaporation system by aspirating a vacuum of approximately 20 mm Hg from absolute. Close up the system and monitor the vacuum for approximately 1 minute. If the vacuum falls more than 25 mm Hg in 1 minute, repair leaks and repeat. Turn off the aspirator and vent vacuum.

8.2.2.3 Deposit approximately 20 ml of sample (inks, paints, etc.) into the rotary evaporation distillation flask.

8.2.2.4 Install the distillation flask on the rotary evaporator.

8.2.2.5 Immerse the distillate collection flask into the ice water bath.

8.2.2.6 Start rotating the distillation flask at a speed of approximately 30 rpm.

8.2.2.7 Begin heating the vessel at a rate of 2 to 3°C per minute.

8.2.2.8 After the hot oil bath has reached a temperature of 50°C or pressure is evident on the mercury manometer, turn on the aspirator and gradually apply a vacuum to the evaporator to within 20 mm Hg of absolute. Care should be taken to prevent material burping from the distillation flask.

8.2.2.9 Continue heating until a temperature of 110°C is achieved and maintain this temperature for at least 2 minutes, or until the sample has dried in the distillation flask.

8.2.2.10 Slowly introduce the N<sub>2</sub> sweep gas through the purge tube and into the distillation flask, taking care to maintain a vacuum of approximately 400-mm Hg from absolute.

8.2.2.11 Continue sweeping the remaining solvent VOC from the

distillation flask and condenser assembly for 2 minutes, or until all traces of condensed solvent are gone from the vessel. Some distillate may remain in the still head. This will not affect solvent recovery ratios.

8.2.2.12 Release the vacuum, disassemble the apparatus and transfer the distillate to a labeled, sealed vial.

### 8.2.3 Preparation of VOC standard bag sample.

8.2.3.1 Assemble the bag sample generation system as shown in Figure 204F-2 and bring the water bath up to near boiling temperature.

8.2.3.2 Inflate the Tedlar bag and perform a leak check on the bag.

8.2.3.3 Evacuate the bag and close the bag inlet valve.

8.2.3.4 Record the current barometric pressure.

8.2.3.5 Record the starting reading on the dry gas meter, open the bag inlet valve, and start the dilution zero air flowing into the Tedlar bag at approximately 2 liters per minute.

8.2.3.6 The bag sample VOC concentration should be similar to the gaseous VOC concentration measured in the gas streams. The amount of liquid VOC required can be approximated using equations in section 9.2. Using Equation 204F-4, calculate C<sub>VOC</sub> by assuming RF is 1.0 and selecting the desired gas concentration in terms of propane, C<sub>C3</sub>. Assuming B<sub>V</sub> is 20 liters, M<sub>L</sub>, the approximate amount of liquid to be used to prepare the bag gas sample, can be calculated using Equation 204F-2.

8.2.3.7 Quickly withdraw an aliquot of the approximate amount calculated in section 8.2.3.6 from the distillate vial with the microliter syringe and record its weight from the analytical balance to the nearest 0.01 mg.

8.2.3.8 Inject the contents of the syringe through the septum of the volatilization vessel into the glass wool inside the vessel.

8.2.3.9 Reweigh and record the tare weight of the now empty syringe.

8.2.3.10 Record the pressure and temperature of the dilution gas as it is passed through the dry gas meter.

8.2.3.11 After approximately 20 liters of dilution gas have passed into the Tedlar bag, close the valve to the dilution air source and record the exact final reading on the dry gas meter.

8.2.3.12 The gas bag is then analyzed by FIA within 1 hour of bag preparation in accordance with the procedure in section 8.2.4.

### 8.2.4 Determination of VOC response factor.

8.2.4.1 Start up the FIA instrument using the same settings as used for the gaseous VOC measurements.

8.2.4.2 Perform the FIA analyzer calibration and linearity checks according to the procedure in section 7.1. Record the responses to each of the calibration gases and the back-pressure setting of the FIA.

8.2.4.3 Connect the Tedlar bag sample to the FIA sample inlet and record the bag concentration in terms of propane. Continue the analyses until a steady reading is obtained for at least 30 seconds. Record the final reading and calculate the RF.

### 8.2.5 Determination of coating VOC content as VOC (V<sub>II</sub>).

8.2.5.1 Determine the VOC content of the coatings used in the process using EPA Method 24 or 24A as applicable.

## 9. Data Analysis and Calculations

### 9.1. Nomenclature.

B<sub>V</sub>=Volume of bag sample volume, liters.

C<sub>C3</sub>=Concentration of bag sample as propane, mg/liter.

C<sub>VOC</sub>=Concentration of bag sample as VOC, mg/liter.

K=0.00183 mg propane/(liter-ppm propane)

L=Total VOC content of liquid input, kg propane.

M<sub>L</sub>=Mass of VOC liquid injected into the bag, mg.

M<sub>V</sub>=Volume of gas measured by DGM, liters.

P<sub>M</sub>=Absolute DGM gas pressure, mm Hg.

P<sub>STD</sub>=Standard absolute pressure, 760 mm Hg.

R<sub>C3</sub>=FIA reading for bag gas sample, ppm propane.

RF=Response factor for VOC in liquid, weight VOC/weight propane.

RF<sub>J</sub>=Response factor for VOC in liquid J, weight VOC/weight propane.

T<sub>M</sub>=DGM temperature, °K.

T<sub>STD</sub>=Standard absolute temperature, 293°K.

V<sub>II</sub>=Initial VOC weight fraction of VOC liquid J.

V<sub>FJ</sub>=Final VOC weight fraction of VOC liquid J.

V<sub>AJ</sub>=VOC weight fraction of VOC liquid J added during the run.

W<sub>II</sub>=Weight of VOC containing liquid J at beginning of run, kg.

W<sub>FJ</sub>=Weight of VOC containing liquid J at end of run, kg.

W<sub>AJ</sub>=Weight of VOC containing liquid J added during the run, kg.

### 9.2 Calculations.

#### 9.2.1 Bag sample volume.

$$B_V = \frac{M_V T_{STD} P_M}{T_M P_{STD}} \quad \text{Eq. 204F-1}$$

#### 9.2.2 Bag sample VOC concentration.

$C_{\text{VOC}} = \frac{M_L}{B_V}$       Eq. 204F-2

$C_{C_3} = R_{C_3} K$       Eq. 204F-3

9.2.4    Response Factor.

$RF = \frac{C_{\text{VOC}}}{C_{C_3}}$       Eq. 204F-4

9.2.3    Bag sample VOC concentration as propane.

9.2.5    Total VOC Content of the Input VOC Containing Liquid.

$$L = \sum_{j=1}^n \frac{V_{rj} W_{rj}}{RF_j} - \sum_{j=1}^n \frac{V_{Fj} W_{Fj}}{RF_j} + \sum_{j=1}^n \frac{V_{Aj} W_{Aj}}{RF_j}$$
      Eq. 204F-5

10. *Diagrams*

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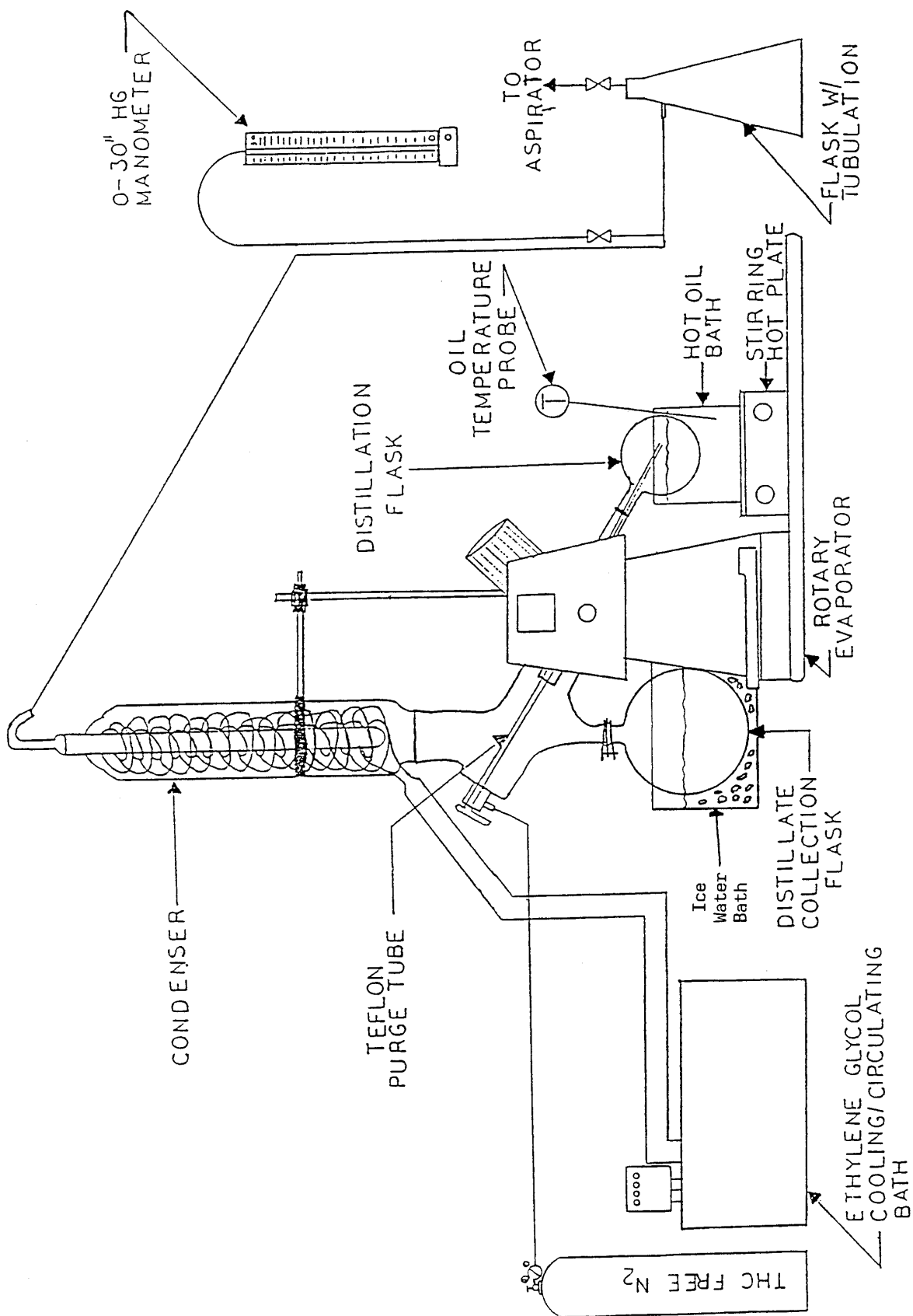


Figure 204F-1. VOC distillation system apparatus.

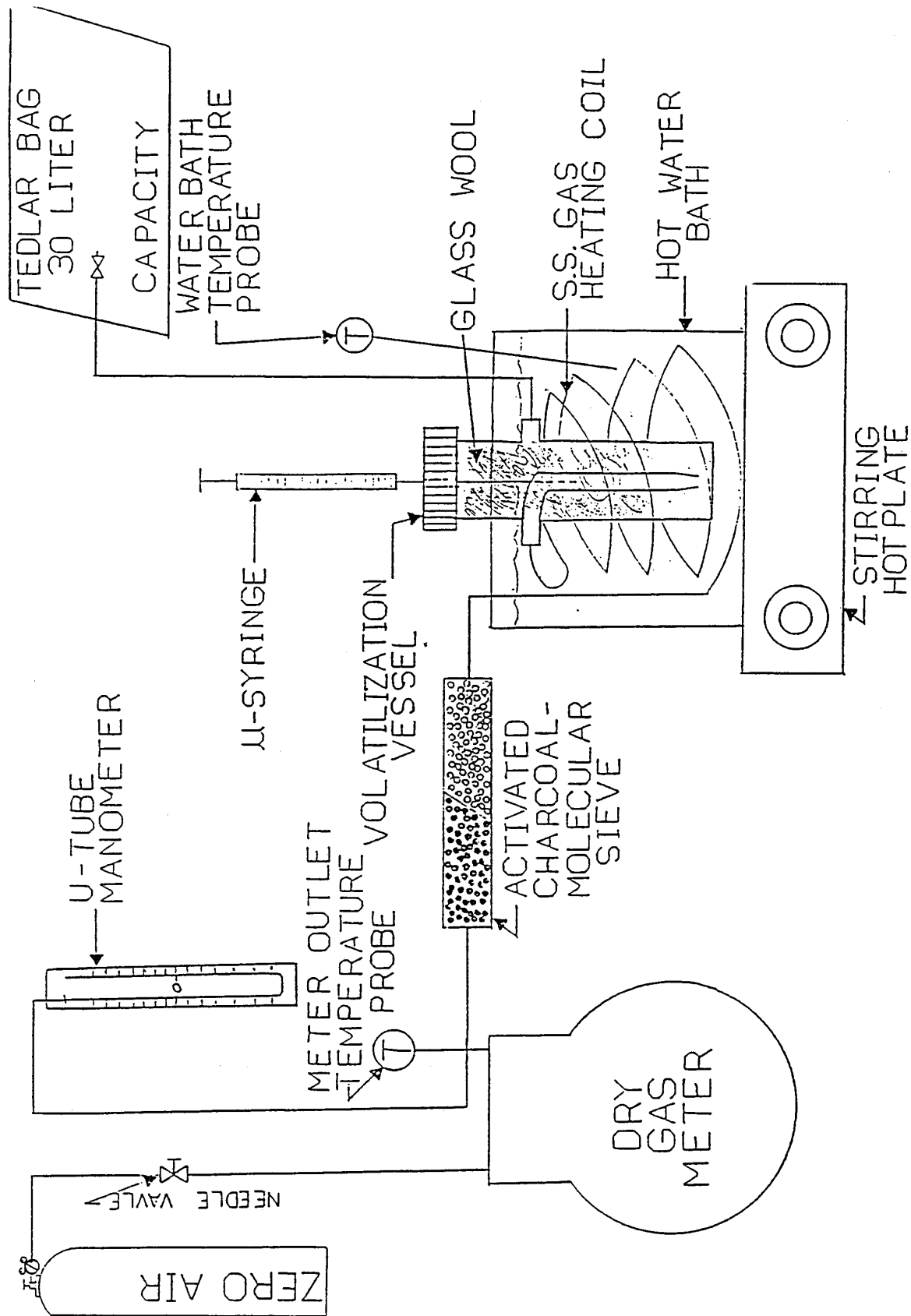


Figure 204F-2. Tedlar gas bag generation system apparatus.